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Crystal Structure and Spectroscopic Properties of $CsVO_2SO_4$

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Dark crystals of the V(V) compound $CsVO_2SO_4$, suitable for X-ray investigations have been obtained from the catalytically important $Cs_2S_2O_7$–V_2O_5 system. By cooling of the mixture with the composition $X_{V_2O_5} = 0.5$, some crystals were obtained in the otherwise glassy sample. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 6.6688(13)$ Å, $b = 10.048(2)$ Å, and $c = 17.680(4)$ Å at 20 °C and $Z = 8$. It contains a coordination sphere with a short V–O bond of 1.595(2) Å and trans to this the closest VO distance at 3.4 Å and four equatorial V–O bonds in the range 1.725(1)–1.984(2) Å. The deformation of the VO_6 octahedron is thus much more pronounced compared to other known oxo sulfato V(V) compounds, and the coordination polyhedron of V(V) should be regarded as a tetragonal pyramid with the vanadium atom in the center. Each VO_2^+ group is coordinated to the neighboring groups by oxygen and sulfate double bridges in a zigzag structure where two sulfate oxygens virtually remain uncoordinated—one is found at the very long nonbonding V–O distance from the neighboring chain. This is the first time that we find pentacoordination of vanadium in the 12 different V(III), V(IV), and V(V) compounds examined so far. The FTIR and Raman spectra of the compound are in agreement with the simple formula unit of the investigated compound.

Introduction

This paper constitutes a continuation of our comprehensive studies of sulfuric acid catalysts and their model systems which are considered well described by the molten salt−gas systems $M_2S_2O_7-V_2O_5/SO_2-O_2-SO_3-N_2$ (M = Na, K, Cs) at 400−600 °C, supported on a porous kieselguhr carrier.[1−3] To get information on the lowest possible temperature of use of the SO_2 oxidation catalysts we have previously[4−7] studied the phase diagrams of the binary systems $M_2S_2O_7-V_2O_5$ (M = K, Rb, Cs, and 80% K + 20% Na). The phase diagrams indicate formation of compounds at the molar ratios M/V = 1 and 2 (M = K, Rb, Cs) and K/V = 3, but usually the melts form glasses upon cooling preventing isolation of crystalline compounds suitable for X-ray investigations. However, previously, we have succeeded in obtaining single crystals and solved the structure of the dimeric V(V) compounds $M_4(VO)_2O(SO_4)_4$ (M = K,[8] Rb,[8] and Cs[9]) and very recently the compounds $Na_2K_6(VO)_2(SO_4)_7$[10] and $K_8(VO)_2O(SO_4)_6$.[11]

In this study we report the crystal structure and spectroscopic properties of yet another V(V) oxo sulfato compound, $CsVO_2SO_4$, which corresponds to the compound formed at the composition $X_{V_2O_5} = 0.5$ (equal to Cs/V = 1) according

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to the phase diagram of the $Cs_2S_2O_7-V_2O_5$ system. The existence of this compound had earlier been claimed,[12] but no single-crystal X-ray investigation had previously been carried out. Only X-ray powder diffraction and infrared spectra were recorded, and these results will be discussed in relation to the present work.

Characterization of V(V) compounds isolated from the catalyst model systems attract interest since their structure is considered essential for understanding the SO_2 oxidation mechanism at the molecular level as reviewed recently.[13,14]

Experimental Section

Synthesis of Crystalline $CsVO_2SO_4$. Pure and dry $Cs_2S_2O_7$ was prepared by thermal decomposition of synthesized $Cs_2S_2O_8$ at 300 °C in a stream of dry nitrogen as earlier described.[6] None of the compounds are commercially available. V_2O_5 was from Cerac (Pure, 99.9%) and used without further treatment. All handling of chemicals was performed in an air-filled drybox with a water content less than 10 ppm. The sample from which crystals of $CsVO_2SO_4$ were isolated was prepared for NMR investigations reported earlier,[15] consisting of approximately 5 g of a $Cs_2S_2O_7-V_2O_5$ mixture with the composition $X_{V_2O_5} = 0.5$, sealed in a quartz tube under 0.5 atm O_2 to prevent a possible auto reduction of V(V) to V(IV). During cooling of this sample from 550 °C after finishing the NMR measurements the partly crystalline sample was obtained from which a crystal of $CsVO_2SO_4$ suitable for X-ray investigations was selected.

Spectroscopy. For recording of the IR spectrum of $CsVO_2SO_4$ in pressed KBr disk, ~3 mg of $CsVO_2SO_4$ was mixed with 150 mg of KBr inside a N_2-atmosphere glovebox to avoid contact with humidity. The IR spectrum was recorded on a Perkin-Elmer 1600 infrared spectrometer. Raman spectra were obtained with the 647.1 nm line of a Spectra Physics 2017 Stabilite krypton ion laser on a sample handled inside the glovebox and sealed in a quartz cell under O_2 atmosphere.

X-ray Investigation. The single crystal used for the X-ray investigation had the dimensions $0.09 \times 0.09 \times 0.40$ mm^3 and was covered completely with epoxy glue to protect it against moisture from the atmosphere. X-ray diffraction data were collected at room temperature on a Siemens SMART diffractometer using Mo Kα ($\lambda = 0.710\,73$ Å) monochromatic radiation. Unit cell dimensions were refined and intensity data reduced by SAINT. The structure was solved by direct methods and refined in the space group *Pbca* including full-matrix least-squares fitting of positional and anisotropic thermal parameters.[16,17] Data were calculated with atomic scattering factors and anomalous dispersion corrections obtained from SHELXTL.[16] Correction for absorption was performed by the Siemens SADABS program. Structure drawings were made using the Ortep III[18] thermal ellipsoid plot software. Crystallographic data are given in Table 1.

Table 1. Crystallographic Data for $CsVO_2SO_4$

chem formula	fw 311.91
$CsVO_2SO_4$	space group *Pbca*
$a = 6.6688(13)$ Å	$T = 20$ °C
$b = 10.048(2)$ Å	$\lambda = 0.710\,73$ Å
$c = 17.680(4)$ Å	$D_{calc} = 3.498$ g cm^{-3}
$V = 1184.6(4)$ Å^3	$R_1{}^a = 0.0194$
$Z = 8$	$R_2{}^b = 0.0526$

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

Results and Discussion

Description of the Structure. Each asymmetric unit contains eight identical pentacoordinated V(V) atoms and eight sulfate tetrahedra. An ORTEP III stereo plot is shown in Figure 1. The bond lengths and angles are given in Tables 2 and 3. Each vanadium(V) pentahedron is coordinated in two positions to neighboring pentahedra by oxygen bridges and in two other positions by oxygens from bidentate bridging sulfate groups while the fifth position is occupied by an unshared oxygen atom as shown in Figure 2. The length of the latter V−O bond is 1.595 Å, which is shorter than the shortest V−O bond of VO_2^+-containing oxo sulfato V(V) compounds reported so far.[10]

This indicates rather strong double bond character while the four other V−O bonds of the pentahedron have lengths in the range 1.725−1.984 Å characteristic for single bonds. The closest distance to a possible sixth oxygen atom is 3.40 Å, far too long to be considered as a V−O bond. This feature may explain the presence of the very short V═O double bond since there is low electron density in the $3d_{z^2}$ orbital. This geometry of $CsVO_2SO_4$ is unique among the 12 different oxo sulfato vanadates(III, IV, or V) of which we have solved the X-ray structure so far. Hexacoordination was always found earlier. As far as we know the only oxo vanadium(V) compound to compare with is V_2O_5. In the case of V_2O_5, pentacoordination is also found with a short V−O bond of 1.58 Å and the four other V−O bonds in the range 1.78−2.02 Å. The sixth V−O distance is found to be around 2.79 Å—too long to be regarded as a regular bond.

A striking feature of both $CsVO_2SO_4$ and V_2O_5 is the relatively short vanadium bonds at 1.72−1.78 Å to the corner-shared oxygen (O3 in $CsVO_2SO_4$) and the relatively long V−O bond at 1.98−2.02 Å found opposite to this bond. Thus, in both structures the O−V(═O)−O−V(═)−O−V(═O) chains seem to be formed. However, this vanadium-rich system exhibits different structural properties, compared to the complex formation of V(V) found in the molten $M_2S_2O_7-V_2O_5$ systems (M = K and Cs) with lower vanadium content (M/V = 2−5; typical composition range of SO_2 oxidation catalyst used industrially), where the dimeric V(V) complex $(VO)_2O(SO_4)_4^{4-}$ dominates.[19−21] Structurally the present compound is more comparable to the compound $V_2O_3(SO_4)_2$ obtained from a system with no

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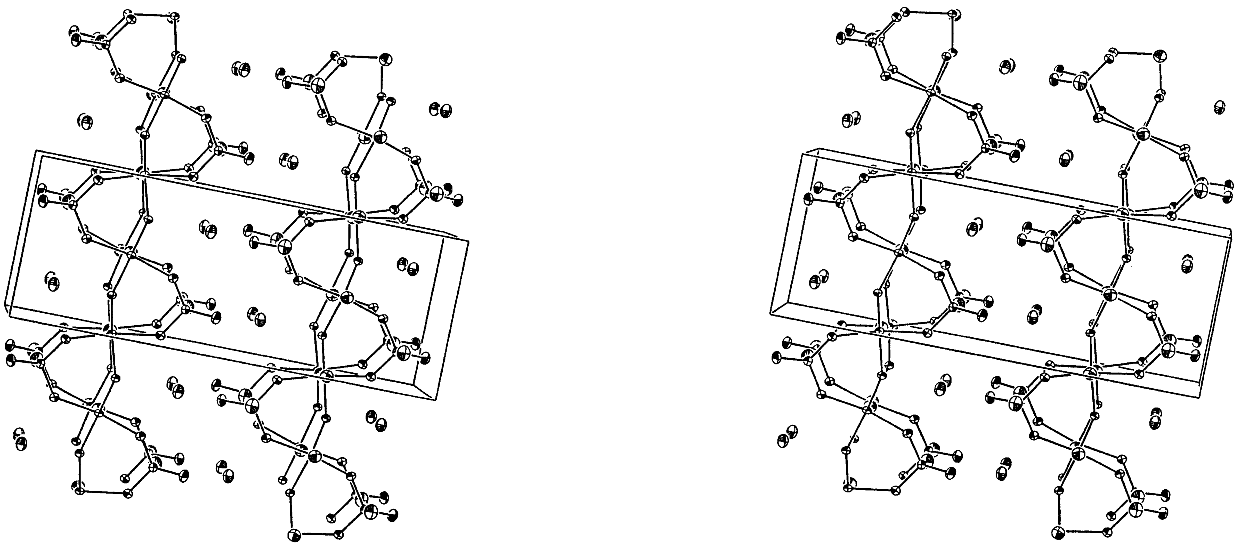

Figure 1. ORTEP-III stereo plot of the unit cell of $CsVO_2SO_4$.

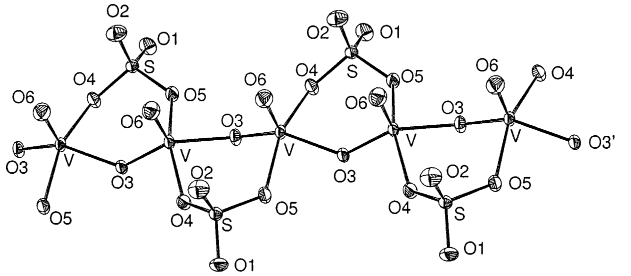

Figure 2. ORTEP-III plot of $CsVO_2SO_4$ showing a part of the zigzag chain. O3′ is only indicated for the terminal complex unit. The cations (Cs^+) are omitted for clarity. Ellipsoids are plotted at the 50% probability level.

Table 2. V−O and S−O Bond Lengths in $CsVO_2SO_4$ (in Å)

V−O6	1.595(2)	S−O1	1.447(2)
V−O3	1.7249(14)	S−O2	1.447(2)
V−O3	1.9188(14)	S−O4	1.526(2)
V−O4	1.971(2)	S−O5	1.530(2)
V−O5	1.984(2)		

Table 3. V−O and S−O Bond Angles in $CsVO_2SO_4$ (deg)

O6−V−O3	108.29(9)	O3−V−O5	81.23(7)
O6−V−O3	110.50(8)	O4−V−O5	157.26(8)
O3−V−O3	141.13(11)	O1−S−O2	114.35(12)
O6−V−O4	101.84(8)	O1−S−O4	108.81(10)
O3−V−O4	90.49(7)	O2−S−O4	109.60(10)
O3−V−O4	84.07(7)	O1−S−O5	107.99(10)
O6−V−O5	99.53(7)	O2−S−O5	109.44(10)
O3−V−O5	90.14(8)	O4−S−O5	106.35(11)

alkali metal ions present,[22] which also exhibits the combination of V−O−V and V−SO_4−V bridges. The latter compound, however, grows in a three-dimensional network, opposite to the $(VO_2SO_4^-)_n$ chain structure of $CsVO_2SO_4$.

Vibrational Spectra. General Considerations. One may consider the $CsVO_2SO_4$ crystal as composed of Cs^+ and $VO_2SO_4^-$ ions. In turn, the $VO_2SO_4^-$ ion, according to the structure shown in Figure 2, consists of VO^{3+} units linked by V−O−V bridges and bidentate sulfate groups. The band due to the $\nu(V^V{=}O)$ stretching mode is expected above 1000 cm^{-1}. The four fundamentals ($\nu_1 - \nu_4$) of the SO_4^{2-} ion are known to span the following representation for a regular tetrahedral (T_d) configuration:

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

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 stretching and ν_2 and ν_4 are angle bending. The wavenumbers of the fundamentals are well-known:[23] $\nu_1(A_1) \approx 983$ cm^{-1}, $\nu_2(E) \approx 450$ cm^{-1}, $\nu_3(F_2) \approx 1105$ cm^{-1}, and $\nu_4(F_2) \approx 611$ 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_5 distorted tetragonal pyramid units will give rise to (apart from the V=O stretch in the apical direction) bands due to V−O stretches along V−O3−V, V−O3′−V, V−O5−S, and V−O4−S coordination bridges extending out of the pyramid base.

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 4. Some of the observed bands are common to both kinds of spectra. The characteristic $V^V{=}O$ stretching is found at 1017 cm^{-1} in the Raman spectra, whereas a careful examination of the IR and Raman spectra leads to assignment of the S−O and V−O stretching and of the split components of sulfate bending. Extensive degeneracy of most of the normal modes must prevail.

Geometry of the SO_4^{2-} Groups. The bond lengths of the bidentate bridging sulfate group reflect the coordination: The usual sulfur−oxygen bond lengths in undistorted sulfate groups are around 1.47 Å. In the present compound relatively long bonds (S−O4 and S−O5) of 1.53 Å are found for the oxygens bonded to both sulfur and the electron-attracting

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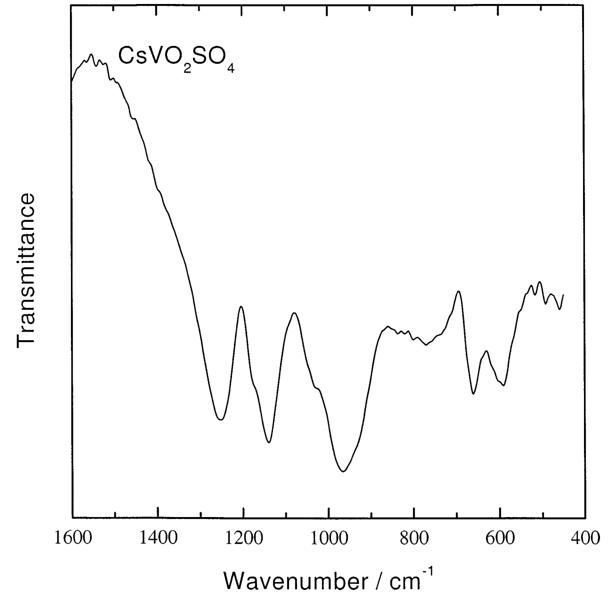

Figure 3. Infrared spectrum of $CsVO_2SO_4$ powder in a pressed KBr disk at room temperature. Resolution: ca. 5 cm^{-1}.

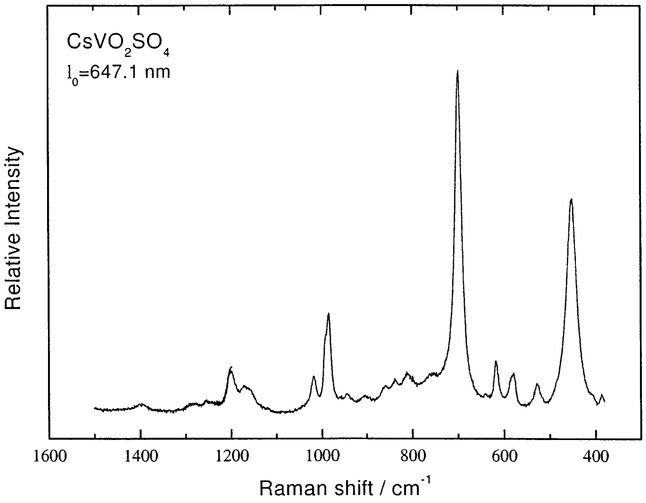

Figure 4. Raman spectrum of $CsVO_2SO_4$ powder at room temperature: λ_0, 647.1 nm; laser power, 90 mW; resolution, 6 cm^{-1}.

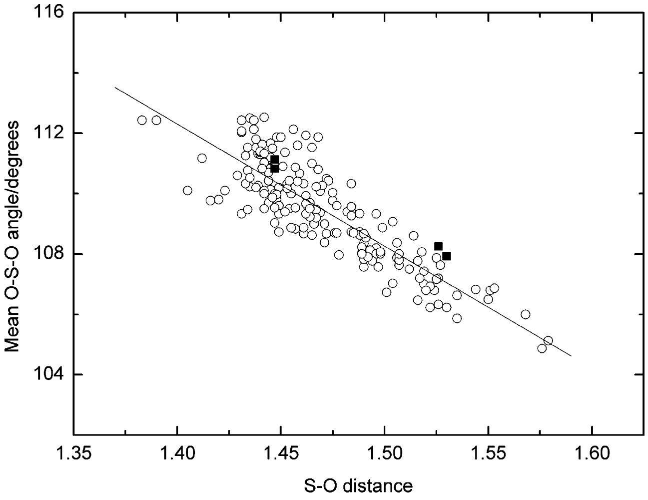

Figure 5. Plot of S−O distances for a particular bond versus the average of the three angles involving that bond and the other S−O bonds of the sulfate tetrahedron (four solid squares for $CsVO_2SO_4$). Also shown are 184 points (open circles) for $K_4(VO)_3(SO_4)_5$, $KV(SO_4)_2$, $K_6(VO)_4(SO_4)_8$, $K_8(VO)_2(SO_4)_6$, $Na_2VO(SO_4)_2$, $Na_8(VO)_2(SO_4)_6$, $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $Na_2K_6(VO)_2(SO_4)_7$, $CsV(SO_4)_2$, $Cs_4(VO)_2O(SO_4)_4$, and β-$VOSO_4$, which result in the regression line $y = ax + b$: y = mean O−S−O angle, deg; x = S−O distance, Å; $a = -40.455$; $b = 168.94$.

Table 4. Infrared and Raman Bands (in cm^{-1}) for $CsVOSO_4$ and Their Tentative Assignments[a]

IR powder in KBr disk	Raman powder ($\lambda_0 = 647.1$ nm)	tentative assgnt
	1284 w	ν_3(str, SO_4^{2-})
1251 s	1254 w	
	1202 m	
1177 sh	1172 m	
1139 s	1158 sh	
1029 sh	1017 m	ν(str, $V{=}O^{3+}$)
	990 sh	ν_1(str, SO_4^{2-})[b]
967 s	983 s	
	945 w	ν[(S−(O−V)][c]
	906 w	
	860 w	
	840 w	
	812 m	
772 m		ν[(V−O)−V]
	701 vs	
660 m		ν[(V−O)−V] and ν_4(bend, SO_4^{2-})
604 sh	616 m	
590 m	579 m	
516 w	527 m	ν_2(bend, SO_4^{2-}) and ν[V−(O−S)]
494 w		
460 w	452 vs	

[a] Intensity codes: s, strong; m, medium; w, weak; sh, shoulder; v, very. [b] S−O$_{terminal}$ modes. [c] S−O$_{bridging}$ modes along V−O−S coordination bridges.

V(V) atom. Consequently, the length of the S−O bonds of the uncoordinated oxygen atoms, i.e. S−O1 and S−O2, are shorter; both have a value of 1.447 Å, which is significantly lower than the usual value of undistorted sulfate groups. Also the S−O bond angles within the sulfate group is affected by the coordination. Thus, the O4−S−O5 angle of 106° involving the coordinated oxygens is considerably lower than the ideal tetrahedral angle of 109° found in undistorted SO_4^{2-} groups. In contrast to this, the angle between the bonds involving the uncoordinated oxygens, i.e. O1−S−O2, is 114°, much higher than the ideal angle, reflecting the reduced repulsion from the coordinated oxygens.

As previously, we have plotted the S−O distances of a particular bond in the SO_4^{2-} group versus the average of the three angles between that bond and the other three S−O bonds. The result is shown in Figure 5, where a fairly large linear relationship (linear regression) is found comparable to what is observed for the 46 different sulfate groups in the compounds $K_4(VO)_3(SO_4)_5$, $KV(SO_4)_2$, $K_6(VO)_4(SO_4)_8$, $NaVO(SO_4)_2$, $Na_8(VO)_2(SO_4)_6$, $NaV(SO_4)_2$, $Na_3V(SO_4)_3$, $CsV(SO_4)_2$, $Cs_4(VO)_2O(SO_4)_4$, β-$VOSO_4$, $Na_2K_6(VO)_2(SO_4)_7$,[10] $K_8(VO)_2O(SO_4)_6$,[11] and $CsVO_2SO_4$. Thus, it appears that the geometry of the sulfate group in the $CsVO_2SO_4$ structure does not deviate much from that of the average sulfate group in the above-mentioned compounds; i.e., the hypothesis[24] of sp^3 hybridization of the sulfate groups in the vanadium oxo sulfato compounds holds for $CsVO_2SO_4$.

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Comparison to Previous Work. The only previous report dealing with synthesis and characterization of $CsVO_2SO_4$ is the work of Glazyrin et al.[12] On the basis of our X-ray data for the single crystal, we have calculated the expected powder XRD for $CsVO_2SO_4$ and compared it to a calculated one in the 2θ range 20−50° using the *d* spacing and intensity values given in ref 12. However, there is no reasonable match between the two diagrams and it is obvious that we are not dealing with the same compound. Furthermore the IR spectrum given in ref 12 is not comparable with ours. It shows many more bands than we find in the spectrum of $CsVO_2SO_4$, which indeed appears relatively simple in accordance with the fact that we find only one $VO_2SO_4^-$ complex unit in the crystal. The band-rich spectrum in ref 12 shows bands in the region expected[25] for HSO_4^- indicating that the compound might have been contaminated by moisture since hygroscopic compounds usually are isolated from $M_2S_2O_7-V_2O_5$ systems in general. Thus, it seems that the compound $CsVO_2SO_4$ has possibly not been isolated previously, at least not in its pure form.

The isolation of $CsVO_2SO_4$ has finally proved that indeed a compound is formed at the molar ratio Cs/V = 1 (or $X_{V_2O_5} = 0.5$) in the binary system $Cs_2S_2O_7-V_2O_5$. This lends also support to our conclusions on previous studies of the analogous binary systems of the other alkali metals about formation of a compound at M/V = 1. It should be mentioned that this molar ratio is far from the M/V ratio range of 3−4 found in most industrial SO_2 oxidation catalysts. In this composition range the predominant V(V) compound is $(VO)_2O(SO_4)_4^{4-}$ and not $VO_2SO_4^-$ (or oligomeric forms of this) underlining that the dimeric V(V) compound indeed is the essential species for the catalytic oxidation of SO_2 by O_2 to SO_3.

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Supporting Information Available: Crystallographic data in CIF format containing 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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