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Crystal Structure of $Cs_4(VO)_2O(SO_4)_4$

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Brownish yellow crystals of a V(V) compound, cesium (μ-oxo)bis(oxodisulfatovanadate)(–4), $Cs_4(VO)_2O(SO_4)_4$, suitable for X-ray determination, have for the first time been obtained from the catalytically important $Cs_2S_2O_7/V_2O_5$ system. By slow cooling of a mixture with the composition $X_{V_2O_5} = 0.251$ from 380 (i.e. just below the liquidus temperature) to 350 °C, the crystal growth could be promoted by the solid V_2O_5 present in the melt. The compound crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 8.117(2)$ Å, $b = 11.104(2)$ Å, $c = 11.799(2)$ Å, $\alpha = 79.58(1)°$, $\beta = 87.95(2)°$, and $\gamma = 75.61(2)°$ at 18 °C and $Z = 2$. It contains two very similar distorted VO_6 octahedra joint through corners corresponding to a V–O–V bridge with an angle of 165.3°. Each octahedron exhibits a short V–O bond of 1.58 Å and a longer bond of around 1.77 Å to the bridging oxide ion. The remaining four V–O bonds are associated with two bidentate coordinated sulfate groups with three V–O bonds in the range 1.86–2.02 Å and a long one around 2.40 Å trans to the short V–O bond. The two equatorially coordinated bidentate sulfate groups are strongly distorted from the tetrahedral geometry—the O-S-O angle being only approximately 97°. This distortion may explain the shift and splitting of the sulfate ν_3 bands to unusual high wavenumbers—up to about 1300 cm^{-1}—as observed in the IR spectra of $Cs_4(VO)_2O(SO_4)_4$.

Introduction

The key step in the industrial production of sulfuric acid is the catalyzed oxidation of SO_2 to SO_3 by oxygen. The catalyst consists of a supported melt, and can be described by the molten salt–gas system $M_2S_2O_7/V_2O_5–SO_2/SO_3/O_2/N_2$ where M usually is a mixture of K and Na, but newer catalysts may also contain Cs. The reaction mechanism is not known in spite of numerous kinetic investigations, but it is generally acknowledged that dimeric V(V) species must be involved in the catalytic cycle.[2–4] Structural investigations of the chemical system are rare because of severe experimental difficulties such as hygroscopy, intense coloring, high viscosity, and glass formation ability. None of these investigations actually prove dimer formation, but typically a marked change of the investigated parameter (e.g. conductivity, excess molar volume, heat of mixing, and molar absorptivity) is found at the composition $M_2S_2O_7/V_2O_5 = 2/1$.[5–11] This may be interpreted as the formation of a dimer complex in solution. This paper describes the synthesis and the characterization of the dimeric V(V) compound $Cs_4(VO)_2O(SO_4)_4$, which could be isolated from the $Cs_2S_2O_7/V_2O_5$ system. Recently[8] the phase diagram of the $Cs_2S_2O_7/V_2O_5$ system has been constructed from conductivity measurements. A compound was formed at the molar ratio $Cs_2S_2O_7/V_2O_5 = 2$, but only very small crystals not suitable for X-ray structural investigation could be isolated. EDS analysis on this microcrystalline phase showed that the crystals with respect to Cs, S, and V had a composition, which combined with IR spectroscopy, led to the proposed formula $Cs_4(VO_2)_2(SO_4)_2S_2O_7$ for the compound. However, on the basis of the present investigation, this compound is certainly the stoichiometrically identical compound $Cs_4(VO)_2O(SO_4)_4$. This paper presents the first successful attempt to obtain the crystal structure of V(V) compounds that form in the catalyst model melt system $M_2S_2O_7/V_2O_5$ (M = Na, K or Cs).

Experimental Section

Synthesis of Crystalline $Cs_4(VO)_2O(SO_4)_4$. The compound was prepared by mixing $Cs_2S_2O_7$ and V_2O_5 in a sealed ampule. The hygroscopic $Cs_2S_2O_7$ was prepared by thermal decomposition of $Cs_2S_2O_8$ at 300 °C in N_2 and stored in sealed ampules. The latter compound is not commercially available and was therefore synthesized in the laboratory as described earlier.[8] V_2O_5 was from Cerac (pure, >99.9%). All handling of chemicals was done in a glovebox under nitrogen atmosphere that was dried continuously to approximately 5 ppm H_2O by molecular sieves. Cooling of the liquid $Cs_2S_2O_7/V_2O_5$ mixture with the composition $X_{V_2O_5} = 0.33$ corresponding to the molar ratio Cs/V = 2, found for the dimeric compound, led previously to a microcrystalline phase.[8] In order to grow larger crystals a mixture with the composition $X_{V_2O_5} = 0.251$ (i.e. inbetween the maximum of the phase diagram at $X_{V_2O_5} = 0.33$ and the eutectic at $X_{V_2O_5} = 0.168$) was used. Furthermore the starting temperature of the synthesis was chosen to be 380 °C, i.e. below the liquidus temperature of the mixture as judged from the phase diagram.[8] The temperature of this melt, containing a solid phase of V_2O_5, was gradually lowered to 350 °C during 3 days in steps of around 5 °C. Apparently, the small crystals of $Cs_2(VO)_2O(SO_4)_4$, initially formed at 380°C by a solid–solid transformation on V_2O_5(s), acted as centers of nucleation for the crystal growth during the slow cooling. The components for the synthesis were sealed in an ampule (Pyrex glass) under O_2 atmosphere (0.9 atm at room temperature) to prevent the autoreduction of V(V) to V(IV).[12] The ampule was placed in a kanthal wire wound transparent glass furnace regulated within ca. ±2 °C. From the final temperature of ~350 °C it was taken directly to room temperature. By inspection of the sample in the microscope, brownish yellow crystals could be isolated from an amorphous solid. The crystals appeared fairly stable in the atmosphere while the other part of the sample, dominated by the amorphous phase,

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

(2) Boreskov, G. K.; Polyakova, G. M.; Ivanov, A. A.; Mastikhin, V. M. *Dokl. Akad. Nauk SSSR* **1973**, *210*, 626; *Dokl. Akad. Nauk SSSR (Engl. Transl.)* **1973**, *210*, 423.

(3) Grydgaard, P.; Jensen-Holm, H.; Livbjerg, H.; Villadsen, J. *ACS Symp. Ser.* **1978**, *21*, 744.

(4) Balzhinimaev, B. S.; Ponomarev, V. E.; Boreskov, G. K.; Ivanov, A. A. *React. Kinet. Catal. Lett.* **1984**, *25*, 219.

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

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

(7) Hatem, G.; Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *J. Phys. Chem.* **1987**, *91*, 195.

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

(9) Bandur, V. A.; Eriksen, K. M.; Folkmann, G. E.; Hatem, G.; Fehrmann, R.; Bjerrum, N. J. To be submitted for publication.

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

(11) Hatem, G.; Fehrmann, R.; Gaune-Escard, M. To be submitted for publication.

(12) Abood, H. M. A.; Kerridge, D. H. *Thermochim. Acta* **1991**, *185*, 35.

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Table I. Crystallographic Data

formula: $Cs_4(VO)_2O(SO_4)_4$	fw = 1065.73
$a = 8.117(2)$ Å	space group $P\bar{1}$ (No. 2)
$b = 11.104(2)$ Å	$T = 18$ °C
$c = 11.799(2)$	$\lambda = 0.71069$ Å (Mo Kα)
$\alpha = 79.58(1)°$	$\mu = 84.08$ cm^{-1}
$\beta = 87.95(2)°$	abs cor: empirical
$\gamma = 75.61(2)°$	$R^a = 0.0276$
$V = 1013.06(40)$ Å^3	$R_w{}^b = 0.0348$
$Z = 2$ formula units/cell	$\rho_{calc} = 3.494$ g cm^{-3}

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

was attached over time. An irregularly shaped single crystal, 0.07 × 0.20 × 0.10 mm^3, completely covered with epoxy glue was selected for the X-ray investigation.

X-ray Investigation. Determination of the Crystal Structure. Intensity data with $\Theta \leq 25°$ and $h \geq 0$ were measured at 18 °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 20 high-order reflections. A total of 3560 independent reflections were reduced to 3012 reflections with $I \geq 2\sigma(I)$. The data were corrected for Lorentz and polarization effects, but not for extinction. Absorption correction was carried out by an empirical method,[13] where the crystal shape is approximated by an ellipsoid and the size (in units of μ^{-1}) and orientation is treated as parameters. The refinement of the six parameters is based on ψ-scans, in the present case ψ-scans on four reflections and their Friedel pairs. The quantity minimized was $R = \sum w(I_{obs} - I_{corr}A)^2$, where A is the absorption coefficient. The minimization problem consisted of 157 observations and six parameters and was accomplished by the SIMPLEX method.[14] The initial and final values of $R_w = (R/\sum wI_{obs}^2)^{1/2}$ are 0.1681 and 0.0304, 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 83.9 cm^{-1} was obtained, which is very close to the actual value of 84.08 cm^{-1}. The minimum and maximum transmission coefficients are 0.278 and 0.491, respectively.

The crystal structure was solved by Patterson and Fourier techniques, and the structural parameters were refined by full-matrix least-squares methods.[15] Crystal data are given in Table I. The final positional parameters are listed in Table II. Details on the data collection and the thermal parameters are available as supplementary material.

Discussion

The unit cell contains two separate $(VO)_2O(SO_4)_4{}^{4-}$ ions. The geometric arrangement of such an ion is shown in Figure 1. Each ion has two V atoms with distorted octahedral coordination including two bidentate chelate sulfate ligands and a short V=O bond. A *cis*-positioned oxygen atom—O(16)—is bridging the two octahedra, with a V—O—V angle of 165.3°, and a V—V distance of 3.512 Å. On the basis of the two planes defined by O=V(1)—O(16) and O=V(2)—O(16), the octahedra are twisted 129.1° relatively to each other. The two octahedra are not entirely geometrically identical as indicated by the V–O bond lengths and angles given in Tables III and IV.

Table V gives all bond angles and distances for the four sulfate groups of the dimeric complex. The sulfate groups are bidentate chelate coordinated to vanadium by only two oxygen atoms, leaving the other two uncoordinated. The two sulfate groups that coordinate in the equatorial *cis*-positions are considerably distorted, the O–S–O angle being only ~97 °—far from the tetrahedral angle of 109.5°. For the other two sulfate groups coordinated to the *cis* and *trans* positions of the V=O group, the distortion is less severe, the O—S—O angle is ~101°. However, these latter groups shows unusual long S–O bonds (to the *trans* position) (1.58 Å)—far from the usual value of 1.47 Å found for sulfate groups.[16] A plot of the O–S distances versus the average of the three angles involving this bond is shown in Figure 2 together with the least-squares line obtained previously[17] on the combined data for the compounds $NaV(SO_4)_2$, $K_4(VO)_3(SO_4)_5$, and $Na_2VO(SO_4)_2$.[17-19] The regression line for the points is close to the previous line, except for the two very long S–O distances. These latter points have been omitted in the calculation of the regression line. This discrepancy from linearity is possibly due

Table II. Coordinates of the Atoms in $Cs_4(VO)_2O(SO_4)_4{}^a$

atom	x/a	y/b	z/c	U_{eq},[b] Å^2
Cs(1)	0.18336(5)	–0.19171(4)	0.10014(3)	0.030
Cs(2)	–0.04128(5)	0.30785(4)	0.49421(3)	0.031
Cs(3)	0.46963(5)	0.22716(4)	0.58981(3)	0.032
Cs(4)	0.24135(5)	0.28087(4)	0.11074(3)	0.033
V(1)	0.3413(1)	0.58530(9)	0.81556(8)	0.020
V(2)	0.2745(1)	0.91135(9)	0.71461(8)	0.019
S(1)	–0.0725(2)	0.9671(1)	0.6852(1)	0.022
S(2)	0.6105(2)	0.5127(1)	0.6718(1)	0.021
S(3)	0.1337(2)	0.4418(1)	0.7883(1)	0.026
S(4)	0.3260(2)	1.0506(1)	0.8646(1)	0.023
O(1)	0.2297(5)	1.0881(4)	0.7502(3)	0.022
O(2)	0.5776(5)	0.5278(4)	0.8015(3)	0.025
O(3)	0.1085(5)	0.5857(4)	0.7705(3)	0.024
O(4)	0.2145(6)	1.0813(4)	0.9575(4)	0.036
O(5)	0.0015(6)	0.9242(4)	0.8014(3)	0.030
O(6)	0.4361(5)	0.5524(4)	0.6252(3)	0.028
O(7)	0.6902(6)	0.3814(4)	0.6721(4)	0.031
O(8)	0.3169(5)	0.4065(4)	0.8298(4)	0.028
O(9)	0.3727(5)	0.9079(4)	0.8673(3)	0.026
O(10)	0.4241(6)	0.9234(5)	0.6269(4)	0.037
O(11)	0.0937(5)	0.9609(4)	0.6104(3)	0.025
O(12)	–0.1683(6)	1.0969(4)	0.6659(4)	0.034
O(13)	0.7152(6)	0.5968(5)	0.6246(4)	0.040
O(14)	0.0235(6)	0.4006(5)	0.8767(4)	0.045
O(15)	0.4741(6)	1.0995(5)	0.8573(4)	0.039
O(16)	0.3050(6)	0.7449(4)	0.7484(4)	0.036
O(17)	–0.1609(6)	0.8817(5)	0.6508(4)	0.037
O(18)	0.1209(6)	0.4037(5)	0.6800(4)	0.038
O(19)	0.3354(6)	0.5948(5)	0.9474(4)	0.045

[a] The temperature factor parameters are given in the supplementary material. [b] $U_{eq} = {}^1/_3\sum U_{ij}a_i^*a_j^*\,\mathbf{a}_i\cdot\mathbf{a}_j$.

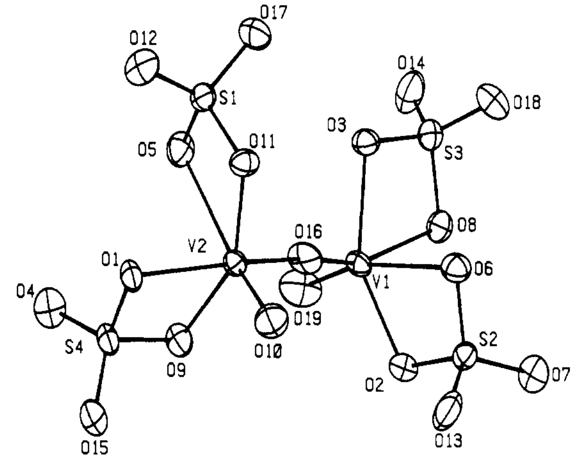

Figure 1. Plot of the structure of the $(VO)_2O(SO_4)_4{}^{4-}$ ion.

Table III. V–O Distances (Å)[a]

V(1)–O		V(2)–O	
O(19)	1.577	O(10)	1.583
O(16)	1.762	O(16)	1.775
O(2)	1.877	O(11)	1.858
O(3)	1.980	O(9)	1.987
O(8)	2.020	O(1)	2.024
O(6)	2.409	O(5)	2.390

[a] Esd = 0.004 Å.

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(13) Nielsen, K. To be submitted for publication.

(14) Nelder, J. A.; Mead, R. *Comput. J.* **1964–1965**, *7*, 308.

(15) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; University of Göttingen: Göttingen, FRG 1976.

(16) Renner, B.; Lehmann, G. *Z. Kristallogr. Kristallgeom., Kristallphys., Kristallchem.* **1986**, *175*, 43.

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

Table IV. O–V–O Angles (deg)[a]

O(2)–V(1)–O(3)	149.5	O(11)–V(2)–O(9)	150.9
O(2)–V(1)–O(6)	65.2	O(11)–V(2)–O(5)	65.7
O(2)–V(1)–O(8)	90.0	O(11)–V(2)–O(1)	91.1
O(2)–V(1)–O(16)	102.0	O(11)–V(2)–O(16)	103.0
O(2)–V(1)–O(19)	98.4	O(11)–V(2)–O(10)	98.8
O(3)–V(1)–O(6)	89.0	O(9)–V(2)–O(5)	89.4
O(3)–V(1)–O(8)	69.7	O(9)–V(2)–O(1)	69.5
O(3)–V(1)–O(16)	89.3	O(9)–V(2)–O(16)	89.4
O(3)–V(1)–O(19)	106.8	O(9)–V(2)–O(10)	104.5
O(6)–V(1)–O(8)	82.3	O(5)–V(2)–O(1)	81.1
O(6)–V(1)–O(16)	81.8	O(5)–V(2)–O(16)	86.4
O(6)–V(1)–O(19)	163.6	O(5)–V(2)–O(10)	164.1
O(8)–V(1)–O(16)	153.7	O(1)–V(2)–O(16)	155.3
O(8)–V(1)–O(19)	98.8	O(1)–V(2)–O(10)	96.4
O(16)–V(1)–O(19)	102.3	O(16)–V(2)–O(10)	101.2

[a] Esd = 0.2°.

Table V. Bond Distances (Å) and Angles (deg) of the Sulfate Groups in $Cs_4(VO)_2O(SO_4)_4$

S(1)–O(5)	1.466(4)	O(5)–	S(1)–	O(11)	100.7(2)
O(11)	1.579(4)	O(5)–	S(1)–	O(12)	113.0(3)
O(12)	1.440(4)	O(5)–	S(1)–	O(17)	113.3(3)
O(17)	1.441(5)	O(11)–	S(1)–	O(12)	107.0(3)
		O(11)–	S(1)–	O(17)	107.7(3)
		O(12)–	S(1)–	O(17)	113.9(3)
S(2)–O(2)	1.576(4)	O(2)–	S(2)–	O(6)	101.0(2)
O(6)	1.469(4)	O(2)–	S(2)–	O(7)	106.8(2)
O(7)	1.440(4)	O(2)–	S(2)–	O(13)	106.8(3)
O(13)	1.440(5)	O(6)–	S(2)–	O(7)	113.5(3)
		O(6)–	S(2)–	O(13)	113.6(3)
		O(7)–	S(2)–	O(13)	113.8(3)
S(3)–O(3)	1.535(4)	O(3)–	S(3)–	O(8)	96.9(2)
O(8)	1.516(4)	O(3)–	S(3)–	O(14)	110.8(3)
O(14)	1.435(5)	O(3)–	S(3)–	O(18)	109.9(3)
O(18)	1.431(5)	O(8)–	S(3)–	O(14)	111.5(3)
		O(8)–	S(3)–	O(18)	111.0(3)
		O(14)–	S(3)–	O(18)	115.2(3)
S(4)–O(1)	1.522(4)	O(1)–	S(4)–	O(4)	110.9(3)
O(4)	1.431(4)	O(1)–	S(4)–	O(9)	97.0(2)
O(9)	1.530(4)	O(1)–	S(4)–	O(15)	110.8(3)
O(15)	1.431(5)	O(4)–	S(4)–	O(9)	110.3(3)
		O(4)–	S(4)–	O(15)	115.0(3)
		O(9)–	S(4)–	O(15)	111.5(3)

to the breakdown of the hypothesis[18] of an sp^3-hybridization of the sulfur atom of those two sulfate groups.

To our knowledge, $Cs_4(VO)_2O(SO_4)_4$ is the first published structure of a vanadium compound with bidentate chelate coordination of sulfate ligands.

Analysis of the Geometry of the $(VO)_2O(SO_4)_4^{4-}$ ion. The halves of the $(VO)_2O(SO_4)_4^{4-}$ ion almost coincide if the V(2) half is translated to V(1) and the atoms are inverted through V(2) and rotated as to obtain the minimum of the sum of squared distances between related atoms. The root mean square distance is 0.086 Å. The bridging oxygen atom [O(16)] and the vanadyl oxygen atoms [O(10), O(19)] are responsible for ~44% of the sum of squared distances. Similar examinations of the sulfate groups show that these are almost pairwise identical, the maximum distance being ~3 times the standard deviation of the S–O distance. It may be concluded that the major differences between the halves are found between the vanadium coordination spheres.

IR Spectra. The part of the solidified sample used for IR spectroscopy in KBr was examined in the microscope. The amorphous phase (probably the frozen eutectic) and the brownish yellow microcrystalline phase gave two very different IR spectra. The spectrum of the crystalline phase was essentially identical to the spectrum obtained earlier[8] although minor bands of the amorphous solid also were present. It is therefore obvious that we are dealing with the same compound, which should be formulated as $Cs_4(VO)_2O(SO_4)_4$ and not $Cs_4(VO_2)_2(SO_4)_2S_2O_7$. The IR spectrum given previously[8] should therefore be attributed to $Cs_4(VO)_2O(SO_4)_4$. The IR spectrum shows SO_4^{2-} ν_3 bands shifted to unusual high wavenumbers. Previously[8,20] these bands were attributed to coordinated $S_2O_7^{2-}$ since $Cs_2S_2O_7$ is known to have bands in this region. This led to the erroneous formula showing pyrosulfate being present in the compound. However, the strong distortion of the SO_4^{2-} groups found in the crystal may cause the unusual large shifts observed. Also the double oxo-bridged structure of the K analogue suggested earlier[6] seems less likely based on the present investigation. Attempts to prepare crystals of the K salt have however not succeeded yet.

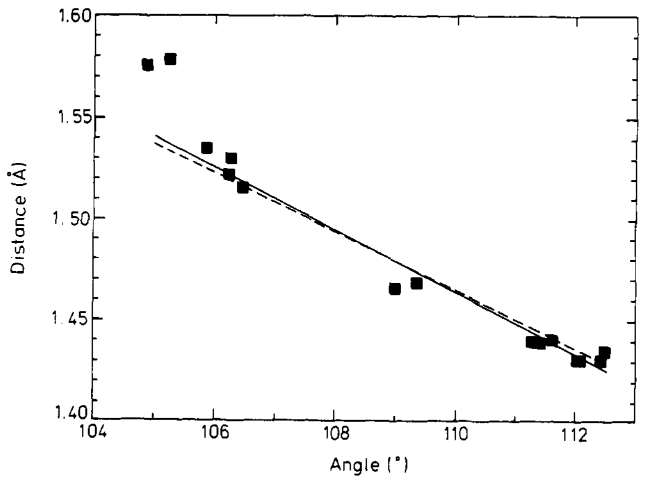

Figure 2. Plot of the S–O distances versus the average of the O–S–O angles involving this bond and the other three S–O bonds of the sulfate tetrahedron. The full line is a regression line for $Cs_4(VO)_2O(SO_4)_4$ where the two long S–O bonds have been omitted from the regression. The dashed line is an average for the compounds $Na_2VO(SO_4)_2$, $K_4(VO)_3(SO_4)_5$, and $NaV(SO_4)_2$ taken from ref 17.

Comparison of the Structure to other Binuclear V(V) Compounds. Only a few binuclear compounds of V(V) containing the $(VO)_2O$ unit seem to be known. None of them contain purely inorganic ligands except for the peroxo compound $(NH_4)_4[(VO(O_2))_2O]$.[21] This contains however a heptacoordinated vanadium complex, and it cannot be structurally compared to the compounds of Table VI where the published analogue structures are represented by bond distances and angles characteristic of the octahedral coordination. During the reviewing of this paper our attention has been attracted to a very recent paper,[27] describing the crystal structure of the binuclear compound $V_2O_3(SO_4)_2$. The characteristic features of this compound has been included in Table VI. For comparison our compound, $Cs_4(VO)_2O(SO_4)_4$, is also given. It can be seen that very similar features are found for all the compounds except for the V–O–V angle of the oxide bridge, which varies between 148 and 180°. The smallest V–O–V angle is found in $V_2O_3(SO_4)_2$ possibly due to the additional bridging of two SO_4^{2-} groups between the vanadium atoms. As in $Cs_4(VO)_2O(SO_4)_4$, the SO_4^{2-} ν_3 bands in the vibrational spectra

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

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

(20) Glazyrin, M. P.; Krasil'nikov, V. N.; Ivakin, A. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1982**, *27*, 1740.

(21) Stomberg, R.; Olson, S.; Svensson, I.-B. *Acta Chem. Scand.* **1984**, *A38*, 653.

(22) Casselato, V.; Vigato, P. A.; Graziani, R.; Vidali, M.; Milani, F.; Musiani, M. M. *Inorg. Chim. Acta.* **1982**, *61*, 121.

(23) Yamada, S.; Katayama, C.; Tanaka, J.; Tanaka, M. *Inorg. Chem.* **1984**, *23*, 253.

(24) Knopp, P.; Wieghart, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363.

(25) Saussine, L.; Mimoun, H.; Mitschler, A.; Fisher, J. *Nouv. J. Chim.* **1980**, *4*, 253.

(26) Diamantis, A. A.; Frederiksen, J. M.; Abdus-Salam, M.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1986**, *61*, 121.

(27) Richter, K.-L.; Mattes, R. *Z. Anorg. Allg. Chem.* **1992**, *611*, 158.

Table VI. Hexacoordinated V(V) Compounds Containing the $(VO)_2O$ Unit[a]

	$D[(VOL)_2O]_2$[b]	$[(VOL_2)_2O]$[d]	$[(VOL(OH))_2O](ClO_4)_2$[e]	$[(VOL_2)_2O]$[f]	$[(VOL)_2O]$[g]	$V_2O_3(SO_4)_2$[h]	$Cs_4[(VO)_2O(SO_4)_4]$[i]
V═O, Å	1.56	1.59	1.61	1.59	1.57	1.57	1.58
$V—O_{br}$, Å	1.79	1.78	1.81	1.81	1.78	1.78	1.77
$(O═V)—L_{tr}$, Å	2.51	2.31	2.33	2.08		2.33	2.40
$(O_{br}—V)—L_{tr}$, Å	2.16[c]	2.20	2.25	1.87	2.08	1.97	2.03
$V—L_{eq}$, Å	1.83, 2.17	1.89, 1.93	1.78, 2.22	1.86, 2.08	1.83, 1.89	1.95, 1.96	1.86, 1.99
$V—O_{br}—V$, deg	156	173.4	180	154.3	180.0	148.4	165.3
$O═V—O_{br}$, deg	106	105.7	103.3	117.7	109.2	98.2	101.2

[a] Key: br, bridging; eq, equatorial; tr, trans. Averaged distances for the two V octahedra are given. [b] H_2L = 2-(2′-hydroxyphenyl)iminomethylphenol; D = Dioxan.[22] [c] L_{tr} = Dioxan. [d] HL = 8-quinolinol.[23]. [e] L = 1,4,7-trimethyl-1,4,7-triazacyclononane.[24] [f] HL = *N*,*N*-diethylhydroxyamine.[25] [g] H_2L = *N*′-(1-methyl-3-oxo-3-phenylpropylidene)benzohydrazide.[26] [h] Reference 27. [i] This work.

of $V_2O_3(SO_4)_2$ and in the oxosulfatovanadates $KVO(SO_4)_4$, $NH_4VO(SO_4)_2$,[27] and $K[VO_2(SO_4)(H_2O)_2]\cdot H_2O$[28] were split widely and shifted to high wavenumbers, i.e. ~1300 cm^{-1}. This is in accordance with the strong distortion of the SO_4^{2-} groups also found in these compounds.

Relation of the Structure to the Reaction Mechanism. It is likely that the strained coordination of the sulfate ligands may break in solution at catalytically relevant temperatures (above 400 °C) in such a way that the ligands becomes only monodentate, leaving the complex coordinatively unsaturated. Such a species is the initial component in the mechanism, proposed by Balzhinimaev et al.[29] In this mechanism the μ-O of a suggested dimeric V(V) complex is attacked by SO_2 while O_2 is bridging with both oxygen atoms—one on each octahedral V atom. Two electrons are transferred to the O_2 ligand from SO_2, oxidizing S(IV) to S(VI). The resulting O_2^{2-} ligand is then attacked by another SO_2 and two SO_3 molecules are released whereby the initial complex is reestablished. However, although the present compound can be transformed into the needed initial species in the mechanism, it cannot coordinate O_2 as required. Assuming that (1) the V—O—V angle is almost unaffected by the SO_2 coordination to the μ-O, (2) the (μ-O)—V distance remains 1.77 Å, (3) the O═O distance is 1.208 Å (as in the gas phase), and (4) the V atoms remain in octahedral coordination, the $V—O_2$ distance would have to be ~9 Å. In order to get an acceptable $V–O_2$ bond distance, the V–O–V angle must decrease to ~121°. If SO_2 is coordinated in a similar way (bridging), the angle has to decrease to 151°—assuming a S–O distance of 1.432 Å and a S–O angle of 119.5° as observed for SO_2 in the gas phase. This possibility is supported by the structure[27] of $V_2O_3(SO_4)_2$, where the bidentate bridging of SO_4^{2-} groups are obtained together with an O^{2-} bridge with a V–O–V angle of 148.4°. Consequently, SO_2 rather than O_2 coordination seems much more likely in $(VO)_2O(SO_4)_4^{4-}$, since it leads to much less strain in the V–O–V bridge. A strong coordination of SO_2 to V(V) complexes without reduction to V(IV) or V(III) seems to take place in the melt judged from ongoing spectroscopic investigations.[30]

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Supplementary Material Available: Tables A and B, listing, respectively, all crystallographic data and the thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(28) Richter, K.-L.; Mattes, R. *Inorg. Chem.* **1991**, *30*, 4367.

(29) Balzhinimaev, B. S.; Ivanov, A. A.; Lapina, O. B.; Mastikhin, V. M.; Zamaraev, K. I. *Faraday Discuss. Chem. Soc.* **1989**, *87*, 227.

(30) Work in progress.