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# Synthesis and Characterization of New Oxidopolysulfidovanadates

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The alkali-metal oxidopolysulfidovanadates $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**), $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**), and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**) have been synthesized by means of methanothermal methods at 170 °C or 175 °C. These compounds each contain a $V^{5+}$ ion coordinated by an oxo ligand and two $\eta^2\text{-}S_2{}^{2-}$ groups. In **I**, two such $[VO(\eta^2\text{-}S_2)_2]^-$ units are bridged by an $S_2{}^{2-}$ unit. In **II** and **III**, two such $[VO(\eta^2\text{-}S_2)_2]^-$ units are joined by a V−S−V bond to form $[(VO(\eta^2\text{-}S_2)_2)_2]^{2-}$ units; in **II**, such a $[(VO(\eta^2\text{-}S_2)_2)_2]^{2-}$ unit is bridged to a $[VO(\eta^2\text{-}S_2)_2]^-$ unit by an $S_4{}^{2-}$ group; in **III**, two such $[(VO(\eta^2\text{-}S_2)_2)_2]^{2-}$ units are bridged by an $S_3{}^{2-}$ group. Crystallographic data at $T = 153$ K (compound, space group, $Z$, $a$, $b$, $c$, $\beta$): **I**, $P2_1/n$, 2, 7.4366(3), 10.3743(5), 13.1151(6) Å, 101.097(1)°; **II**, $P2_1/c$, 4, 8.4451(6), 24.5144(18), 14.0995(10) Å, 101.325(1)°; **III**, $C2/c$, 4, 31.037(3), 12.5355(11), 8.7822(8) Å, 93.127(2)°.

## Introduction

Polychalcogenometalates are a remarkably diverse group of anions, both structurally and in their method of synthesis, which ranges from solution to solid-state to solvothermal.[1−5] The oxidopolychalogenometalates are an interesting subgroup. These are formed by oxyphilic metals, such as Ti, V, and Mo. Examples include $[Ti_6OS_8(S_2)_6]^{6-}$,[6] $[V_2O_2(\eta^2\text{-}Se_2)(\eta^2\text{-}Se_4)Se_2]^{4-}$,[7] $[V_2O_2(\eta^2\text{-}Se_4)_2]^{4-}$,[7] $[[(S_2)OMo(\mu\text{-}S)_2MoO(S_4)]^{2-}$,[5] and $[(\eta^2\text{-}S_2)OMo(\mu\text{-}S)]_2{}^{2-}$.[8] Although a number of oxidopolysulfidomolybdates are known,[9] few oxidopolysulfidotitanates or oxidopolysulfidovanadates have been reported. Here we present the synthesis and characterization of the three new oxidopolysulfidovanadates $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**), $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**), and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**) prepared by methanothermal methods.

## Experimental Details

**Syntheses.** The following reagents were used as obtained: $V_2O_5$ (Fisher, 99.9%), $VO_2$ (Aldrich, 99.9%), S (Mallinckrodt, 99.6%), Cs (Strem, 99.9%), and K (Aldrich, 98%). $Cs_2S_3$ and $K_2S$ were prepared by the stoichiometric reactions of the elements in liquid $NH_3$.

A reaction mixture was loaded into a fused-silica tube under an Ar atmosphere in a glovebox. Then, 0.4 mL of $CH_3OH$ was added via syringe. The tube was frozen, evacuated to $\sim 10^{-3}$ Torr, flame-sealed, and thawed. It was then loaded into a high-pressure autoclave along with 1700 mL of $CH_3OH$ to counter the pressure. The autoclave was heated at 170 °C (175 °C for **II**) for 3 days and then cooled to room temperature. The solid products were recovered by suction filtration and washed with methanol. Red crystals of the reported materials were obtained in 40−50% yields. Examination of these crystals with an EDX-equipped Hitachi S-3500 SEM gave results consistent with the stated compositions.

$Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**) and $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**) were obtained from the reaction of $V_2O_5$ (0.0197 g, 0.10 mmol) and $Cs_2S_3$ (0.054 g, 0.15 mmol). $K_6(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)\cdot 2CH_3OH\cdot 0.6H_2O$ was obtained from reaction of $VO_2$ (0.017 g, 0.20 mmol), $K_2S$ (0.044 g, 0.40 mmol), and S (0.0032 g, 0.10 mmol).

**Crystallography.** Single-crystal X-ray diffraction data were collected with the use of the program SMART[10] on a Bruker Smart 1000 CCD diffractometer[10] at 153 K. Monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) was employed. The diffracted intensities generated by a scan of 0.3° in $\omega$ were recorded on four sets of 606 frames at $\varphi$ settings of 0, 90, 180, and 270°. The exposure times were 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT.[10] Face-indexed absorption corrections were made with the program XPREP.[11] Then, the program SADABS was employed to make incident beam and decay corrections.[10] The structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with the program SHELXL in the SHELXTL-97 suite.[11] Crystallographic details are given in Table 1 and in Supporting Information.

## Result and Discussion

**Syntheses.** The methanothermal syntheses of $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**), $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**), and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**) are reproducible. The starting materials and procedures for the syntheses of **I** and **II** are the same except for the temperature of 170(1)°C used for **I** and 175(1)°C used for **II**. That small temperature differences affect the products formed in solvothermal reactions has been previously noted.[12,13] As one example, the compounds $Cs_2Te_{13}$, $Cs_2Te_5$, $Cs_4Te_{28}$, and $Cs_3Te_{22}$ are produced in varying proportions

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(1) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223−266.

(2) Ansari, M. A.; McConnachie, J. M.; Ibers, J. A. *Acc. Chem. Res.* **1993**, *26*, 574−578.

(3) Young, D. M.; Schimek, G. L.; Kolis, J. W. *Inorg. Chem.* **1996**, *35*, 7620−7625.

(4) Sheldrick, W. S.; Wachhold, M. *Coord. Chem. Rev.* **1998**, *176*, 211−322.

(5) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349−356.

(6) Huang, F. Q.; Ibers, J. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2515−2516.

(7) Liao, J.-H.; Hill, L.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, *32*, 4650−4652.

(8) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476−5477.

(9) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1989**, *28*, 2169−2177.

(10) *SMART*, Version 5.054 Data Collection, and *SAINT-Plus*, Version 6.02A Data Processing Software for the SMART System; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.

(11) Sheldrick, G. M. *SHELXTL* DOS/Windows/NT Version 5.10; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1997.

(12) Korzenski, M. B. Ph.D. Dissertation, Clemson University, Clemson, SC, 1998.

(13) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206−224.

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**Table 1.** Crystal Data and Structure Refinements for $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**), $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**), and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**)

| compound | I | II | III |
|---|---|---|---|
| fw | 986.12 | 1378.33 | 1186.39 |
| space group | $P2_1/n$ | $P2_1/c$ | $C2/c$ |
| $a$, (Å) | 7.4366(3) | 8.4451(6) | 31.047(3) |
| $b$, (Å) | 10.3743(5) | 24.5144(18) | 12.5355(11) |
| $c$, (Å) | 13.1151(6) | 14.0995(10) | 8.7822(8) |
| $\beta$, (deg) | 101.097(1) | 101.325(1) | 93.127(2) |
| $V$, (Å$^3$) | 992.91(8) | 2862.1(4) | 3412.9(5) |
| Z | 2 | 4 | 4 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $T$, (K) | 153 | 153 | 153 |
| $\rho_c$, (g cm$^{-3}$) | 3.298 | 3.199 | 2.309 |
| $\mu$, (cm$^{-1}$) | 92.1 | 84.0 | 29.8 |
| $R(F)^a$ | 0.0195 | 0.0433 | 0.0412 |
| $R_w(F^2)^b$ | 0.0460 | 0.105 | 0.120 |

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$ for all data, where $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

between 150 and 180 °C.[14] In the present instance, the temperature difference is very small, but there is no visual evidence for the formation of mixtures of **I** and **II**; crystals of **I** are large red parallelepipeds of equant habit whereas crystals of **II** are needles.

Given the stoichiometry of the reaction and the yield of product, the water of crystallization in **III** requires not more than about 0.1% $H_2O$ in the $CH_3OH$.

**Structures.** The crystal structures of $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**), $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ (**II**), and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**) comprise well-separated cations and anions. In this latter compound, hydrogen atoms on the oxygen atom (O4) of the water molecule form a hydrogen-bonding network with the O1 atom of the V=O group, with the O4−H···O1 distances being 3.014(7) and 3.119(4) Å. Because the position of the water molecule is not fully occupied, this network need not be continuous.

In these compounds, each anion contains a $V^{5+}$ ion coordinated by an oxo ligand and two $\eta^2\text{-}S_2^{2-}$ groups to form a $[VO(\eta^2\text{-}S_2)_2]^-$ unit. The oxide analogue, $[VO(\eta^2\text{-}O_2)_2]^-$, can be found in the $[(\mu\text{-}O(VO(\eta^2\text{-}O_2)_2)_2]^{4-}$ anion.[15] In **I**, two such $[VO(\eta^2\text{-}S_2)_2]^-$ units are bridged by a $\mu\text{-}S_2^{2-}$ unit (Figure 1). In **II** and **III**, two such $[VO(\eta^2\text{-}S_2)_2]^-$ units are joined by a V−S−V bond to form $[(VO(\eta^2\text{-}S_2)_2)_2]^{2-}$ units; in **II**, such a $[(VO(\eta^2\text{-}S_2)_2)_2]^{2-}$ unit is bridged to a $[VO(\eta^2\text{-}S_2)_2]^-$ by a $\mu\text{-}S_4^{2-}$ group (Figure 2); in **III**, two such $[(VO(\eta^2\text{-}S_2)_2)_2]^-$ units are bridged by a $\mu\text{-}S_3^{2-}$ group (Figure 3). The anion in $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ (**I**) has crystallographically imposed $\bar{1}$ symmetry; the anion in $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ (**III**) has crystallographically imposed 2 symmetry. The $V^{5+}$ centers in these compounds are in distorted tetrahedral environments comprising the oxo ligand, the bridging S atom, and the centers of the two $\eta^2\text{-}S_2^{2-}$ ligands.

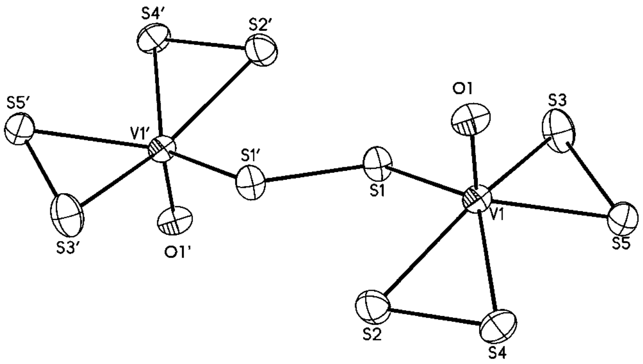

**Figure 1.** The $[(VO)_2(\eta\text{-}S_2)_4(\mu\text{-}S_2)]^{4-}$ anion in $Cs_4[(VO)_2(\eta\text{-}S_2)_4(\mu\text{-}S_2)]$. Here and in succeeding figures, the 70% probability displacement ellipsoids are shown.

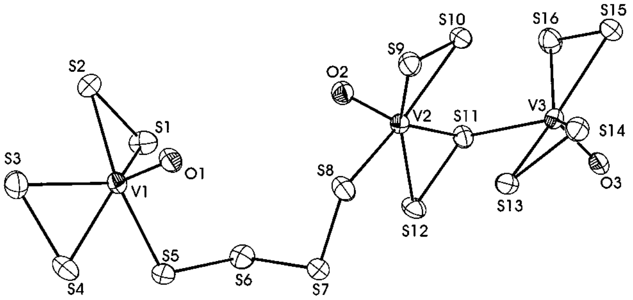

**Figure 2.** The $[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_2)2]^{5-}$ anion in $Cs_5[(VO)_3(\eta\text{-}S_2)_6(\mu\text{-}S_4)]$.

Table 2 provides selected bond distances. These distances are normal and show minimal variations among the three compounds. Thus, the V−S distances range from 2.315(2) to 2.4813(14) Å, compared with 2.284(2) and 2.288(1) Å in Cp*-

**Table 2.** Selected Bond Lengths (Å) for $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$, $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$, and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$

| | | | | | |
|---|---|---|---|---|---|
| | | $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$ | | | |
| V(1)−O(1) | 1.618(2) | V(1)−S(1) | 2.3734(9) | S(1)−S(1) | 2.1044(14) |
| V(1)−S(5) | 2.3257(9) | V(1)−S(4) | 2.3912(9) | S(2)−S(4) | 2.0662(11) |
| V(1)−S(2) | 2.3385(9) | V(1)−S(3) | 2.3975(9) | S(3)−S(5) | 2.0653(12) |
| | | $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$ | | | |
| V(1)−O(1) | 1.598(5) | V(2)−S(9) | 2.380(2) | S(1)−S(2) | 2.055(3) |
| V(1)−S(1) | 2.315(2) | V(2)−S(11) | 2.392(2) | S(3)−S(4) | 2.044(3) |
| V(1)−S(3) | 2.334(2) | V(2)−S(8) | 2.430(2) | S(5)−S(6) | 2.087(3) |
| V(1)−S(4) | 2.373(2) | V(3)−O(3 | 1.625(5) | S(6)−S(7) | 2.063(3) |
| V(1)−S(2) | 2.415(2) | V(3)−S(13) | 2.344(2) | S(7)−S(8) | 2.066(3) |
| V(1)−S(5) | 2.422(2) | V(3)−S(14) | 2.351(2) | S(9)−S(10) | 2.050(3) |
| V(2)−O(2) | 1.626(5) | V(3)−S(15) | 2.361(2) | S(11)−S(12) | 2.062(3) |
| V(2)−S(10) | 2.350(2) | V(3)−S(16) | 2.380(2) | S(13)−S(14) | 2.060(3) |
| V(2)−S(12) | 2.358(2) | V(3)−S(11) | 2.473(2) | S(15)−S(16) | 2.086(3) |
| | | $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$ | | | |
| V(1)−O(1) | 1.619(3) | V(2)−O(2) | 1.605(3) | S(1)−S(2) | 2.0548(16) |
| V(1)−S(2) | 2.3370(14) | V(2)−S(6) | 2.3415(13) | S(3)−S(4) | 2.0576(16) |
| V(1)−S(1) | 2.3487(14) | V(2)−S(8) | 2.3646(14) | S(5)−S(6) | 2.0623(16) |
| V(1)−S(4) | 2.3885(14) | V(2)−S(5) | 2.3661(14) | S(7)−S(8) | 2.0646(17) |
| V(1)−S(3) | 2.3946(14) | V(2)−S(7) | 2.3954(14) | S(9)−S(10) | 2.0604(14) |
| V(1)−S(9) | 2.4251(13) | V(2)−S(4) | 2.4813(14) | | |

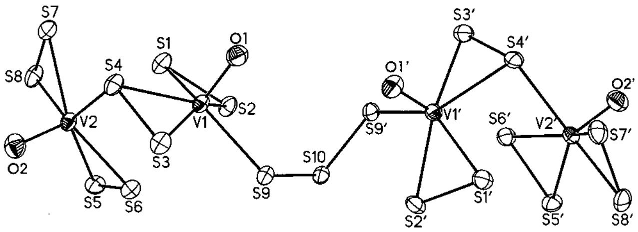

**Figure 3.** The $[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]^{6-}$ anion in $K_6[VO)_4(\eta\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$.

$VO(S_5)$;[16] the S−S distances range from 2.044(3) to 2.1044(14) Å, which is within the normal range for polysulfides;[17] the V═O distances range from 1.598(5) to 1.619(3) Å and are at the centroid of a recent histogram of such vanadyl V═O bonds.[18] The V═O bond length in compound **III** is unaffected by the hydrogen bonding.

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**Supporting Information Available:** Crystallographic files in CIF format for $Cs_4[(VO)_2(\eta^2\text{-}S_2)_4(\mu\text{-}S_2)]$, $Cs_5[(VO)_3(\eta^2\text{-}S_2)_6(\mu\text{-}S_4)]$, and $K_6[(VO)_4(\eta^2\text{-}S_2)_8(\mu\text{-}S_3)]\cdot 2CH_3OH\cdot 0.6H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Sheldrick, W. S.; Wachhold, M. *J. Chem. Soc., Chem. Commun.* **1996**, 607−608.

(15) Stomberg, R.; Olson, S.; Svensson, I.-B. *Acta Chem. Scand., Ser. A* **1984**, *38*, 653−656.

(16) Heberhold, M.; Kuhnlein, M.; Ziegler, M. L.; Nuber, B. *J. Organomet. Chem.* **1988**, *349*, 131−141.

(17) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89−122.

(18) Schindler, M.; Hawthorne, F. C.; Baur, W. H. *Chem. Mater.* **2000**, *12*, 1248−1259.