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Synthesis and molecular structure of $[Cp'_2V(\mu\text{-}S)_2VCp']_2(\mu\text{-}O)$ [1]

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Abstract

$[Cp'_2V(\mu\text{-}S)_2VCp']_2(\mu\text{-}O)$ (**4**) ($Cp' = \eta^5\text{-}CH_3C_5H_4$) was isolated from the reaction of the Na-reduced form of *cyclo*$(CH_3AsS)_{3,4}$ (**1**) and Cp'_2VCl_2 in THF at room temperature. The molecular structure was determined by single-crystal X-ray diffraction. The molecule consists of two oxygen-bridged $Cp'_3V_2S_2$ units. The oxygen-bonded vanadium atoms have each lost one Cp′ group in a reaction that is assumed to be the hydrolysis of $Cp'_2V(\mu\text{-}S)_2VCp'Cl$ (**3**) to give the product (**4**). The most striking structural feature of the molecule is the presence of asymmetrical V–S bond distances; the V–S distances for the oxygen-bonded vanadium atoms are considerably shorter (2.17–2.21 Å) than those for the all-sulfur bridged vanadium atoms (2.36–2.39 Å). The complex is diamagnetic, as was found from its ^1H NMR spectrum, which can be explained either by the presence of a V(IV)–V(IV) bond or the presence of mixed oxidation states as V(III) and V(V). © 1997 Elsevier Science S.A.

Keywords: Vanadium; Cyclopentadienyls; Sulfur complexes

1. Introduction

In our continuing effort to explore the similarities and differences between the isolobal S and RE (E = pnicogen) groups in cluster chemistry, we have borrowed reactions from the much more extensively studied sulfur chemistry as an entry to the related group-15 chemistry. One such area consists of reactions of a metallocene halide with lithium or sodium polysulfide (Li_2S_n, Na_2S_n) to form typically *cyclo*-metallopolysulfides, e.g. Cp_2MS_5 (M = group 4 or 5 metal). [1–5]. To facilitate our work, we have substituted either homocatenated $Na_2(RE)_n$ or heterocatenated $Na_2(RE)_mS_n$, prepared from sodium and the appropriate homoatomic or heteroatomic ring systems, for the polysulfide. Accordingly, in an attempt to synthesize $Cp'_2VS_n(MeAs)_m$ (**2**) ($n + m = 5$) from the reaction of the sodium reduced form of *cyclo*-$(CH_3AsS)_{3,4}$ [6] (**1**) and Cp'_2VCl_2 [2] ($Cp' = \eta^5\text{-}C_5H_4Me$), which was modeled after similar reactions that produce the all-sulfur analogue Cp_2VS_5 [1,2], we have isolated $[Cp'_2V(\mu\text{-}S)_2VCp']_2(\mu\text{-}O)$ (**4**). It is likely that one of the initial reaction products was $Cp'_2V(\mu\text{-}S)_2VCp'Cl$ (**3**) [7] which was subsequently hydrolyzed during attempted purification on alumina to give the product **4** (see Scheme 1).

2. Results and discussion

Compound **4** crystallizes as three chemically identical, but crystallographically independent, molecules without close contacts. The molecule of **4** consists of two oxo-bridged divanadium di(μ)sulfido units, $Cp'_3V_2S_2$, bearing three Cp′ groups (see Fig. 1). The oxygen-bonded vanadium atoms, V(2) and V(3), each carry one Cp′ ligand, while the all-sulfur bridged vanadium atoms V(1) and V(4) retain both Cp′ ligands. One of the striking feature of this molecule is the asymmetrical V–S bond distances. The vanadium–sulfur bond distances (Fig. 2, X = μ-O) are considerably shorter for the oxygen-bonded vanadium atoms, V(2) and V(3) (2.17–2.21 Å) compared to the all-sulfur bridged vanadium atoms, V(1) and V(4), (2.36–2.39 Å). The shorter V–S bond distances at V(2) and V(3) are intermediate between typical V–S single bonds (2.3–2.4 Å) [8–12] and V–S double bonds (2.05–2.10 Å) [11–13]. Closely related to **4** is $Cp_2V(\mu\text{-}S)_2VCpCl$ [7] (Fig. 2, X = Cl), synthesized from Cp_2VCl_2 and H_2S in dimethylform-

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[1] Dedicated to Prof. Dr. Max Herberhold on the occasion of his 60th birthday.

[2] Courtesy of Professor Max Herberhold.

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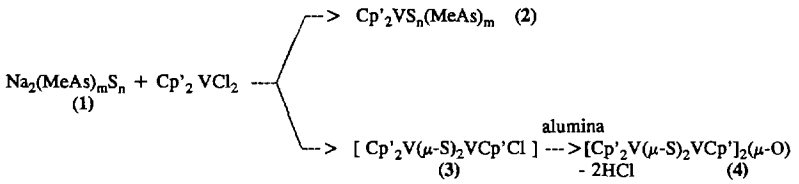

Scheme 1.

amide and methanol, which also shows a nearly identically unsymmetrical V–S bonding, where the V–S bond distances for the chlorine-bonded vanadium atom are 2.169(3) and 2.172(3) Å, compared to the all-sulfur bridged vanadium atom (2.396(3) Å and 2.390(3) Å) [7]. Short V–S (μ-S) bond distances (average 2.21 Å) are also reported for $(i\text{-PrCp})_2V_2S_4$ and are explained by evoking V–S multiple bonding through *full* S to V π-donation [14]. The average V–V distance in **4** (3.043(4) Å) is identical to the value reported for $Cp_2V(\mu_2\text{-}S)_2VCpCl$ [7], but it is much longer than the values reported for other sulfur complexes in which V–V bonds have been established (typically 2.46–2.66 Å) [15]. The V–O distances in **4** (average 1.794(9) Å) agree well with other values reported for bridging vanadium oxides in the range 1.769–1.841 Å [16,17].

The V_2S_2 rings are slightly folded; the average dihedral angle hinged along the V–V vector is 11.5°. The [cnt,V,cnt] (cnt = Cp′ ring centroid) planes intersect the [S,V,S] planes at $90 \pm 2°$. Similarly, the two planes formed by atoms [V(2),S(1),S(2)] and [O(1),V(2),cnt] are also perpendicular. This indicates that the vanadium atoms are in a nearly tetrahedral environment. In the V_2S_2 rings, the largest S–V–S bond angles (100.6(2)–101.0(2)°) are for the oxygen-bonded vanadium atoms, while the smallest bond angles are the V–S–V (82.7(2)–84.2(2)°). The S(1)–V(1)–S(2) and S(3)–V(4)–S(4) bond angles values range from 90.5(2) to 91.5(2)°. The V–O–V bond angle is almost linear (average 166.7(6)°).

Charge balance in the cluster requires the vanadium atoms to be V(IV), which suggests that the vanadium atoms are d^1 systems. These single electrons are expected to render the cluster paramagnetic, if their spins are not paired. However, the proton NMR does not reveal any paramagnetism, as the resonance signals show no evidence for line broadening or anomalous chemical shifts. This suggests that the electrons on the vanadium atoms are spin-paired via the long vanadium–vanadium bonds. An alternative view is to consider the vanadium atoms to be of mixed oxidation states as V(III) and V(V), which could also rationalize the asymmetrical V–S bond distances observed.

3. Experimental

3.1. Synthesis of (4)

A mixture of *cyclo*-$(CH_3AsS)_{3,4}$ [6] (0.183 g, 0.5 mmol) and sodium powder (0.046 g, 2.00 mmol) in 10 ml THF was stirred for 3 h to give a white slurry. $Cp'_2VCl_2^1$ (0.188 g, 0.67 mmol) was added to the white slurry. The color changed instantly to brown. The solu-

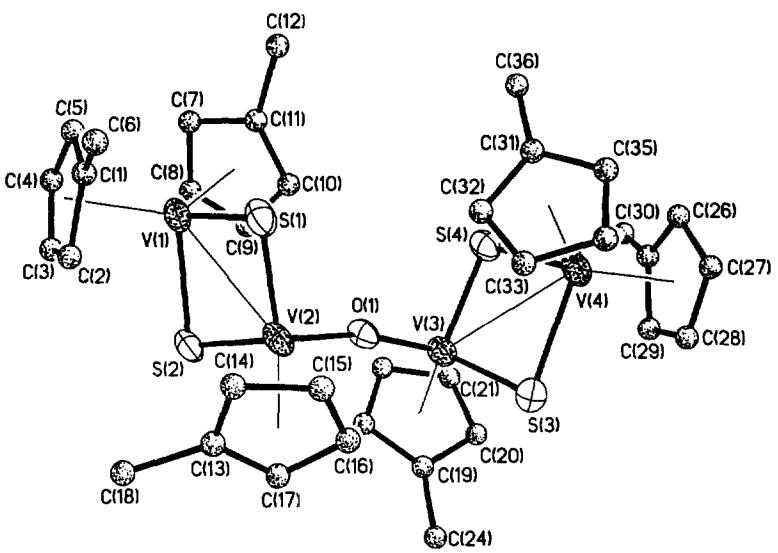

Fig. 1. Molecular structure of $[Cp'_2V(\mu\text{-}S)_2VCp']_2$ (μ-O) (**4**) drawn with 40% thermal ellipsoids.

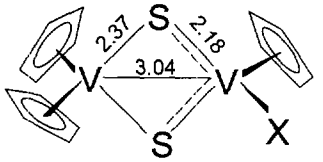

Fig. 2. V–S bond distances in $[Cp'_2V(\mu\text{-}S)_2VCp'X]$ (X = μ-O).

tion was stirred at room temperature for 16 h. The reaction mixture was filtered and the solvent removed. The product obtained was chromatographed on an alumina column. Compound **4** was separated with toluene/THF (90:10) mixture as a dark bluish fraction in 56% yield. ^{1}H NMR (benzene-d_6); 6.60 ppm (q, 2H), 6.55 ppm (q, 2H), 5.23 ppm (q, 2H), 4.89 ppm (m, 4H), 4.81 ppm (m, 6H), 4.68 ppm (q, 2H), 4.48 (q, 2H), 4.08 ppm (q, 2H), 4.02 ppm (q, 2H), 2.08 ppm (s, 6H), 1.84 ppm (s, 6H), 1.82 ppm (s, 6H). M.S.: [%I_{rel}, ion] m/z: [73.5, $V_4S_4Cp'^+_4$] 647.8; [100, $Cp'_4V_4S_3O^+$] 631.8; [10, $Cp'_3V_4S^+_4$] 568.8; [14.2, $Cp'_3V_4O^+$] 552.8; [20.7, $Cp'_2V_4S^+_4$] 489.7; [20, $Cp'_2V_4S_3O^+$] 473.8; [20.7, $Cp'V_4S^+_4$] 410.7; [17.7, $Cp'V_4S_3O^+$] 394.8; [17.9, $V_4S^+_4$] 331.6; [16.0, $V_4S_3O^+$] 315.9; [4.3, $Cp'V^+$] 129.9; [5.8, Cp'^+] 79.0.

3.2. Structural determination

Crystals were grown from a THF solution by slow pentane diffusion and were mounted on a glass fiber with epoxy cement. Systematic absences in the diffraction data limited the space group choices to $C2/c$ or Cc [3]. The centrosymmetric alternative was chosen ini-

Table 1
Crystallographic data for $[Cp'_2V(\mu\text{-}S)_2VCp']_2(\mu\text{-}O)$ (**4**)

(a) Crystal data	
Formula	$C_{36}H_{24}OS_4V_4$
Formula wt	823.74
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	33.308(6)
b (Å)	18.954(2) Å
c (Å)	35.529(4) Å
β (°)	109.53(3)
V (Å^3)	21,140(5)
Z	24
D_{calcd} (g cm^{-3})	1.551
T (K)	298(2) K
Color	Purple
Size (mm)	0.40×0.30×0.20
μ(MoK α) (cm^{-1})	12.94
(b) Data collection and refinement	
Diffractometer	Siemens P4
Reflections collected	13,382
2θ range (°)	4–43
Independent reflections	11,717
Data/parameter	17.1
$R(F)$, $R(wF)$	0.0952, 0.2086
GOF	1.004
$\Delta\rho$ (e Å^3 max, min)	0.67, −0.53

Table 2
Selected bond distances (Å) and bond angles (°) for the three independent molecules of $[Cp'_2V(\mu\text{-}S_2)VCp']_2(\mu\text{-}O)$

	A	B	C
(a) *Bond distances*			
V(1)–V(2)	3.035(2)	3.054(2)	3.039(2)
V(3)–V(4)	3.041(4)	3.039(4)	3.052(4)
V(1)–S(1)	2.365(6)	2.378(5)	2.393(6)
V(1)–S(2)	2.381(6)	2.378(5)	2.359(5)
V(4)–S(3)	2.364(6)	2.372(6)	2.386(6)
V(4)–S(4)	2.364(6)	2.366(6)	2.370(5)
V(2)–S(1)	2.209(6)	2.203(5)	2.200(6)
V(2)–S(2)	2.197(5)	2.186(5)	2.167(5)
V(3)–S(3)	2.197(6)	2.199(6)	2.196(6)
V(3)–S(4)	2.183(5)	2.183(5)	2.201(5)
V(2)–O(1)	1.793(9)	1.795(11)	1.803(11)
V(3)–O(1)	1.797(10)	1.805(11)	1.776(11)
V(1)–cnt1	2.04(1)	1.99(1)	2.01(1)
V(1)–cnt2	2.00(1)	2.01(1)	2.00(1)
V(2)–cnt3	1.99(1)	2.00(1)	2.03(1)
V(3)–cnt4	2.02(1)	2.02(1)	2.01(1)
V(4)–cnt5	2.01(1)	2.03(1)	1.99(1)
V(4)–cnt6	1.98(1)	1.98(1)	1.98(1)
(b) *Bond angles*			
S(1)–V(1)–S(2)	91.5(2)	90.5(2)	90.4(2)
S(3)–V(4)–S(4)	90.9(2)	90.8(2)	91.0(2)
S(1)–V(2)–S(2)	101.0(2)	100.7(2)	101.1(2)
S(3)–V(3)–S(4)	100.6(2)	100.7(2)	100.9(2)
V(1)–S(1)–V(2)	83.1(2)	83.5(2)	82.7(2)
V(4)–S(4)–V(3)	83.9(2)	83.7(2)	83.7(2)
V(1)–S(2)–V(2)	83.0(2)	83.9(2)	84.2(2)
V(4)–S(3)–V(2)	83.5(2)	83.3(2)	83.4(2)
S(1)–V(2)–O(1)	104.8(4)	104.4(4)	104.3(4)
S(2)–V(2)–O(1)	103.7(4)	103.9(4)	105.1(4)
S(4)–V(3)–O(1)	105.0(4)	104.5(4)	102.7(4)
S(3)–V(3)–O(1)	103.9(4)	105.0(4)	103.6(4)
V(2)–O(1)–V(3)	166.8(6)	167.1(6)	166.2(6)
cnt1–V(1)–cnt2	131.3(3)	132.0(3)	132.4(3)
cnt1–V(1)–S(1)	107.7(3)	105.9(3)	106.8(4)
cnt1–V(1)–S(2)	105.0(4)	107.7(4)	105.9(3)
cnt2–V(1)–S(1)	107.3(3)	107.2(3)	108.0(3)
cnt2(V1)–S(2)	106.9(3)	105.7(4)	105.4(3)
cnt3–V(2)–O(1)	114.8(3)	113.6(4)	113.0(2)
cnt3–V(2)–S(1)	114.7(4)	115.5(2)	113.2(4)
cnt3–V(2)–S(2)	116.1(3)	117.0(4)	118.6(3)
cnt4–V(3)–O(1)	113.6(3)	113.0(4)	113.9(3)
cnt4–V(3)–S(3)	115.7(3)	115.5(4)	116.5(3)
cnt4–V(3)–S(4)	116.3(3)	116.5(2)	117.2(3)
cnt5–V(4)–cnt6	130.5(3)	132.2(3)	131.6(3)
cnt5–V(4)–S(3)	104.3(4)	106.6(3)	106.2(3)
cnt5–V(4)–S(4)	108.6(4)	104.8(3)	108.2(3)
cnt6–V(4)–S(3)	108.7(3)	107.3(4)	106.2(3)
cnt6–V(4)–S(4)	106.7(3)	107.5(3)	106.2(2)

[3] Given that Z is 24, readers would be correctly suspicious about missed trigonal symmetry, but cell-reduction methods failed to indicate any symmetry higher than monoclinic.

tially on the statistical distribution of normalized structure factors, and the choice was supported by the reasonable and stable results of refinement. The structure was solved by direct methods and completed from subsequent difference Fourier syntheses. There are three crystallographically independent, but chemically similar, molecules in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. Crystallographic data are given in Table 1, and selected bond distances and bond angles for the three independent molecules are given in Table 2 [4].

Acknowledgements

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[4] Additional information available: additional crystallographic data for **4**, including atomic coordinates, complete tables of bond parameters and anisotropic thermal parameters may be obtained from the authors.