Carbon Disulphide Activation. A *CS*-Bonded Derivative of Vanadocene derived from a Carbon Disulphide Complex: Synthesis and Structure of $[V(\eta\text{-}C_5H_5)_2(CS_2)]$ and $[V(\eta\text{-}C_5H_5)_2(SCSMe)][I_3]$ †

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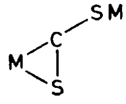
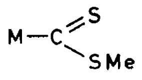
The addition of the ' carbenoid ' $[V(cp)_2]$ (cp = η-C_5H_5) to CS_2 gives the known $[V(cp)_2(CS_2)]$ complex containing the *CS*-side-bonded CS_2, as confirmed by an *X*-ray analysis. A significant lengthening of one of the C–S bonds is observed [1.666(4) Å: average of the two independent molecules in the asymmetric unit] with respect to the non-bonded CS moiety [1.617(4) Å]. Alkylation of the co-ordinated CS_2 produces a vanadium dithiomethoxycarbonyl complex $[V(cp)_2(CS_2Me)I]$ [ν(C=S) (Nujol) at 1 125 cm^{-1}] which reacts with I_2 giving $[V(cp)_2(CS_2Me)][I_3]$ [ν(C=S) (Nujol) at 1 105 cm^{-1}]. The trend in C–S bond distances, as deduced from *X*-ray analyses, allows the *CS*-bonded dithiomethoxycarbonyl group to be described as a three-electron ligand, with carbenoid character for the carbon atom bonded to the metal. In both the complexes $[V(cp)_2(CS_2)]$ and $[V(cp)_2(CS_2Me)][I_3]$ the two cp are bent away so as to make a cavity in the equatorial plane for the CS_2 and SCSMe ligands, which are nearly coplanar with the vanadium atom. Crystallographic details: $[V(cp)_2(CS_2)]$, space group $P2_1/c$, a = 11.803(2), b = 12.310(2), c = 14.463(3) Å, β = 90.07(3)°, Z = 8, final R factor = 0.030 for 2 857 observed reflections; $[V(cp)_2(CS_2Me)][I_3]$, space group $P2_1/n$, a = 9.377(2), b = 26.601(3), c = 7.579(1) Å, β = 108.95(2)°, Z = 4, final R factor = 0.084 for 2 842 observed reflections.

THE interest in metal-promoted activation of CS_2 comes from the fact that CS_2 is the usual source of the ' CS ' ligand [1,2] and dithiocarbenes, $=C(SR)_2$.[3-5] These two kinds of transformation of co-ordinated CS_2 can be accomplished by nucleophilic reagents, *i.e.* tricovalent phosphorus,[1,2] or electrophilic reagents, *i.e.* alkyl halides.[3-5] Moreover, a further interest in CS_2 co-ordinated to metals is that it can be used as a model for CO_2, which is much more difficult to investigate. Carbon disulphide displays various anchoring modes to metals,[1,6-8] the most common being the addition of a carbene-like metal to a C=S bond, which is exemplified by $[Pt(PPh_3)_2(CS_2)]$.[9]

The preparation of complexes containing the dithiomethoxycarbonyl group (SCSMe) as a ligand has been recently reported.[4,10] The ligand is generated by the reaction of MeI on co-ordinated CS_2. The group SCSMe displays the two bonding modes sketched below:



(I)



(II)

Confirmation of these bonding modes has been obtained from an *X*-ray analysis on $[Ru(SCSMe)(CO)_2(PPh_3)_2]^+$,[11] in which the SCSMe group is *CS* bonded, while the unidentate attachment, (II), was found in $[OsH(CS_2Me)(CO)_2(PPh_3)_2]$.[12]

Herein we report an *X*-ray structure analysis on $[V(cp)_2(CS_2)]$ [13,14] (cp = η-C_5H_5), which reacts with MeI and I_2 producing $[V(cp)_2(CS_2Me)][I_3]$ containing the dithiomethoxycarbonyl ligand *CS*-bonded to the metal.

EXPERIMENTAL

All the reactions described were carried out under an atmosphere of purified nitrogen; solvents were purified by standard methods. (Carbon disulphide)bis(η-cyclopentadienyl)vanadium (2) was prepared as previously described.[14] Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer. Magnetic susceptibility measurements were made with a Faraday balance. *X*-Ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer by use of niobium-filtered Mo-K_α radiation and the ω—2θ scan technique.

Preparations.— *Bis(η-cyclopentadienyl)(dithiomethoxycarbonyl)(iodo)vanadium*(IV). A tetrahydrofuran (thf) (50 cm^3) solution of $[V(cp)_2(CS_2)]$ (1.25 g, 4.86 mmol) was treated with MeI (0.7 cm^3, 11.24 mmol). On standing for 1 d the solution gave light green crystals, which were washed with thf (20 cm^3) and dried *in vacuo* (1.82 g, *ca.* 94%) (Found: C, 36.35; H, 3.60; I, 31.0; S, 15.1. Calc. for $C_{12}H_{13}IS_2V$: C, 36.1; H, 3.25; I, 31.8; S, 16.05%). The solid is rather insoluble in most common solvents. Its i.r. spectrum (Nujol mull) shows a strong broad C=S band at 1 125 cm^{-1}. $\mu_{eff.}$ = 1.83 B.M.‡ at 293 K.

Bis(η-cyclopentadienyl)(dithiomethoxycarbonyl)vanadium(IV) *Tri-iodide*, (4).—A thf (50 cm^3) suspension of $[V(cp)_2(CS_2Me)I]$ (1.216 g, 3.05 mmol) was treated with solid I_2 (0.83 g, 3.27 mmol) which caused the solid to dissolve giving a deep brown solution. By addition of toluene (100 cm^3) to the solution and partial evaporation, a brown crystalline compound was obtained (1.54 g, *ca.* 77%). (Found: C, 22.2; H, 2.10; I, 58.5; S, 10.4. Calc. for $C_{12}H_{13}I_3S_2V$: C, 22.05; H, 2.00; I, 58.3; S, 9.80%). The solid is stable in air. Its i.r. spectrum (Nujol mull) shows a strong C=S band at 1 105 cm^{-1}. $\mu_{eff.}$ = 1.84 B.M. at 293 K.

X-*Ray Crystallography.—Crystal data.* (2) $C_{11}H_{10}S_2V$, M = 257.3, Monoclinic, a = 11.803(2), b = 12.310(2), c = 14.463(3) Å, β = 90.07(3)°, U = 2 101.4 Å^3, Z = 8, D_c = 1.626 g cm^{-3}, $F(000)$ = 1 048, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 13.3 cm^{-1}, space group $P2_1/c$.

(4) $C_{12}H_{13}I_3S_2V$, M = 653.0, Monoclinic, a = 9.377(2), b = 26.601(3), c = 7.579(1) Å, β = 108.95(2)°, U = 1 788.0 Å^3, Z = 4, D_c = 2.425 g cm^{-3}, $F(000)$ = 1 196,

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† The complexes whose formulae are shown are (carbon disulphide-*CS*)bis(η-cyclopentadienyl)vanadium and bis(η-cyclopentadienyl)(dithiomethoxycarbonyl-*CS*)vanadium(IV) tri-iodide respectively.

‡ Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 60.2$ cm^{-1}, space group $P2_1/n$.

Cell dimensions were determined from rotation and Weissenberg photographs and those quoted were obtained by a least-squares refinement of the 2θ values of 27 ($2\theta > 30°$) and 33 ($2\theta > 40°$) reflections for complex (2) and (4) respectively.

Intensity-data collection. For both compounds three-dimensional intensity data were taken at room temperature from crystals of lengths 0.95 and 0.43 mm, and of cross sections 0.18 × 0.29 and 0.12 × 0.35 mm for complex (2) and (4) respectively. The crystals, sealed in glass capillaries under a nitrogen atmosphere, were mounted with *a* along the Φ axis of the diffractometer. The moving-counter–moving-crystal scan technique was used with a drive speed related to the number of counts on the peak (lowest speed 2.5° min^{-1}). No significant change in the intensity of a standard reflection monitored every 20 reflections was observed during data collection. For measuring intensity and background the five-point technique [15] was used. The intensities were measured in the interval $5 < 2\theta < 50°$ for (2) and $5 < 2\theta < 58°$ for (4). For (2), 3 704 independent reflections were collected, of which 2 857 having $I > 2\sigma(I)$ were considered observed and used in the analysis; for (4) the number of independent reflections was 4 603, 2 842 $[I > 2\sigma(I)]$ being used in the analysis. No correction for absorption was applied because of the poor shape of the crystals [$\mu\bar{r} \sim 0.2$ and 0.7 for complex (2) and (4) respectively] and therefore the thermal coefficients, in particular for (4), are influenced by this omission.

Solution and refinement of the structure. (a) *For complex* (2). Initial co-ordinates for the two independent vanadium atoms were obtained from a vector analysis of a three-dimensional Patterson function. A successive Fourier synthesis yielded the positions of all other non-hydrogen atoms. Refinement by full-matrix least squares with anisotropic vanadium and sulphur atoms gave $R = 0.067$. This was improved to 0.063 by adding the contribution of all the hydrogen atoms located from a difference-Fourier map. A further refinement, anisotropic for the non-hydrogen and isotropic for the hydrogen atoms, converged to the final $R = 0.030$. The final difference-Fourier map showed no significant features. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$ with unit weights. In the last stage of the refinement no parameter shifted by more than 0.3 times its standard deviation. No evidence for secondary extinction was found.

(*b*) *For complex* (4). The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Two further Fourier syntheses were necessary to obtain the co-ordinates of all the non-hydrogen atoms. Refinement was by full-matrix least squares, isotropically down to $R = 0.17$ and anisotropically down to $R = 0.085$. The lack of correction for absorption resulted in data which do not yield an improved fit. A subsequent difference Fourier revealed three pairs of peaks of *ca.* 1.5 e Å^{-3} each pair at *ca.* 0.9 Å from the three iodine atoms. No other peak exceeded 0.7 e Å^{-3}. The presence of these peaks, to which a real physical meaning cannot be attributed, prevented the direct location of the hydrogen atoms which were thus introduced in calculated positions as fixed atom contributions with free isotropic temperature factors. Refinement was stopped at $R = 0.084$, no parameters shifting by more than 0.3σ in the last cycle. The function minimized was $\Sigma w|\Delta F|^2$, first with unit weights, then with $w = 0.176\,9/[\sigma^2(F_o) + 0.003F_o^2]$.

TABLE 1

Final atomic fractional co-ordinates for $C_{11}H_{10}S_2V$ (2) with standard deviations in parentheses

	x/a	y/b	z/c
V(1)	0.139 8(1)	0.276 9(1)	0.591 6(0)
V(2)	0.641 2(1)	0.224 3(1)	0.164 1(0)
S(1)	0.087 5(1)	0.325 3(1)	0.434 2(1)
S(2)	0.336 7(1)	0.261 5(1)	0.411 7(1)
S(3)	0.589 7(1)	0.143 0(1)	0.312 4(1)
S(4)	0.842 3(1)	0.189 3(1)	0.340 2(1)
C(1)	0.118 0(5)	0.102 9(4)	0.538 1(3)
C(2)	0.202 2(4)	0.100 9(4)	0.604 8(4)
C(3)	0.153 7(5)	0.131 8(4)	0.685 3(4)
C(4)	0.039 6(5)	0.152 4(4)	0.671 6(4)
C(5)	0.017 5(8)	0.134 3(4)	0.579 1(4)
C(6)	0.081 5(4)	0.418 4(4)	0.682 4(3)
C(7)	0.164 8(5)	0.360 7(4)	0.729 4(3)
C(8)	0.265 0(4)	0.367 9(4)	0.680 5(3)
C(9)	0.243 8(4)	0.430 7(4)	0.604 5(3)
C(10)	0.131 8(4)	0.462 1(3)	0.605 8(3)
C(11)	0.546 0(6)	0.366 1(4)	0.102 8(4)
C(12)	0.660 0(6)	0.388 6(4)	0.095 3(4)
C(13)	0.705 1(5)	0.398 5(4)	0.181 2(5)
C(14)	0.619 3(5)	0.382 4(4)	0.243 1(4)
C(15)	0.518 7(4)	0.361 8(4)	0.194 9(4)
C(16)	0.673 5(6)	0.172 7(4)	0.017 3(3)
C(17)	0.765 3(4)	0.143 7(5)	0.067 9(4)
C(18)	0.730 3(5)	0.066 9(4)	0.128 5(3)
C(19)	0.615 8(5)	0.050 6(4)	0.115 9(4)
C(20)	0.579 8(4)	0.117 7(5)	0.047 2(4)
C(21)	0.217 8(3)	0.285 6(3)	0.463 3(3)
C(22)	0.721 0(4)	0.183 6(3)	0.288 4(3)
H(1)	0.132(7)	0.086(7)	0.480(6)
H(2)	0.275(7)	0.091(7)	0.602(5)
H(3)	0.201(5)	0.130(5)	0.730(4)
H(4)	−0.034(7)	0.179(7)	0.700(5)
H(5)	−0.050(7)	0.152(7)	0.558(6)
H(6)	0.005(7)	0.422(7)	0.695(5)
H(7)	0.169(6)	0.342(6)	0.774(5)
H(8)	0.327(7)	0.341(7)	0.687(5)
H(9)	0.292(7)	0.444(7)	0.573(6)
H(10)	0.094(7)	0.507(7)	0.559(6)
H(11)	0.497(5)	0.356(5)	0.059(4)
H(12)	0.715(7)	0.393(7)	0.056(6)
H(13)	0.780(7)	0.404(7)	0.190(5)
H(14)	0.625(6)	0.396(6)	0.284(5)
H(15)	0.447(7)	0.345(7)	0.213(6)
H(16)	0.699(7)	0.212(7)	−0.016(5)
H(17)	0.835(7)	0.154(7)	0.078(6)
H(18)	0.769(6)	0.046(6)	0.154(5)
H(19)	0.565(7)	0.010(7)	0.150(6)
H(20)	0.498(7)	0.119(7)	0.034(5)

Complex scattering factors were included in refinements. Atomic scattering factors used throughout the calculations were taken from ref. 16 for vanadium and iodine, from ref. 17 for carbon and sulphur, and from ref. 18 for hydrogen. All the calculations were made on a CYBER 7600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), using the SHELX-76 system of programs.[19] The final positions for the atoms are in Tables 1 and 2. Observed and calculated structure factors together with the thermal parameters are listed in Supplementary Publication No. SUP 22549 (30 pp.).* The most relevant bond distances and angles and the equations of molecular planes are given in Tables 3—5. All the average values were calculated using the formulae $\mu_{\text{av.}} = \sum_i (\mu_i/\sigma_i^2)/\sum_i \sigma_i^{-2}$ and $\sigma_{\text{av.}} = (\sum_i \sigma_i^{-2})^{-\frac{1}{2}}$ where μ_i are the individual observations and σ_i their standard deviations.

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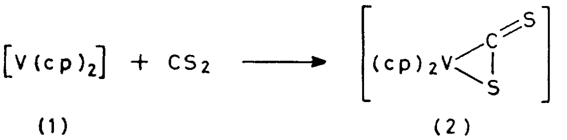
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

RESULTS AND DISCUSSION

As was reported previously,[13,14] the reaction between bis(η-cyclopentadienyl)vanadium(II), [V(cp)$_2$] (cp = η-C$_5$H$_5$), and CS$_2$ gives the adduct (2):



(i)

Much of the chemistry of [V(cp)$_2$] with unsaturated substrates could be described as the addition of the carbene-like vanadium to unsaturated groups, *i.e.* –N=N–,[20] –C≡C–,[21,22] C=C,[14] *etc.* The spectroscopic properties of co-ordinated CS$_2$ have been reported, while the *X*-ray structure analysis will be described below. The structure (see below) confirms that a vanadium atom is added to one of the C=S double bonds, as sketched in (2). The addition of CS$_2$ to the metal generates two potentially nucleophilic centres, the carbon and sulphur atoms bonded to the metal, susceptible to attack by electrophilic reagents.[1] Reaction of co-ordinated CS$_2$ with alkyl halides has been recently reported to produce dithioalkoxycarbonyl or dithiocarbene ligands,[1,3-5,10] and this corresponds to an electrophilic attack on the sulphur atom bonded to the metal.

A tetrahydrofuran solution of [V(cp)$_2$(CS$_2$)] (2) reacts at room temperature with MeI, producing (3) as a light

$$[V(cp)_2(CS_2)] + MeI \longrightarrow \underset{(3)}{[V(cp)_2(CS_2Me)I]} \qquad (ii)$$

green microcrystalline solid. Complex (3), which analy-

TABLE 2

Final atomic fractional co-ordinates for C$_{12}$H$_{13}$I$_3$S$_2$V (4) with standard deviations in parentheses

	x/a	y/b	z/c
I(1)	0.181 8(1)	0.170 6(0)	0.360 0(2)
I(2)	0.193 0(1)	0.098 9(0)	0.070 5(1)
I(3)	0.206 5(1)	0.028 6(0)	−0.214 2(2)
V	0.308 6(2)	−0.118 8(1)	0.264 6(3)
S(1)	0.112 0(4)	−0.169 6(1)	0.326 7(5)
S(2)	0.390 7(4)	−0.218 8(1)	0.592 1(5)
C(11)	0.290 9(15)	−0.178 8(4)	0.432 1(18)
C(12)	0.243 3(19)	−0.258 7(6)	0.630 1(26)
C(1)	0.482 3(19)	−0.142 2(6)	0.133 2(21)
C(2)	0.397 3(19)	−0.104 6(6)	0.023 8(21)
C(3)	0.246 1(18)	−0.123 6(7)	0.050 8(19)
C(4)	0.249 9(23)	−0.170 8(7)	0.012 7(24)
C(5)	0.386 9(19)	−0.184 0(5)	0.124 4(20)
C(6)	0.479 2(16)	−0.065 4(5)	0.451 7(18)
C(7)	0.386 3(16)	−0.038 0(4)	0.297 7(19)
C(8)	0.237 1(17)	−0.038 9(5)	0.296 6(21)
C(9)	0.235 2(19)	−0.066 7(6)	0.460 2(24)
C(10)	0.385 5(20)	−0.082 3(5)	0.551 5(18)
H(1)	0.600 7	−0.139 8	0.212 9
H(2)	0.436 7	−0.068 2	−0.002 8
H(3)	0.149 5	−0.103 3	−0.139 0
H(4)	0.152 8	−0.195 3	−0.023 3
H(5)	0.419 1	−0.219 7	0.194 2
H(6)	0.599 0	−0.071 8	0.486 4
H(7)	0.424 6	−0.019 5	0.194 5
H(8)	0.141 5	−0.021 9	0.193 0
H(9)	0.138 6	−0.073 9	0.504 3
H(10)	0.422 9	−0.104 1	0.678 6

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for complex (2)

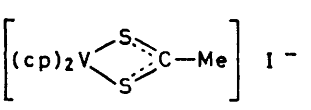
V(1)–C(1)	2.292(5)	V(1)–C(6)	2.288(5)
V(1)–C(2)	3.296(5)	V(1)–C(7)	2.263(5)
V(1)–C(2)	2.248(5)	V(1)–C(8)	2.256(5)
V(1)–C(4)	2.256(5)	V(1)–C(9)	2.264(5)
V(1)–C(5)	2.280(5)	V(1)–C(10)	2.291(4)
Average	2.274(2)	Average	2.274(2)
V(2)–C(11)	2.257(6)	V(2)–C(16)	2.249(5)
V(2)–C(12)	2.265(5)	V(2)–C(17)	2.252(6)
V(2)–C(13)	2.287(5)	V(2)–C(18)	2.264(5)
V(2)–C(14)	2.272(5)	V(2)–C(19)	2.269(5)
V(2)–C(15)	2.271(5)	V(2)–C(20)	2.259(6)
Average	2.271(2)	Average	2.259(2)
V(1)–S(1)	2.432(2)	V(2)–S(3)	2.444(2)
V(1)–C(21)	2.075(4)	V(2)–C(22)	2.090(5)
V(1)–Cp(1)	1.949(5)	V(2)–Cp(3)	1.946(5)
V(1)–Cp(2)	1.948(5)	V(2)–Cp(4)	1.938(6)
S(1)–C(21)	1.667(4)	S(3)–C(22)	1.665(5)
S(2)–C(21)	1.618(4)	S(4)–C(22)	1.617(5)
C(1)–C(2)	1.384(7)	C(6)–C(7)	1.390(7)
C(1)–C(5)	1.382(8)	C(6)–C(10)	1.368(6)
C(2)–C(3)	1.353(8)	C(7)–C(8)	1.382(7)
C(3)–C(4)	1.384(8)	C(8)–C(9)	1.367(6)
C(4)–C(5)	1.381(8)	C(9)–C(10)	1.377(7)
Average	1.377(3)	Average	1.376(3)
C(11)–C(12)	1.378(10)	C(16)–C(17)	1.355(8)
C(11)–C(15)	1.372(8)	C(16)–C(20)	1.367(8)
C(12)–C(13)	1.357(9)	C(17)–C(18)	1.354(8)
C(13)–C(14)	1.367(9)	C(18)–C(19)	1.378(8)
C(14)–C(15)	1.399(8)	C(19)–C(20)	1.360(8)
Average	1.376(4)	Average	1.363(3)
C(1)–V(1)–C(2)	35.1(2)	C(6)–V(1)–C(7)	35.6(2)
C(1)–V(1)–C(5)	35.2(2)	C(6)–V(1)–C(10)	34.8(2)
C(2)–V(1)–C(3)	34.6(2)	C(7)–V(1)–C(8)	35.6(2)
C(3)–V(1)–C(4)	35.8(2)	C(8)–V(1)–C(9)	35.2(2)
C(4)–V(1)–C(5)	35.4(2)	C(9)–V(1)–C(10)	35.2(2)
Average	35.2(1)	Average	35.3(1)
S(1)–V(1)–C(21)	42.5(1)	Cp(1)–V(1)–Cp(2)	138.8(3)
S(1)–V(1)–Cp(1)	110.6(2)	V(1)–S(1)–C(21)	57.2(2)
S(1)–V(1)–Cp(2)	109.5(2)	V(1)–C(21)–S(1)	80.3(2)
C(21)–V(1)–Cp(1)	107.5(2)	V(1)–C(21)–S(2)	142.1(2)
C(21)–V(1)–Cp(2)	108.3(2)	S(1)–C(21)–S(2)	137.5(3)
C(11)–V(2)–C(12)	35.5(3)	C(16)–V(2)–C(17)	35.0(2)
C(11)–V(2)–C(15)	35.3(2)	C(16)–V(2)–C(20)	35.3(2)
C(12)–V(2)–C(13)	34.7(2)	C(17)–V(2)–C(18)	34.9(2)
C(13)–V(2)–C(14)	34.9(2)	C(18)–V(2)–C(19)	35.4(2)
C(14)–V(2)–C(15)	35.9(2)	C(19)–V(2)–C(20)	35.0(2)
Average	35.2(1)	Average	35.1(1)
S(3)–V(2)–C(22)	42.2(1)	Cp(3)–V(2)–Cp(4)	138.1(3)
S(3)–V(2)–Cp(3)	111.0(2)	V(2)–S(3)–C(22)	57.4(2)
S(3)–V(2)–Cp(4)	109.4(2)	V(2)–C(22)–S(3)	80.4(2)
C(22)–V(2)–Cp(3)	109.0(2)	V(2)–C(22)–S(4)	141.9(3)
C(22)–V(2)–Cp(4)	108.0(2)	S(3)–C(22)–S(4)	137.8(3)
C(1)–C(2)–C(3)	106.9(5)	C(6)–C(7)–C(8)	108.8(4)
C(2)–C(3)–C(4)	109.9(5)	C(7)–C(8)–C(9)	107.0(4)
C(3)–C(4)–C(5)	107.0(5)	C(8)–C(9)–C(10)	108.8(4)
C(4)–C(5)–C(1)	107.4(5)	C(9)–C(10)–C(6)	108.6(4)
C(5)–C(1)–C(2)	108.8(4)	C(10)–C(6)–C(7)	106.8(4)
Average	108.1(2)	Average	108.0(2)
C(11)–C(12)–C(13)	109.2(6)	C(16)–C(17)–C(18)	106.8(5)
C(12)–C(13)–C(14)	107.3(5)	C(17)–C(18)–C(19)	108.4(5)
C(13)–C(14)–C(15)	109.2(5)	C(18)–C(19)–C(20)	108.3(5)
C(14)–C(15)–C(11)	106.1(5)	C(19)–C(20)–C(16)	106.2(5)
C(15)–C(11)–C(12)	108.3(5)	C(20)–C(16)–C(17)	110.2(5)
Average	108.0(2)	Average	108.0(2)

TABLE 4

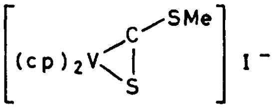
Bond distances (Å) and angles (°) with estimated standard deviations in parentheses for complex (4)

V–C(1)	2.26(2)	V–C(6)	2.26(1)
V–C(2)	2.27(2)	V–C(7)	2.26(1)
V–C(3)	2.27(1)	V–C(8)	2.27(1)
V–C(4)	2.28(2)	V–C(9)	2.29(2)
V–C(5)	2.28(2)	V–C(10)	2.27(1)
Average	2.27(1)	Average	2.27(1)
C(1)–C(2)	1.38(2)	C(6)–C(7)	1.41(2)
C(1)–C(5)	1.42(2)	C(6)–C(10)	1.41(2)
C(2)–C(3)	1.44(2)	C(7)–C(8)	1.40(2)
C(3)–C(4)	1.34(3)	C(8)–C(9)	1.45(2)
C(4)–C(5)	1.34(3)	C(9)–C(10)	1.42(2)
Average	1.40(1)	Average	1.42(1)
S(1)–C(11)	1.63(1)	V–S(1)	2.452(4)
S(2)–C(11)	1.66(1)	V–C(11)	2.08(1)
S(2)–C(12)	1.84(1)	V–Cp(1)	1.94(2)
I(1)–I(2)	2.935(3)	V–Cp(2)	1.92(1)
I(2)–I(3)	2.889(3)		
C(1)–V–C(2)	35.4(6)	C(6)–V–C(7)	36.4(5)
C(1)–V–C(5)	36.4(6)	C(6)–V–C(10)	36.1(6)
C(2)–V–C(3)	36.9(6)	C(7)–V–C(8)	36.0(6)
C(3)–V–C(4)	34.3(7)	C(8)–V–C(9)	37.1(6)
C(4)–V–C(5)	34.1(7)	C(9)–V–C(10)	36.1(6)
Average	35.6(3)	Average	36.3(3)
S(1)–V–C(11)	41.0(4)	V–S(1)–C(11)	57.1(4)
S(1)–V–Cp(1)	110.0(5)	V–C(11)–S(1)	81.8(5)
S(1)–V–Cp(2)	110.6(6)	V–C(11)–S(2)	143.4(9)
C(11)–V–Cp(1)	108.7(6)	S(1)–C(11)–S(2)	134.8(9)
C(11)–V–Cp(2)	108.8(6)	C(11)–S(2)–C(12)	102.2(8)
Cp(1)–V–Cp(2)	137.9(7)	I(1)–I(2)–I(3)	179.5(1)
C(1)–C(2)–C(3)	106.6(1.5)	C(6)–C(7)–C(8)	110.1(1.3)
C(2)–C(3)–C(4)	106.3(1.6)	C(7)–C(8)–C(9)	107.1(1.4)
C(3)–C(4)–C(5)	112.4(1.8)	C(8)–C(9)–C(10)	106.3(1.5)
C(4)–C(5)–C(1)	106.7(1.4)	C(9)–C(10)–C(6)	109.9(1.3)
C(5)–C(1)–C(2)	108.0(1.5)	C(10)–C(6)–C(7)	106.5(1.3)
Average	107.7(7)	Average	108.1(6)

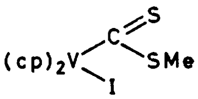
ses correctly, is a vanadium(IV) derivative with a magnetic moment of 1.83 B.M. at 293 K. The three following possibilities can be devised for its structure:



(A)



(B)



(C)

A structure like (A) requires alkylation of the carbon bonded to the metal in (2). However, this possibility can be ruled out on the basis of both the *X*-ray structure analysis of complex (4) (see below) and the i.r. spectrum [ν(C=S) at 1 125s, ν(C–S) 740 cm^{-1}], which is typical for a dithioalkoxycarbonyl group.[4] The dithiomethoxycarbonyl group can either behave in a bidentate fashion [structure (B)] or be carbon-bonded to the metal [structure (C)]. In fact, the i.r. spectrum seems to support (B) rather than (C) as a possible structure for (3). The *CS*-bonded dithiomethoxycarbonyl ligand shows a C=S band at *ca.* 1 100 cm^{-1}, while a shift of the C=S band to *ca.* 1 000 cm^{-1} is expected for the alternative unidentate attachment.[10,12] Complex (3), which is completely insoluble in thf, dissolves in the presence of I_2 producing a deep brown solution, from which (4) was recovered as brown crystals. The solubilization process may probably be related to the higher solubility of $[I_3]^-$ than I^- derivatives.

No significant shift in the C=S stretching frequency is observed when (3) is converted into (4) [Δν(C=S) *ca.* 20 cm^{-1}]. This gives further support to the suggestion that the SCSMe ligand displays the same bonding mode in both (3) and (4). A final point must be considered, the alkylation of co-ordinated CS_2 yet again regenerates two reactive centres, S and C bonded to the metal, for a further alkylation reaction.[3-5,10] Other structural features of (4) will be described together with the structure of (2), since both complexes contain the same basic $(\mathrm{cp})_2\overline{\mathrm{VCS}}$ unit.

TABLE 5

Equations of least-squares mean planes and, in square brackets, distances (Å) from these planes

(*a*) Complex (2)

Plane (1): V(1), S(1), C(21)

$$-0.2527X - 0.9505Y - 0.1806Z = -5.1993$$

[S(2) 0.062]

Plane (2): V(2), S(3), C(22)

$$0.2112X - 0.9074Y - 0.3633Z = -1.7699$$

[S(4) −0.034]

Plane (3): cyclopentadienyl ring, C(1)—C(5)

$$0.2133X + 0.9560Y - 0.2013Z = -0.0634$$

[C(1) 0.003, C(2) −0.004, C(3) 0.003, C(4) −0.002, C(5) −0.001, V(1) 1.949]

Plane (4): cyclopentadienyl ring, C(6)—C(10)

$$-0.2433X - 0.8187Y - 0.5201Z = -9.5868$$

[C(6) 0.006, C(7) −0.005, C(8) 0.002, C(9) 0.001, C(10) −0.003, V(1) 1.947]

Plane (5): cyclopentadienyl ring C(11)—C(15)

$$-0.2021X + 0.9793Y - 0.0106Z = 3.0954$$

[C(11) 0.000, C(12) 0.000, C(13) −0.001, C(14) 0.001, C(15) 0.000, V(2) −1.946]

Plane (6): cyclopentadienyl ring C(16)—C(20)

$$0.1961X - 0.7186Y - 0.6672Z = -0.1455$$

[C(16) 0.010, C(17) −0.009, C(18) 0.004, C(19) 0.005, C(20) −0.009, V(2) −1.938]

The transformation matrix from monoclinic x,y,z to orthogonal X,Y,Z is (1 0 cosβ||0 1 0||0 0 sinβ).

(*b*) Complex (4)

Plane (1): V, S(1), C(11), S(2)

$$0.2719x - 0.6389y - 0.7196z = 1.2636$$

[V 0.000, S(1) 0.0001, C(11) −0.001, S(2) 0.001, C(12) 0.081]

Plane (2): cyclopentadienyl ring C(1)—C(5)

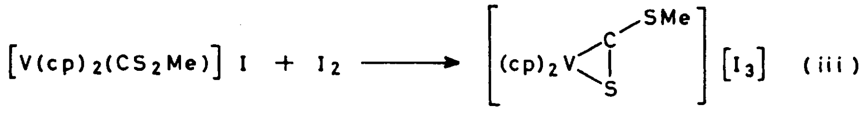
$$0.4985x - 0.3484y - 0.7938z = 2.6554$$

[C(1) −0.004, C(2) 0.007, C(3) −0.008, C(4) 0.008, C(5) −0.002, V −1.942]

Plane (3): cyclopentadienyl ring C(6)—C(10)

$$0.0043x - 0.8412y - 0.5408z = -0.2820$$

[C(6) 0.009, C(7) −0.009, C(8) 0.009, C(9) −0.005, C(10) −0.005, V 1.924]



(3) (4)

Description of the Structures of (2) *and* (4).—In the asymmetric unit of complex (2) there are two crystallographically independent molecules, $[V(cp)_2(CS_2)]$ (Figure 1), whose geometries are not significantly different. The crystals of (4) are built up by the monomeric cations $[V(cp)_2(SCSMe)]^+$ and $[I_3]^-$ anions (Figure 2), separated by the usual van der Waals interactions. In both cases, the two cp rings, which are η^5-bonded to vanadium, make a cavity in the equatorial plane for the CS_2 unit *CS*-bonded to the metal. Sulphur which is not bonded to the metal displays the following displacements from the plane defined by the VCS unit: S(2) +0.062; S(4) −0.034 Å. The non-bonded sulphur lies in the plane of the VCS unit in $[V(cp)_2(SCSMe)]^+$ (Table 5). The reciprocal orientation of the cp rings is staggered in (2) and eclipsed in (4) with cp–V–cp angles of 138.5(3)° (average for the two independent molecules) and 137.9(7)° in (2) and (4), respectively. V–C(cp) and V–cp(centroid) distances (Tables 3 and 4) fall in the usual range,[23] as do the C–C bond distances within the cp rings, which are planar.

The structural features of the VCS_2 unit deserve attention in both complexes. The CS_2 group is essentially planar in both complexes, the same deviations from the ideal trigonal angles being observed at atoms C(21), C(22), and C(11) (Tables 3 and 4), while significant differences could be found in the C–S bond distances which are in accord with the chemical differences in the two units. The C(12)–S(2) distance of 1.84(1) Å agrees well with the C–S single bond length determined in SMe_2 (1.81 Å).[24] However, all the other C–S distances in complexes (2) and (4) are shorter than this indicating some multiple bonding. In detail, the C–S double bond character in C(21)–S(2) and C(22)–S(4) [1.618(4) and 1.617(5) Å] compared with C(21)–S(1) and C(22)–S(3) [1.667(4) and 1.665(5) Å] appears evident, while the difference between C(11)–S(1) [1.63(1) Å] and C(11)–S(2) [1.66(1) Å] is not significant. An interesting comparison of the C–S bond distances for various CS_2 and SCSMe complexes is given in Table 6. Even the V–S and V–C distances are quite comparable in both complexes ranging from 2.432(2)—2.444(2) to 2.452(4) Å for V–S

TABLE 6

C–S bond distances (Å) in CS_2- and SCSMe-containing complexes

Compound [a]	C–S(1)	C–S(2)	Ref.
$[Nb(cp)_2(C_3H_5)\{S(1)C{=}S(2)\}]$	1.720(24)	1.574(23)	*b*
$[Fe\{S(1)C{=}S(2)\}(CO)_2(PMe_3)(PPh_3)]$	1.671(9)	1.623(10)	*c*
$[Pt\{S(1)C{=}S(2)\}(PPh_3)_2]$	1.72(5)	1.54(5)	9
$[Pd\{S(1)C{=}S(2)\}(PPh_3)_2]$	1.65(3)	1.63(3)	*d*
$[V(cp)_2\{S(1)C{=}S(2)\}]$	1.666(4)	1.618(4)	*e*
$[V(cp)_2\{S(1)C{-}S(2)Me\}]^+$	1.63(1)	1.66(1)	*e*
$[Ru\{S(1)C{-}S(2)Me\}(CO)_2(PPh_3)_2]^+$	1.66	1.65	11
$[Os\{C[{=}S(1)]S(2)Me\}H(CO)_2(PPh_3)_2]$	1.648(4)	1.724(5)	12
S=C=S	1.554		*f*

[a] C_3H_5 = σ-Allyl. [b] M. G. B. Drew and L. S. Pu, *Acta Cryst.*, 1977, **B33**, 1207. [c] H. Le Bozec, P. Dixneuf, N. J. Taylor, and A. J. Carty, *J. Organometallic Chem.*, 1977, **135**, C29. [d] T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 296. [e] This work. [f] A. H. Guenther, *J. Chem. Phys.*, 1959, **31**, 1095.

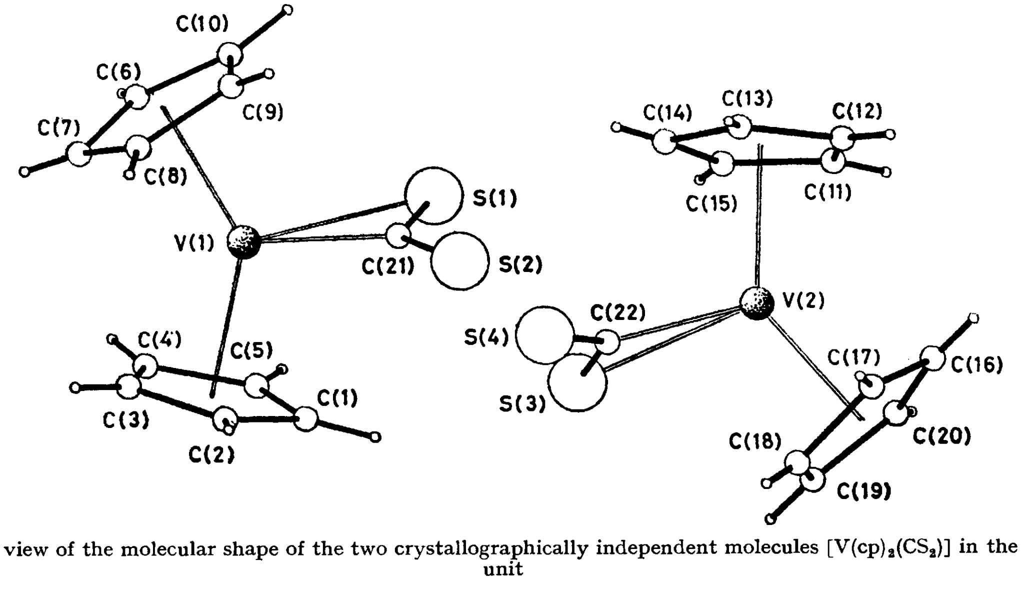


FIGURE 1 A view of the molecular shape of the two crystallographically independent molecules $[V(cp)_2(CS_2)]$ in the asymmetric unit

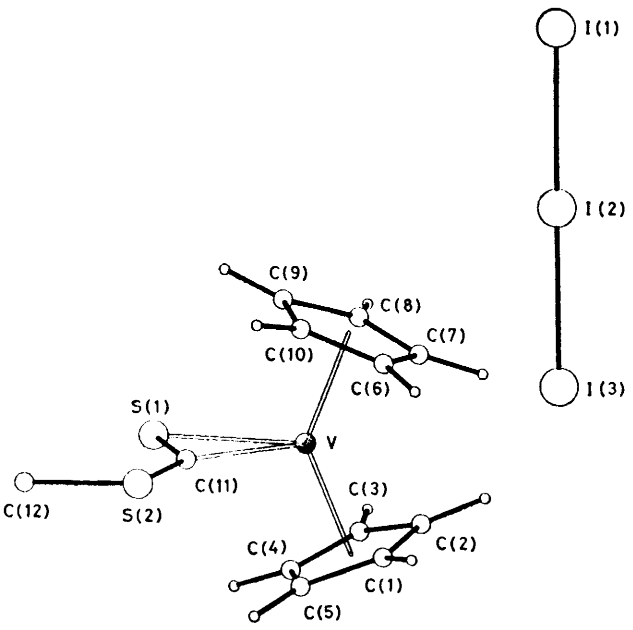
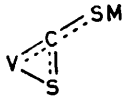


FIGURE 2 A view of the molecular structure of complex (4) showing the cation $[V(cp)_2(CS_2Me)]^+$ and the anion $[I_3]^-$

and from 2.075(4) and 2.090(5) to 2.08(1) Å for V–C in (2) and (4), respectively.

The distances and angles in the dithiomethoxycarbonyl ligand are consistent with a trigonally hybridized donor carbon atom in which the unhybridized *p* orbital probably has some interaction with orbitals on the metal. On the other hand, this orbital interacts with appropriate orbitals on both sulphur atoms, so that considerable electronic delocalization occurs over the three atoms. This is the pattern observed in many carbenoid complexes where the major π interaction is between the carbon and its adjacent donor heteroatoms,



with the π contribution from the metal being less significant. Some qualitative idea concerning this contribution should come from a comparison with other V–C bond distances in bis(cyclopentadienyl) derivatives. The relevant literature, however, is rather sparse and the values reported here could only be compared with V–C bond lengths, in $[V(cp)_2(EtO_2C\text{–}HC\text{=}CH\text{–}CO_2Et)]$ [2.186(12) and 2.213(12) Å] and $[V(cp)_2(MeO_2CC{\equiv}CCO_2Me)]$ [2.097(3) and 2.084(3) Å], respectively.[25] We note that the acetyl group in $[Zr(cp)_2(COMe)Me]$ [26] and $[Ti(cp)_2(COMe)Cl]$ [27] displays a bonding mode which has been described in the terms employed above for the dithiomethoxycarbonyl group.

The counter anion $[I_3]^-$ has the usual structural features (Table 4) [28] and does not interact significantly with the cation, the shortest contact distance being I(3) · · · C(9) 3.61(2) Å.

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