Reaction of Elemental Sulphur with Bis(pentamethylcyclopentadienyl)-vanadium Derivatives: Disulphido and μ-Sulphido Complexes. Crystal Structures of $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ and $[V_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$[‡]

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Reactions of elemental sulphur with $[V(\eta\text{-}C_5Me_5)_2]$, (**1**), and $[V(\eta\text{-}C_5Me_5)_2Cl]$, (**6**), are reported. The compound $[V(\eta\text{-}C_5Me_5)_2]$ reacted with S_8 forming $[V(\eta\text{-}C_5Me_5)_2(S_2)]$, (**2**) [V–S 2.415(4); S–S 2.028(4) Å; $(\eta\text{-}C_5Me_5)$–V–$(\eta\text{-}C_5Me_5)$, 141.7(4)°], which is paramagnetic, having one unpaired electron ($\mu_{\text{eff.}}$ = 1.89 at 297 K). Desulphurization of (**2**) with [Fe(salen)] [salen = *NN'*-ethylenebis(salicylideneiminate)] led to $[V(\eta\text{-}C_5Me_5)_2]$ and $[\{Fe(salen)\}_2(\mu\text{-}S)]$. Alkylation of the disulphido ligand with $MeSO_3F$ gave $[V(\eta\text{-}C_5Me_5)_2(S_2Me)][SO_3F]$, (**5**). Reaction of elemental sulphur with $[V(\eta\text{-}C_5Me_5)_2Cl]$, (**6**), in tetrahydrofuran, at room temperature gave a mixture of $[V(\eta\text{-}C_5Me_5)_2Cl_2]$, (**8**), and $[V(\eta\text{-}C_5Me_5)_2(S_2)]$, (**2**), while reaction in refluxing benzene gave a diamagnetic dimeric vanadium(IV) complex $[V_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$, (**9**) [V–S 2.16(2) and 2.23(1) Å; V$\cdots$V 2.829(3) Å].

Complexation of S_n units by cyclopentadienyl and substituted cyclopentadienyl complexes is a subject of considerable interest.[1–4] Monocyclopentadienyl fragments have provided numerous examples of co-ordinated S_n units, which display a variety of bonding modes and molecular complexity. The bent $M(cp)_2$ (cp = $\eta\text{-}C_5H_5$) fragment provides a reactive cavity, whose size is determined by the ionic radius of the metal, and by substitution at the cp ring. Steric constraints control the length, bonding mode, and reactivity of the co-ordinated S_n fragments obtained from reaction of the $M(cp)_2$ moiety with elemental sulphur, S_8. An interesting aspect of this chemistry is the large variety of rearrangement of the polysulphido ligands[4a,4b,5] caused mainly by the thermal lability of the S–S bond.

A number of reports, and a recent review by Draganjac and Rauchfuss,[1] emphasize many aspects of the M(cp) and $M(cp)_2$ chemistry outlined above. This paper concerns the reaction of $[V(\eta\text{-}C_5Me_5)_2]$[6] and $[V(\eta\text{-}C_5Me_5)_2Cl]$ with elemental sulphur. Reduction in size of the reactive cavity of the $M(cp)_2$ fragment, caused by permethylation at the cp rings, gives rise to the formation of a bidentate S_2 unit in $[V(\eta\text{-}C_5Me_5)_2(S_2)]$[3b,3c] which was the subject of a previous communication. The diamagnetic binuclear vanadium(IV) complex $[V_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}S)_2Cl_2]$ forms from the reaction of $[V(\eta\text{-}C_5Me_5)_2Cl]$ with elemental sulphur.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. I.r. spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibilities were found by use of a Faraday balance. Synthesis of $[V(\eta\text{-}C_5Me_5)_2]$ (**1**),[6] $[V(\eta\text{-}C_5Me_5)_2Cl]$ (**6**),[6] and [Fe(salen)][7] [salen = *NN'*-ethylenebis(salicylideneiminate)] was carried out as described in the literature. Diamagnetic corrections were taken from ref. 8.

Reaction of $[V(\eta\text{-}C_5Me_5)_2]$ *with Elemental Sulphur, Synthesis of* $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ (**2**).—A tetrahydrofuran (thf) solution (50 cm^3) of $[V(\eta\text{-}C_5Me_5)_2]$ (1.52 g, 4.72 mmol) was stirred with elemental sulphur (0.30 g, 1.17 mmol) until no more solid sulphur could be seen. On standing, at room temperature, the solution gave $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ as a crystalline solid. The yield may be increased by concentration and cooling to -30 °C (*ca.* 40%) (Found: C, 62.75; H, 8.05; S, 16.35. $C_{20}H_{30}S_2V$ requires C, 62.35; H, 7.80; S, 16.6%); $\mu_{\text{eff.}}$ = 1.78, $\mu_{\text{eff.}}^{\text{corr.}}$ = 1.89 at 297 K.

Reaction of $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ *with* $MeSO_3F$, *Synthesis of* $[V(\eta\text{-}C_5Me_5)_2(S_2Me)][SO_3F]$ (**5**).—To a toluene solution (25 cm^3) of $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ (0.30 g, 0.78 mmol), $MeSO_3F$ (0.13 g, 1.58 mmol) was added. After a few hours at room temperature, the solution became deep maroon then yellow, and, on standing for 2 d, gave a yellow-maroon microcrystalline solid (*ca.* 49%) (Found: C, 51.00; H, 6.35; S, 18.75. $C_{21}H_{33}FO_3S_3V$ requires C, 50.50; H, 6.60; S, 19.25%); $\mu_{\text{eff.}}$ = 1.74, $\mu_{\text{eff.}}^{\text{corr.}}$ = 1.88 at 298 K. A small amount of a green solid crystallized afterwards. Complete characterization of this compound was not possible.

Sulphur Transfer from $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ *to* [Fe(salen)].—To a thf solution (50 cm^3) of $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ (0.39 g, 1.01 mmol) solid [Fe(salen)] (0.65 g, 1.99 mmol) was added. After stirring the suspension at room temperature for a few days, microcrystalline $[\{Fe(salen)\}_2(\mu\text{-}S)]$ was filtered off (0.50 g). Evaporation of the solution to dryness left a residue which, when dissolved in toluene, gave a solution of $[V(\eta\text{-}C_5Me_5)_2]$, which reacted with carbon monoxide to give $[V(\eta\text{-}C_5Me_5)_2(CO)]$ [ν(CO) 1 845 cm^{-1}].[6]

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[‡] Bis(η-pentamethylcyclopentadienyl)(disulphido-*SS'*)vanadium and di-μ-sulphido-bis[chloro(η-pentamethylcyclopentadienyl)vanadium].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystal data and summary of intensity data collection and structure refinement[a]

	Complex (**2**) $C_{20}H_{30}S_2V$	Complex (**9**) $C_{20}H_{30}Cl_2S_2V_2$
M	385.5	507.4
Cell dimensions at 295 K[b]		
a/Å	17.664(9)	8.925(2)
b/Å	26.199(14)	13.054(3)
c/Å	8.664(3)	10.702(2)
α/°	90	90
β/°	90	112.92(1)
γ/°	90	90
U/Å^3	4 009(3)	1 148.4(4)
Z	8	2
D_c/g cm^{-3}	1.277	1.467
Space group	$Fdd2$	$C2$
Max. crystal dimensions, mm	0.24 × 0.29 × 0.58	0.18 × 0.29 × 0.40
μ/cm^{-1}	6.77	12.0
F(000)	1 640	524
Scan type	ω	ω—2θ
Scan speed/° s^{-1}	0.050	0.050
Scan width/°	1.50	1.20
2θ range/°	5—53	6—48
Reflections measured	$h, k, \pm l$	$\pm h, k, l$
Total measured data	2 050	983
Agreement between equiv. reflections		0.049
Total unique data	2 050	918
Unique observed data (N_o) [$I > 3\sigma(I)$]	996	545
R[c]	0.060	0.052
R'[c]	0.062	
Goodness of fit[d]	1.97	
N_o/N_v	9.6	5.2

[a] Details pertaining to both complexes: graphite monochromated Mo-K_α radiation (λ = 0.7107 Å); equatorial diffraction geometry; 104 parameters varied. [b] Unit-cell parameters were obtained by least-squares refinement of the setting angles of 20 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$. [d] Defined as $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is the number of observations and N_v is the number of variable parameters.

Table 2. Fractional atomic co-ordinates (× 10^4) for [V(η-C_5Me_5)$_2$(S_2)] (**2**)

Atom	X/a	Y/b	Z/c
V	7 500	2 500	0
S	7 901(2)	2 223(1)	2 530(5)
C(1)	7 877(6)	3 353(3)	−144(15)
C(2)	7 753(6)	3 190(4)	−1 583(14)
C(3)	8 283(7)	2 818(5)	−1 900(10)
C(4)	8 720(5)	2 736(4)	−680(13)
C(5)	8 485(6)	3 093(4)	493(10)
C(11)	7 522(10)	3 795(5)	576(27)
C(12)	7 252(10)	3 459(6)	−2 723(25)
C(13)	8 508(10)	2 620(7)	−3 529(15)
C(14)	9 395(7)	2 397(6)	−498(21)
C(15)	8 892(8)	3 201(6)	1 953(14)

Reaction of [V(η-C_5Me_5)$_2$Cl] *with Elemental Sulphur, Synthesis of* [V_2(η-C_5Me_5)$_2$$Cl_2$($\mu$-S)$_2$] (**9**).—(*a*) *At room temperature.* A thf solution (50 cm^3) of [V(η-C_5Me_5)$_2$Cl] (0.90 g, 2.52 mmol) was treated with crystalline S_8 (0.50 g, 1.95 mmol). The suspension was stirred at room temperature until the sulphur was completely dissolved. The solution changed from blue to green, and finally to yellow. On standing overnight, the solution gave a crystalline yellow-brown material, 'V(η-C_5Me_5)$_2$(S)Cl' (0.30 g, 30%) (Found: C, 60.30; H, 7.60; Cl, 9.10; S, 8.30. $C_{20}H_{30}ClSV$ requires C, 61.75; H, 7.70; Cl, 9.15; S, 8.25%); $\mu_{eff.}$ = 1.60, $\mu_{eff.}^{corr.}$ = 1.73 at 296 K.

(*b*) *In refluxing benzene.* The compound [V(η-C_5Me_5)$_2$Cl] (2.07 g, 5.81 mmol) was treated with S_8 (0.20 g, 0.78 mmol) in refluxing benzene (50 cm^3) for 4 d. The resulting solution, when concentrated to *ca.* 20 cm^3 and cooled, gave, after 4 d, red-violet crystals of [V_2(η-C_5Me_5)$_2$$Cl_2$($\mu$-S)$_2$] (Found: C, 47.2; H, 5.95; Cl, 13.65; S, 12.75. $C_{20}H_{30}Cl_2S_2V_2$ requires C, 47.35; H, 5.90; Cl, 14.00; S, 12.6%).

X-*Ray Crystallography.*[9a]—Crystals of complexes (**2**) and (**9**) examined were wedged into thin-walled glass capillaries and sealed under nitrogen. They were mounted on a Philips PW 1100 diffractometer in a random orientation. The reduced cells were obtained using TRACER[9b] (see Table 1 for crystal data and data collection parameters). Intensity data were collected at 295 K using the three-point technique. The structure amplitudes were obtained after usual Lorentz and polarization correction. The quality and absorption effects of the crystals were studied with ψ scans and considered to be non-negligible for complex (**9**). Therefore, the data for this complex were corrected for absorption following a semi-empirical method[10] with maximum and minimum corrections of 1.238 and 1.004 respectively. Only the observed reflections were used in the structure solution and refinement.

Full-matrix least-squares refinement was based on F, and the function minimized was $\Sigma w|\Delta F|^2$. Unit weights were used for complex (**9**), since these gave acceptable agreement analyses, while for complex (**2**) the weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$ was applied. At convergence the values for k and g were 1.6482 and 0.00107 respectively. The atomic scattering factors for all non-hydrogen atoms were taken from ref. 11*a* and those for H from ref. 12. The effects of anomalous dispersions were included in F_c by using the values from ref. 11*b*. There was no evidence for secondary extinction among low-angle reflections for the two complexes. Structure solution and refinement was carried out on a GOULD SEL 32/77 computer.

Structure solution and refinement for complex (**2**). The structure was solved by the heavy-atom method assuming the vanadium atom to lie on a two-fold axis according to the number of molecules in the unit cell (Z = 8). In the initial stages of refinement the cp rings were considered as rigid groups.[9a] In the final refinement all constraints were removed and all non-hydrogen atoms were allowed to vary anisotropically. Refinement was continued until shifts in all parameters were less than 0.3 times the standard deviation in the respective parameter. The hydrogen atoms, partly located in a ΔF map and partly placed in calculated positions, were introduced in calculations prior to the final refinement as fixed isotropic contributors (U_{iso} = 7.8 Å^2). In the final difference map there were no peaks above the general background. Final atomic co-ordinates are given in Table 2.

Structure solution and refinement for complex (**9**). The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Some difficulties were found in the structure refinement, because the two space groups $C2/m$ and $C2$ seemed equally probable. E-statistics calculated as a function of sinθ did not provide a clear choice between them, $\langle|E^2 - 1|\rangle$ being 0.88. The centrosymmetric space group implied a statistical distribution of the cyclopentadienyl and chlorine ligands over two positions about the mirror plane. The non-centrosymmetric space group did not require any assumption of disorder. As it was not possible to test for centrosymmetry by direct experiment, anisotropic refinement in both space groups was tried using full-matrix least

Table 3. Fractional atomic co-ordinates (× 10^4) for $[V(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$ (**9**)

Atom	*X/a*	*Y/b*	*Z/c*
V	−654(2)	0	−1 435(2)
Cl	−3 372(4)	−65(19)	−2 287(4)
S(1)	0	−1 254(16)	0
S(2)	0	1 326(12)	0
C(1)	1 530(15)	475(19)	−1 968(13)
C(2)	1 244(15)	−592(19)	−2 190(13)
C(3)	−316(15)	−725(19)	−3 245(13)
C(4)	−993(15)	261(19)	−3 675(13)
C(5)	148(15)	1 003(19)	−2 886(13)
C(11)	2 980(44)	1 149(40)	−1 256(36)
C(12)	2 721(63)	−1 221(51)	−1 151(57)
C(13)	−1 014(70)	−1 870(49)	−3 621(60)
C(14)	−2 612(25)	435(35)	−4 895(21)
C(15)	−158(61)	2 071(27)	−3 181(48)

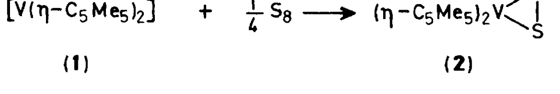
squares and a rigid-body constraint for the cp ring. Refinement converged at $R = 0.053$ ($R_G = 0.059$) $[R_G = (\Sigma w|\Delta F|^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ for the undisordered non-centrosymmetric model and $R = 0.053$ ($R_G = 0.061$) for the disordered centrosymmetric one. In order to choose between the two models, Hamilton's significance test[13] was applied indicating that the disordered centrosymmetric model could be rejected at the 0.005 significance level. It is worth noticing that the two refinements did not result in significantly different structural parameters as far as the co-ordination polyhedron is concerned. So, whatever the model, from the chemical point of view the results are practically the same, at the level of accuracy achieved by this analysis.

At this point, since the *C*2 space group is polar, the chirality of the crystal was tested by inverting all co-ordinates ($x, y, z \rightarrow \bar{x}, \bar{y}, \bar{z}$) and refining to convergence once again. The resulting values ($R = 0.052$, $R_G = 0.058$) indicated that the 'inverted' structure should be accepted. So the atomic co-ordinates given in Table 3 refer to this.

The C(2) carbon atom was not allowed to vary anisotropically, since it gave 'non-positive definite' conditions in all refinements. The methyl hydrogen atoms could not be directly located and this aspect of the structure was not pursued further. In the final difference map the greatest peaks of *ca.* 0.3—0.4 e $Å^{-3}$ were at *ca.* 1 Å from vanadium in the directions of the V–S and V–Cl bonds.

Results and Discussion

Bis(cyclopentadienyl) derivatives of Group 4 metals and vanadium gave, regardless of the synthetic route used, $[M(cp)_2(S_5)]$[1,2a,2b] on reaction with elemental sulphur or polysulphides. Reaction of $[V(\eta\text{-}C_5Me_5)_2]$ with S_8 in thf leads, however, to the formation of complex (**2**) [equation (1)], which crystallizes from the solution at room temperature. Complex (**2**) is a paramagnetic vanadium(IV) derivative with one unpaired electron ($\mu_{eff.} = 1.89$ at 297 K). Formation of the $M(S_2)$ fragment in the $[V(\eta\text{-}C_5Me_5)_2]$ derivative is attributed to the angular compression caused by permethyl substitution at the cp ring, the (C_5Me_5)–V–(C_5Me_5) angle [141.7(4)°] being among the highest found for bis(cyclopentadienyl)vanadium derivatives.[6] This steric constraint controls other reactions of $[V(\eta\text{-}C_5Me_5)_2]$. The same angular compression, for example, is responsible for the formation of the trisulphido derivative $[M(\eta\text{-}C_5Me_5)_2(S_3)]$ (**3**) (M = Ti or Zr), of the Group 4 elements.[3a] In addition, the $V(S_2)$ unit appears to be particularly stable, since it forms from sulphur-containing substrates like COS,[14] or by sulphur transfer from other complexes, like $[\{Co(salphen)\}_2(\mu\text{-}S_2)Na]^+$ [salphen = *NN'*-*o*-phenylenebis(salicylideneiminate)].[3c]



$$[V(\eta\text{-}C_5Me_5)_2] + \tfrac{1}{4}S_8 \longrightarrow (\eta\text{-}C_5Me_5)_2V{<}\overset{S}{\underset{S}{|}} \qquad (1)$$

(**1**) (**2**)

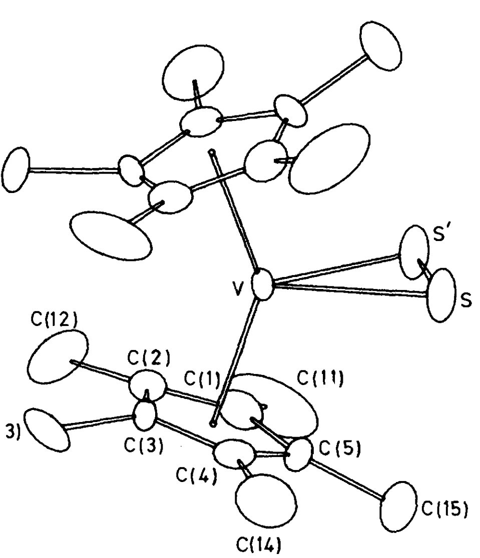
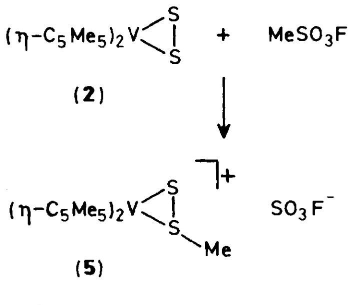


Figure 1. An ORTEP diagram for $[V(\eta\text{-}C_5Me_5)_2(S_2)]$, (**2**). The prime indicates the transformation ($\frac{3}{2} - x$, $\frac{1}{2} - y$, z) (20% probability ellipsoids)

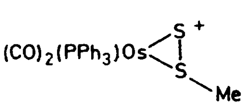
Complex (**2**) has the structure reported in Figure 1. Relevant bond distances and angles are listed in Table 4. The molecule has a C_2 axis passing through the S–S bond and the vanadium atom. The V–S bond distance of 2.415(4) Å is close to those found in $[V(cp)_2(S_5)]$,[2b] (**4**), and other $[V(cp)_2]$ derivatives containing V–S bonds.[15] The S–S bond distance is typical of co-ordinated disulphides.[16] Permethylation at the cp rings results in a long vanadium–ring distance {2.01(1) *vs.* 1.92—1.96 Å in $[V(cp)_2]$ derivatives} and a wide (C_5Me_5)–V–(C_5Me_5) bond angle of 141.7(4)°.[6] The mutual repulsion of methyl groups on the rings is reduced by their significant deviation out of the plane of the ring [from 0.075(15) to 0.407(17) Å] in the opposite direction to vanadium, in such a way that the pentamethylcyclopentadienyl group assumes a 'butterfly' conformation.

The ligand S_2 is electron-rich and undergoes reaction with electrophiles.[17,18] The alkylation of (**2**) was performed with $MeSO_3F$ [equation (2)]. Compound (**5**), isolated as a crystalline solid, is paramagnetic ($\mu_{eff.} = 1.88$ at 298 K). Related alkylation of a disulphido ligand has been reported to give $[Os(CO)_2(PPh_3)(S_2Me)]^+$,[17] while a peralkylation of $[Nb(cp)_2(S_2)Cl]$ led to the formation of Me_2S_2.[18] Though not supported by *X*-ray data, analogy with both the observed bonding mode of $S\text{–}SMe^-$ in the osmium complex,[17] (**A**), and the C,S and C,N bonding modes of the alkylated CS_2[15b] and *p*-tolylcarbodi-imide[19] in complexes (**B**) and (**C**) (R = C_6H_4Me-*p*, R' = Me), supports the proposed SS' bonding of (**5**).

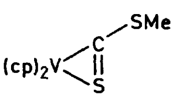


$$(\eta\text{-}C_5Me_5)_2V{<}\overset{S}{\underset{S}{|}} + MeSO_3F \longrightarrow \left[(\eta\text{-}C_5Me_5)_2V{<}\overset{S}{\underset{S\text{–}Me}{|}}\right]^+ SO_3F^- \qquad (2)$$

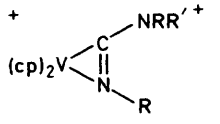
(**2**) (**5**)



(A)

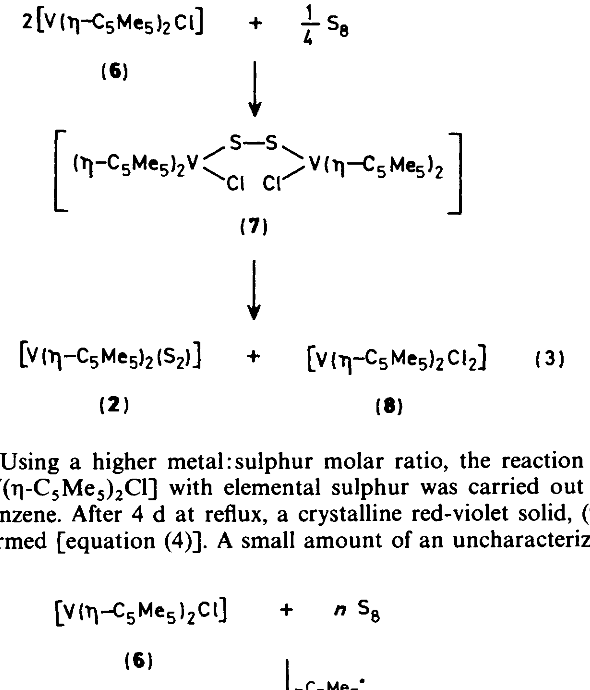


(B)

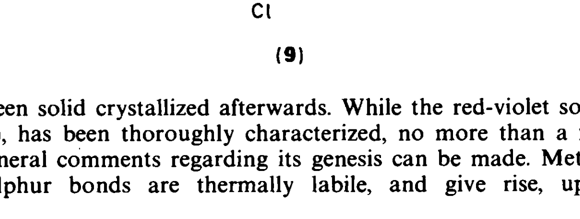


(C)

The vanadium(III) derivative $[V(\eta\text{-}C_5Me_5)_2Cl]$ (**6**), which behaves as a one-electron donor system, may be viewed as a metallic free radical.[6] The attempts to synthesize a disulphido-bridged vanadium(IV) dimer by reaction of $[V(\eta\text{-}C_5Me_5)_2Cl]$ with an excess of elemental sulphur led, however, to a different result. Complex (**6**) reacted with elemental sulphur in thf to give a blue solution which changed to green, then to yellow, and on standing a crystalline yellow-brown material was obtained. Elemental analysis of the solid was consistent with the formula $[\{V(\eta\text{-}C_5Me_5)_2Cl\}_2(\mu\text{-}S_2)]$, (**7**). In accord with such a formula, the magnetic moment of the compound at 296 K was 1.73 per vanadium atom. Available *X*-ray data, however, excluded the structure shown for (**7**) [see equation (3)] (complete solution of the structure was not achieved). The structure appears to be either $[V(\eta\text{-}C_5Me_5)_2(S_2)]$ or $[V(\eta\text{-}C_5Me_5)_2Cl_2]$. This information, along with the analytical results, are in agreement with a crystalline solid containing both (**2**) and (**8**) in a 1 : 1 molar ratio. The i.r. spectrum of the solid and of an equimolar mixture of complexes (**2**) and (**8**) are superimposable. As suggested in equation (3), (**2**) and (**8**) may form through the intermediacy of (**7**).



Using a higher metal : sulphur molar ratio, the reaction of $[V(\eta\text{-}C_5Me_5)_2Cl]$ with elemental sulphur was carried out in benzene. After 4 d at reflux, a crystalline red-violet solid, (**9**), formed [equation (4)]. A small amount of an uncharacterized green solid crystallized afterwards. While the red-violet solid, (**9**), has been thoroughly characterized, no more than a few general comments regarding its genesis can be made. Metal–sulphur bonds are thermally labile, and give rise, upon dissociation, to sulphur radicals that are known to react with cyclopentadienyl rings, leading to their transformation or displacement.[4a,5] The formation of (**9**), as well as the facile conversion of $[V(cp)_2(S_5)]$ to $[V_2(cp)_2(S_5)]$[4a] or the thermal conversion of $[Ti(cp)_2(S_5)]$ into the so-called β form[5] may be attributed to this well known behaviour of the M–S moiety.



(9)

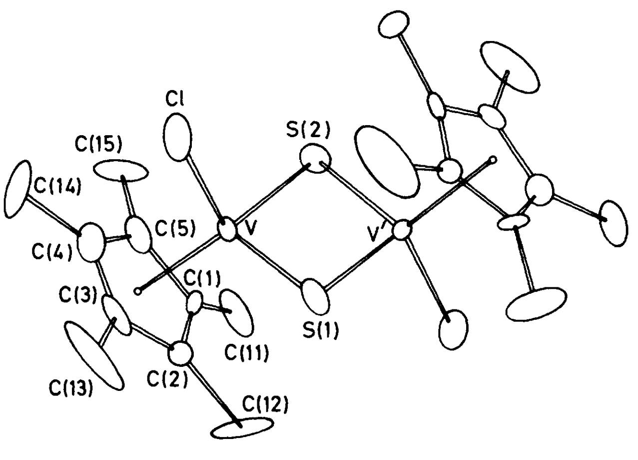


Figure 2. An ORTEP diagram for $[V_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$, (**9**). The prime indicates the transformation ($\bar{x}$, y, $\bar{z}$) (20% probability ellipsoids)

The structure of (**9**) is shown in Figure 2. The dimer has a crystallographic C_2 symmetry, the sulphur atoms lying on a two-fold axis, and a pseudo *m* symmetry with a non-crystallographic mirror plane perpendicular to the C_2 axis and running roughly through V, Cl, C(4), and C(14). Due to strong correlations between pseudo symmetry-related atoms, severe difficulties were encountered in the structure refinement (see Experimental section). The co-ordination sphere around vanadium consists of a single pentamethylcyclopentadienyl ring η^5-bonded to the metal, a chlorine atom, and two bridging sulphido ligands (Table 5). Within the dimer, the atoms V, S(2), S(1), and V′ define a plane. The V–S distances [mean 2.20(2) Å] are significantly shorter than that observed in complex (**2**) [2.415(4) Å] and other vanadium complexes.[15] Similar V–S bond distances are found in the μ-sulphido derivatives $[(\eta\text{-}C_5H_4Me)_2V_2(S_3)Fe(CO)_3]$ [2.23(1) Å][4b] and $[V_2(\eta\text{-}C_5H_4Me)_2(S_5)]$ [2.267(1) and 2.263(1) Å].[4a] Shortening of the V–Cl [2.236(4) Å] and V–S distances, relative to those found in bis(cyclopentadienyl)vanadium compounds, may be attributed to the lower co-ordination number of the mono(cyclopentadienyl) derivative. The hypothesis that the compound should be formulated as $[V_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_2(S)_2]$ can be excluded on the basis of the value of the V–S distance which is too long to be considered as a V=S double bond, *i.e.* 2.06(1) in [S=V-(acen)] [acen = *NN*′-ethylenebis(acetylacetoneiminate)].[20] The geometry of the η-C_5Me_5 ring, which is nearly planar, with C(11) alone deviating significantly from planarity, is as expected. Unfortunately the low accuracy of the data due to the presence of pseudo-symmetry (and/or disorder) prevents a reliable discussion of bond distances and angles in the ring.

Complex (**9**) is diamagnetic both in the solid state (magnetic susceptibility) and in solution (the ^1H n.m.r. spectrum in C_6D_6 shows a very sharp singlet at δ 1.82). This diamagnetism may be due to the presence of a metal–metal bond, or to anti-ferromagnetic exchange. The V–V distance [2.829(3) Å] is significantly longer than those of $[V_2(\eta\text{-}C_5H_4Me)_2(S_5)]$ [2.658(1) Å],[4a] $[V_2(\eta\text{-}C_5H_4Pr^i)_2(S_4)]$ [2.610(1) Å],[4b] $[V_2(cp)_2(S_4)\cdot C_2(CF_3)_2]$ [2.574(3) Å],[4b] $[(\eta\text{-}C_5H_4Me)_2V_2(S_3)\text{-}Fe(CO)_3]$ [2.51(1) Å],[4c] $[V_2(cp)_2(CO)_5]$ [2.462(2) Å],[21a] and $[V_2(cp)_2(CO)_4(PPh_3)]$ [2.466(1)],[21b] in which V–V bonds have been established. Nevertheless, the existence of a V–V bond

Table 4. Selected interatomic distances (Å) and angles (°) for complex (**2**)*

V–cp	2.01(1)	S–V–cp	108.8(3)
V–S	2.415(4)	S′–V–cp	105.9(3)
S–S′	2.028(4)	S–V–S′	49.7(1)
		cp–V–cp′	141.7(4)
		V–S–S′	65.2(2)

* Primes refer to the position $\frac{3}{2} - x, \frac{1}{2} - y, z$, cp to the centroid of the C(1) — C(5) ring.

Table 5. Selected interatomic distances (Å) and angles (°) for complex (**9**)*

V–cp	2.07(2)	S(1)–V–cp	120.0(5)
V–S(1)	2.16(2)	S(2)–V–cp	113.8(5)
V–S(2)	2.23(1)	S(1)–V–S(2)	99.9(1)
V–Cl	2.236(4)	Cl–V–cp	113.8(4)
V···V	2.829(3)	Cl–V–S(1)	102.2(2)
		Cl–V–S(2)	105.1(2)
		V–S(1)–V′	81.7(1)
		V–S(2)–V′	78.5(1)

* Primes refer to the position $\bar{x}, y, \bar{z}$, cp to the centroid of the C(1) — C(5) ring.

would explain the rather small V–S–V angles observed [V–S(1)–V′ 81.7(1) and V–S(2)–V′ 78.5(1)°]. Alternatively, the coupling observed in complex (**9**) may result from antiferromagnetic exchange, facilitated by the two μ-sulphido ligands. In the absence of a temperature-dependent measurement of the magnetic susceptibility, neither mechanism can be excluded.

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