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PREPARATION OF $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ AND STEREOCHEMICAL CHARACTERIZATION OF $M(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ (M = Ti, V): THE GEOMETRICAL EFFECT OF AN UNPAIRED ELECTRON ON A $M(h^5\text{-}C_5H_5)_2L_2$ COMPLEX

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Summary

The synthesis of the d^1 vanadium(IV) compound $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ from the reaction of $V(h^5\text{-}C_5H_5)_2$ with $(C_6H_5)_2S_2$ and its stereochemical characterization from X-ray diffraction data (as well as from infrared, solution EPR, and temperature-dependent magnetic susceptibility data) were performed in conjunction with a previous structural determination by X-ray diffraction of the corresponding d^0 titanium(IV) compound $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ in order to provide an operational test of the qualitative bonding model proposed by Ballhausen and Dahl and widely utilized by others for d^1 and d^2 metal(IV) complexes ($M(h^5\text{-}C_5H_5)_2L_2$). The isomorphous $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ and $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ compounds crystallize with eight molecules in a monoclinic unit cell of symmetry $C2/c$ and of dimensions a 31.76(10), b 7.97(2), c 15.45(5) Å, β 104.87(17)° for the titanium compound and a 31.454(5), b 7.835(1), c 15.545(2) Å, β 104.35(1)° for the vanadium compound. The molecular configuration, comprised of a distorted tetrahedral array of the two cyclopentadienyl rings and two phenylmercapto sulfur atoms about the central metal atom, conforms closely to C_2-2 symmetry. The crystallographic results, which show the S—V—S bond angle of 94.1(1)° to be 5° less than the S—Ti—S bond angle of 99.3(3)°, are taken as strong evidence for the nonvalidity of the Ballhausen—Dahl model applied to $M(h^5\text{-}C_5H_5)_2L_2$ systems. The structural determination and rigid-body least-squares refinement of the titanium compound were based on 1048 observed maxima collected by photographic methods, while the corresponding refinement of the vanadium compound utilized 1793 reflections above background obtained with a four-circle diffractometer. Efforts to obtain $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ from the reaction of $V(h^5\text{-}C_5H_5)_2Cl_2$ with thio-

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phenol led instead to the $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ dimer, which is presumed on the basis of its determined magnetic moment of μ_{eff}^{300} 1.15 BM to be structurally similar to the previously reported methylmercapto homolog.

Introduction

A structural investigation by Watkins [1] of the stable diamagnetic compound $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$, prepared by Giddings [2] originally from the heterogeneous reaction of dicyclopentadienyltitanium dichloride with $NaSC_6H_5$ [2a] and later from the reaction of thiophenol and $Ti(h^5\text{-}C_5H_5)_2Cl_2$ with triethylamine as base [2b*], provided impetus to the idea that a structural comparison with the analogous vanadium compound would serve as an operational test of the qualitative bonding model proposed by Ballhausen and Dahl [3] for d^1 and d^2 metal(IV) complexes $M(h^5\text{-}C_5H_5)_2L_2$. Their model predicts that the unpaired electron in the d^1 vanadium(IV) molecule $V(h^5\text{-}C_5H_5)_2\text{-}(SC_6H_5)_2$ would occupy a metal hybrid orbital located between the two mercapto ligands. An electron in this orbital would be expected from electron—electron repulsion arguments to cause an *increase* in the sulfur—metal—sulfur bonding angle for the vanadium complex compared with that for the analogous titanium derivative from which this electron has been formally removed. In addition, the vanadium complex was considered to be a suitable candidate for a dilute single-crystal EPR study [4] from which further insight into the distribution of the unpaired electron might be gained.

Our initial attempts to prepare the desired vanadium compound by the method employed by Giddings [2] for the preparation of $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ led instead to the compound $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ [5]. The desired paramagnetic compound, $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$, was obtained by a different synthetic route and characterized by physical measurements including a crystallographic determination by X-ray diffraction. This paper presents the results of our studies on both the d^0 titanium(IV) and d^1 vanadium(IV) molecules.

Experimental

Preparation of $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$

To 150 ml of toluene were added $V(h^5\text{-}C_5H_5)_2$ (1.81 g, 10 mmol), prepared from the reaction of VCl_3 and NaC_5H_5 by the general method outlined by Eisch and King [6], and $(C_6H_5)_2S_2$ (2.18 g, 10 mmol) under an atmosphere of nitrogen, and the mixture was refluxed for $\frac{1}{2}$ h; the color of the reaction mixture changed slowly from purple to dark green (red to transmitted light). The resulting mixture was filtered, and the solvent was removed under vacuum. The remaining residue was washed with 100 ml of hot hexane and extracted with 50 ml of boiling benzene; upon cooling of the benzene solution dark violet crystals of $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ formed which were collected on a filter and washed with pentane. Yield: ≈50%, based on $V(h^5\text{-}C_5H_5)_2$. The compound is

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* The latter preparation was independently utilized by Köpf and Schmidt [31] to prepare dicyclopentadienyltitanium mercaptides (both alkyl and aryl) in good yields.

stable in air for short periods and melts at approximately 140°C with considerable decomposition. $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ decomposes under vacuum (≈0.1 torr) at ca. 100°C and evolves $(C_6H_5)_2S_2$. (Found*: C, 65.9; H, 5.2; V, 12.5; S, 16.2. $C_{22}H_{20}VS_2$ calcd.: C, 66.1; H, 5.0; V, 12.8; S, 16.1%.)

Preparation of $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$

To 100 ml of toluene were added $N(C_2H_5)_3$ (10 ml), $V(h^5\text{-}C_5H_5)_2Cl_2$ (2.53 g, 0.01 mol), and C_6H_5SH (2 ml) under a nitrogen atmosphere. The resulting black mixture was stirred for 2 h and refluxed for 30 min, and the solvent then removed under vacuum. The remaining brown residue was washed with water, acetone, and ether, leaving $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$. Yield: ≈90% based on $V(h^5\text{-}C_5H_5)_2Cl_2$. The compound is stable to water and air and highly insoluble in common solvents. (Found: C, 57.9; H, 4.6; V, 15.7; S, 19.6. $C_{17}H_{15}VS_2$ calcd.: C, 61.1; H, 4.5; V, 15.2; S, 19.2%.)

Infrared spectra

Spectra of $M(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ (M = Ti, V) and $V_2(h^5\text{-}C_5H_5)_2\text{-}(\mu_2\text{-}SC_6H_5)_4$ were obtained from KBr discs with a Beckman IR-8 spectrometer. The IR frequencies, calibrated with polystyrene film, are given in Table 2 with a tentative assignment of the cyclopentadienyl ring frequencies being made on the basis of a discussion of localized vibrational modes by Fritz [7]. The spectra of the titanium and vanadium analogs are nearly identical, while the spectrum of $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ is very similar.

Magnetic susceptibility

(a) $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. Magnetic susceptibility measurements were made via the Faraday method over a temperature range of 95—296 K. The gram susceptibility for each temperature was obtained by the averaging of values from four different magnetic field strengths (viz., 4.62, 5.53, 6.50, and 7.47 kG). A diamagnetic correction of -231×10^{-8} cgsu/mol was applied to the molar susceptibility. The compound follows the Curie—Weiss Law, $\chi_M^{corr} = C/(T-\theta)$, in the measured temperature range. From a least-squares analysis of the linear relationship $1/\chi_M^{corr}$ vs. T(K), the constants C and θ were determined to be 0.394 ± 0.014 (estimated error at 95% *CL*) and —18.95, respectively. An effective magnetic moment of 1.78 ± 0.03 BM was obtained from the formula $\mu_{eff} = 2.828\,[\chi_M^{corr}\,(T-\theta)]^{1/2}$.

(b) $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$. The magnetic susceptibility was measured by the utilization of a Gouy balance with field strengths of 2.1, 2.6, and 3.1 kG. For calibration, a $Hg[Co(NCS)_4]$ sample was used. From the determined susceptibility of 1.08×10^{-6} cgsu obtained at 300 K together with an estimated diamagnetic correction of -192×10^{-6} cgsu/mol for a $V(C_5H_5)(SC_6H_5)_2$ moiety, the corrected molar susceptibility, χ_M^{corr}, was determined to be 552×10^{-6} cgsu. An effective magnetic moment of 1.15 BM per vanadium atom was calculated from the formula, $\mu_{eff} = 2.828\,[\chi_M^{corr}T]^{1/2}$.

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* Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. and by A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr), West Germany.

TABLE 1

MAGNETIC SUSCEPTIBILITY DATA FOR $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$

T (K)	$10^6\ \chi_g$ (cgsu/gm)	$10^6\ \chi_M^{corr}$ (cgsu/mol)
94.66	8.05	3447
110.38	7.14	3083
126.10	6.39	2784
141.82	5.71	2512
157.54	5.09	2264
173.26	4.63	2081
188.98	4.32	1957
204.70	3.90	1789
220.42	3.60	1669
251.86	2.99	1425
295.86	2.65	1290

Solution EPR spectrum of $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$

EPR spectra of the compound in various solutions were recorded on a Varian E-3 spectrometer at room temperature. An EPR spectrum of a saturated benzene solution (Fig. 1) displays the characteristic eight-line pattern resulting from the hyperfine interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$, 99.8%). This spectrum shows that the separations between adjacent lines are not equivalent in that the lines at the higher magnetic field have wider separations. On the basis of the system being represented by a spin Hamiltonian $H = \langle g\rangle \beta H \cdot S + \langle a\rangle I \cdot S$, it follows from second-order perturbation theory [8] that the relative hyperfine line positions H are related to the central magnetic-field position H_0 (corresponding to $\langle g\rangle$) by the equation $H(\text{gauss}) = H_0 - \langle a\rangle m_I/\langle g\rangle\beta - (1/H)(\langle a\rangle^2/2\langle g\rangle^2\beta^2)[I(I+1) - m_I^2]$. This equation indicates that the hyperfine line positions and the separations between adjacent lines are a function of the nuclear magnetic quantum number (m_I), as observed in the spectrum of $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ given in Fig. 1, in which the line separations increase from 59 to 67 gauss. In accord with the discussions by Rogers and Pake [8] and by Kivelson [9], the line-width variations (which also are a function of m_I) may be attributed to solute—solvent interactions such that the Zeeman and hyperfine interactions are not completely isotropic, as would be the case for freely tumbling molecules in a noninteracting solvent. The rather large line widths in the EPR spectrum are seen to give rise to considerable overlap of the hyperfine lines; this feature precluded a precise evaluation of the EPR parameters $\langle g\rangle$ and $\langle a\rangle$. An isotropic $\langle g\rangle$ value of 2.00 ± 0.02 was estimated directly from the calibrated Varian chart recording, while an isotropic $\langle a\rangle$ value of 62.6 ± 0.5 gauss was also determined directly from the spectrum by use of the equation $\langle a\rangle\ (\text{gauss}) = (H_{(-m_I)} - H_{(+m_I)})/2|m_I|$ which necessitates taking the difference between pairs of hyperfine lines with the same $|m_I|$*.

Data collection and reduction

(a). $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. Deep red crystals of $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$

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* Weil's treatment of large hyperfine splittings in EPR spectra arising from $S = 1/2$ systems [32] gives $\langle a\rangle$ (gauss) = $[(H_{(-m_I)} - H_{(+m_I)})/2|m_I|][1 - (\langle a\rangle/2h\nu_0)^2]$, where in the case of our particular system the term inside the latter square brackets approximates to 1.00.

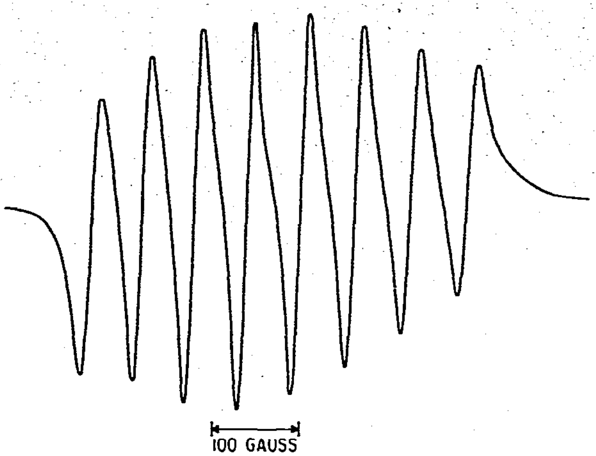

Fig. 1. The EPR spectrum of a benzene solution of $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ showing the characteristic eight-line hyperfine pattern due to the interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$; 99.8%).

TABLE 2

INFRARED SPECTRA OF $M(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ (M = Ti, V) AND $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$

$Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$	$V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$	$V_2(h^5\text{-}C_2H_5)_2\text{-}(\mu_2\text{-}SC_6H_5)_4$	Tentative assignment
C_5H_5 ring			
3118m	3118w		C—H str. (ν CH)
1435m	1438m	1437m	C—C str. (ω CC)
1359w	1362w(br)	1389w(br)	C—C str. (ω CC)
1129vw	1126vw(br)		
1022m	1023m	1025m	C—H def. (δ CH)
1018m	1012w	1017m	C—H def. (δ CH)
920w(br)	920m(br)	900w(br)	
851m	830s	814m(br)	C—H def. (γ CH)
823s(br)	810s(br)	794s(br)	C—H def. (γ CH)
C_6H_5 ring and others			
3068m	3061w	3078w(br)	
1572m	1572m	1580m	
1565w	1565w		
1471m	1471m	1476m	
1462m	1457w	1467m	
1172vs	1167w(br)	1160m	
1155vw(br)	1142vw(br)		
1082m	1080w	1083m	
1066m	1066w	1066m	
941w	939w(br)	966w	
744s	742s(br)	744s	
697s	696m(br)	695s(br)	
690s	690s(br)	690m	
		1298w	
		1000m(br)	
		844m	
		753m	
		736s	

were kindly supplied by Dr. S.A. Giddings of the American Cyanamid Company, Stamford, Connecticut (now at Formica Corporation, Cincinnati, Ohio). Preliminary X-ray photographs of several crystals mounted in thin-walled glass capillaries showed the Laue symmetry to be C_{2h}-$2/m$. Intensity data were recorded on multiple-film equi-inclination Weissenberg photographs exposed with Zr-filtered Mo-K_α radiation. Intensities of reflections from reciprocal levels $h0l$ through $h8l$ were estimated on the upper half of each film by visual comparison with a set of timed exposures of one standard reflection. A total of 1048 independent diffraction maxima was obtained. In addition, time exposure $hk0$ precession data were collected and used initially for inter-layer Weissenberg correlation to* place all data on the same relative scale. However, only Weissenberg data scaled with separate reciprocal level scale factors were used in the final stages of refinement.

Lattice parameters (Table 3) were determined from $h0l$ Weissenberg and $hk0$ precession photographs. Analytical corrections for Lorentz and polarization effects, as well as for spot extension [10], were applied to all data. Absorption corrections were not made, since the small linear absorption coefficient of 7 cm^{-1} made such corrections negligible. The estimated variance applied to

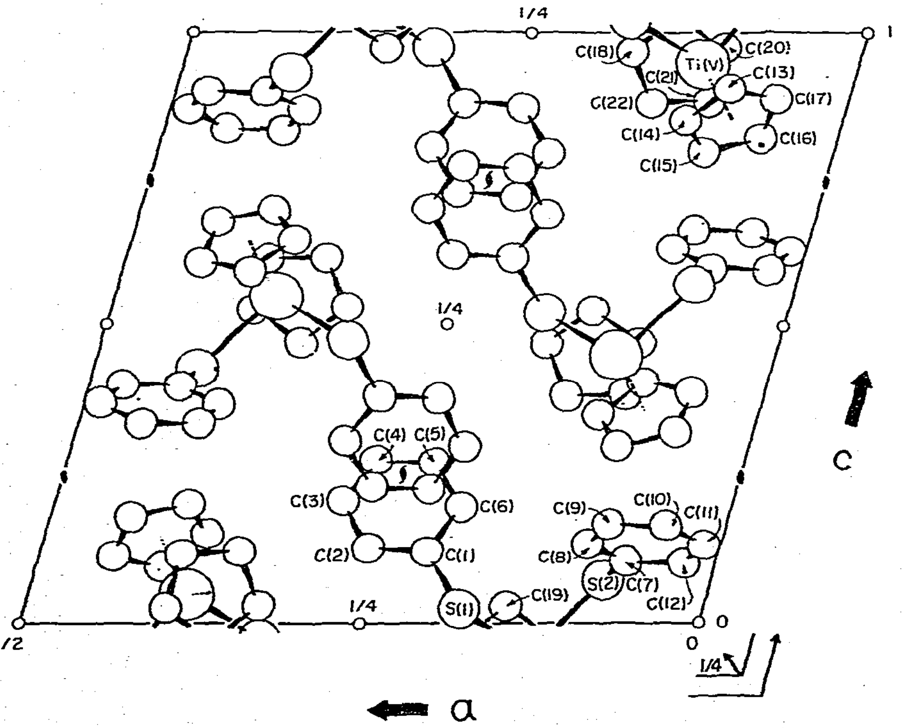

Fig. 2. An [010] projection showing the molecular arrangement of the isomorphous $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ and $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ compounds in one-half of the monoclinic unit cell of symmetry $C2/c$.

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* The programs utilized for the data collection and reduction, the structural analysis, least-squares refinement, and error analysis are listed elsewhere [1,5,11,12], if not otherwise referenced.

TABLE 3

CRYSTAL DATA FOR $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ AND $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$

	$Ti(h^5\text{-}C_5H_5)_2$-$(SC_6H_5)_2$	$V(h^5\text{-}C_5H_5)_2$-$(SC_6H_5)_2$
a (Å)	31.76(10)[a]	31.454(5)
b (Å)	7.97(2)	7.835(1)
c (Å)	15.45(5)	15.545(2)
β (deg.)	104.87(17)	104.35(1)
Volume (Å^3)	3780	3713
Density (obsd.) (g/cm^3)	1.44	[b]
Density (calcd.) (g/cm^3)	1.40	1.43
Z	8	8
Conditions limiting possible reflections		
$\{hkl\}$	$h + k = 2n$	$h + k = 2n$
$\{h0l\}$	$l = 2n$	$l = 2n$
Space group	$C2/c$ (C^6_{2h})	$C2/c$ (C^6_{2h})
Atomic positions in unit cell	$(8f)$[c]	$(8f)$

[a] Estimated standard deviations of the last significant figures are given in parentheses in this and the following tables. [b] Rapid dissolution of the crystals precluded a precise determination of the density. [c] Ref. 13.

each observed structure amplitude was computed in a manner described elsewhere [1,11].

(b). $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. A dark purple prismatic-shaped crystal of approximate dimensions 0.10 × 0.19 × 0.40 mm was mounted in a thin-walled glass capillary. Preliminary oscillation and Weissenberg photographs taken with Cu-K_α radiation indicated monoclinic symmetry. The crystal was then aligned on a General Electric—Datex card-controlled diffractometer (equipped with an E and A full circle) with the long dimension parallel to the spindle axis, and 16 diffraction peaks were carefully centered. The lattice constants (Table 3), obtained by least-squares refinement of the measured angle settings of these 16 reflections, were used to generate the angle settings for collection of all data, which were measured at a take-off angle of 2.0° by the $\theta - 2\theta$ scan technique with symmetric 2θ scans over a range of 1.5° at 1.0°/min rate. (Stationary-crystal)—(stationary-counter) background counts of 20 sec were taken at the beginning and end of each scan. A counter aperture of 2 mm diameter was placed at 31 mm from the crystal. Zirconium-filtered Mo-K_α radiation was employed with a scintillation detector with the pulse-height analyzer adjusted to accept approximately 90% of the pulse.

Intensity data (hkl, $\bar{h}kl$, $\bar{h}k\bar{l}$, $hk\bar{l}$) were collected for $2\theta \leq 50°$. Four standard reflections, measured every 100 reflections to monitor the electronic stability and crystal alignment and/or decay, showed no significant changes during the entire data collection. The data were corrected and averaged, and $\sigma(I)$'s and $\sigma(|F|)$'s (based on an E value of 0.0016) were obtained as previously described [12]. This procedure yielded 1793 independent reflections with $|F| \geq 10\sigma(|F|)$ which were used in the structural determination and refinement. No corrections for absorption were made in that the transmission coefficients (based on a linear absorption coefficient of 7.8 cm^{-1} for Mo-K_α radiation) calculated for a small set of reflections with widely differing orientations were found to vary from only 0.92 to 0.93.

Solution and refinement of the structures

(a). $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. The observed systematic absences (Table 3) are satisfied by two space groups, $Cc(C_s^4$, No. 9) and $Cs/c(C_{2h}^6$, No. 15) [13] which require (with an assumption of no crystal order-disorder phenomenon) that either one or two formula units, respectively, comprise the crystallographically independent unit.

Different interpretations based on $C2/c$ symmetry of the computed three-dimensional Patterson map yielded several possible positions for the independent titanium atom. Application of successive Fourier syntheses phased on each of these titanium positions failed to resolve the positions of all carbon atoms, although one or more images of a triangular TiS_2 group always appeared accompanied by presumed fragments of the phenyl rings which were invariably badly distorted. Attempted least-squares refinement* of these partial structures failed to reduce the unweighted discrepancy factor to less than 35%.

The diffraction results displayed a pseudo-lattice with a c' lattice vector equal to one-half of the true c lattice vector, since the reflections with an l-odd index were weak and comprised only 30% of the observed data. Accordingly, two sets of normalized structure factors were prepared for direct phase determination [14]. The statistical averages of the normalized structure factors (scaled so that $\langle |E| \rangle = 1$) for the first set, which included observed and unobserved data for the true unit cell, were $\langle |E| \rangle = 0.854$ and $\langle |E^2 - 1| \rangle = 0.901$, with a distribution of 0.05% for $E > 3$, 3.4% for $E > 2$, and 31.87% for $E > 1$. The second set of normalized structure factors contained the data for the pseudo-cell ($l' = l/2$, with l-odd reflections deleted) and gave $\langle |E| \rangle = 0.866$ and $\langle |E^2 - 1| \rangle = 0.824$, with a distribution of 0.00% for $E > 3$, 1.82% for $E > 2$, and 37.79% for $E > 1$. A comparison of these results with the corresponding theoretical averages [15] (based on a random distribution of equal atoms**) for centrosymmetric crystals vs. those for non-centrosymmetric crystals indicated that the distribution and determined averages for the real-cell data are inconclusive, whereas those for the pseudo-cell data appeared to support a non-centrosymmetric space group. An application of the Hauptman—Karle Σ_2 formula [14,16] to determine the phases of the real-cell structure factors under centrosymmetric $C2/c$ symmetry failed to yield a sufficient number of high probability phase relations even when five letters were assigned as unknown starting phases in the symbolic procedure. The conclusion thus formed was that the space group was the non-centrosymmetric Cc.

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* In all least-squares refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and $w = 1/\sigma^2(F_o)$. The discrepancy factors are defined as $R_1 = (\Sigma ||F_o| - |F_c||/\Sigma|F_o|) \times 100$ and $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2} \times 100$.

** The electron density in $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ was later found to be distributed such that 60% of the contribution of the scattering lies within 30% of the cell volume. This nonrandom distribution presumably accounts for the disparity between the final results and the conclusion formed on the basis of the statistical tests.

The existence of one short unit cell dimension (viz., *b* 7.97 Å) indicated that the packing of the molecules (or of the heavy Ti and S atoms at least) could probably be resolved in projection. Consequently a [010] Patterson projection was computed, and an interpretation on the basis of the projected space group *Cc* yielded initial *x* and *z* coordinates for the titanium and sulfur atoms. Successive two-dimensional Fourier maps appeared to resolve the positions of 23 carbon atoms with additional indications of the phenyl and cyclopentadienyl ring positions. Figure 2 shows the contents of one-half of the centered unit cell projected down the [010] direction.

A reinterpretation of the three-dimensional Patterson map on the basis of space group *Cc* not only yielded the *y* coordinates of the titanium, sulfur, and five carbon atoms but also showed that the maxima initially assumed to represent titanium—titanium vectors were accidentally degenerate titanium—sulfur vectors. Two successive three-dimensional Fourier maps yielded the approximate positions of all nonhydrogen atoms for two independent molecules of $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. Full-matrix least-squares for this noncentrosymmetric model, in which all carbon and hydrogen atoms were constrained to vary as rigid group cyclopentadienyl and phenyl rings (a description of the rigid-body refinement [1] is outlined in Table 4), converged smoothly and rapidly to R_1 and R_2 values of 8.6 and 8.9%, respectively. This refinement was not satisfactory, however, due to the very high correlations (of approximate magnitude 0.8) between all corresponding positional parameters in the two molecules. Furthermore, unreasonable

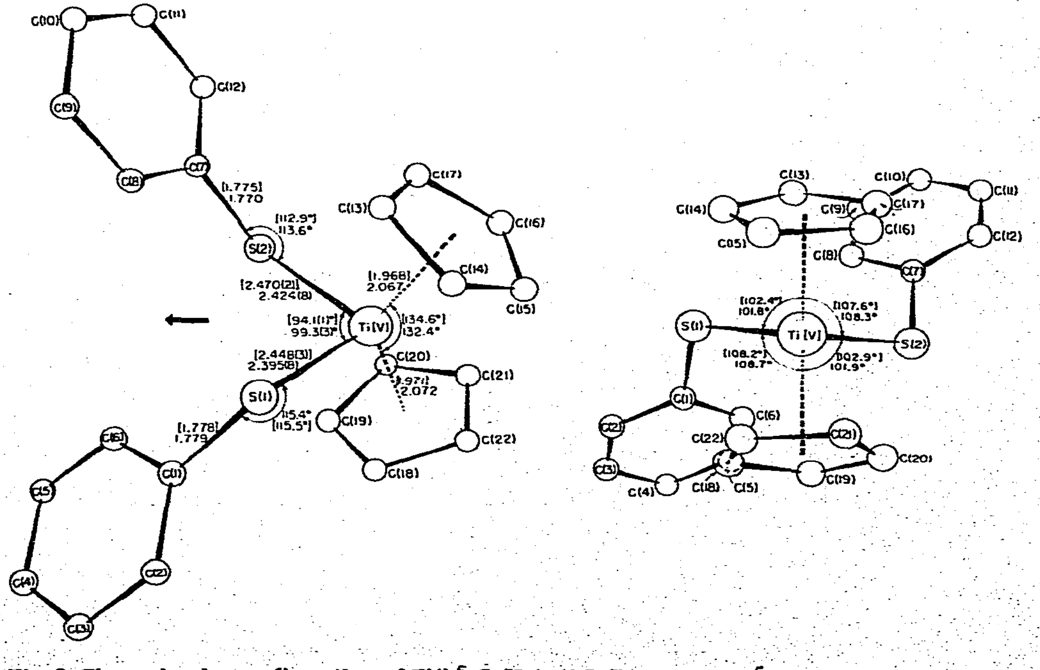

Fig. 3. The molecular configuration of $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ and $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. The molecular parameters for the titanium and vanadium analogs are given without and with square brackets, respectively.

variations in certain molecular parameters were conspicious (e.g., the four independent Ti—S bond lengths varied over a range of 0.14 Å). On the basis of these observations, it was noted that the two assumed independent molecules in *Cc* were approximately related by a screw-axis symmetry operation of space group *C*2/*c*. Refinement was therefore continued in the centrosymmetric space group with the C and H of the two Cp and two Ph rings in the resulting single independent molecule treated as rigid groups [1]. The final discrepancy factors for this constrained centrosymmetric model were R_1 10.7% and R_2 11.7%. When the rigid group constraints were released, neither a significant improvement in the refinement (R_1 10.8%, R_2 11.6%) nor significant variations between the corresponding molecular parameters were observed. An electron-density difference synthesis of the final rigid-group model under *C*2/*c* indicated no unusual features with no peaks above the general background. While the overall fit of the calculated structure factors to the observed data is better in space group *Cc* when judged only by the gross indicators, R_1 and R_2, we are highly prejudiced toward the actual space group being *C*2/*c* due to: (1) the existence of large correlation coefficients (vide supra) between all corresponding parameters of the two supposedly independent molecules in *Cc*; (2) the inexplicable distortions observed in the noncentrosymmetric model being absent in the centrosymmetric refinement; and (3) the e.s.d.'s of all positional parameters obtained in space group *Cc* being larger than the corresponding values in space group *C*2/*c*. These considerations have led to our adoption of the rigid-group refinement model in *C*2/*c* as the best structural solution consistent with the criterion of minimum variance [17]. The atomic parameters for this model are given in Table 4*, while interatomic distances and bond angles are presented in Table 5.

(b). $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$. Refinement was undertaken at the onset based on the final coordinates determined for $\mathrm{Ti}(h^5\text{-}\mathrm{C_5H_5})_2(\mathrm{SC_6H_5})_2$ being utilized as initial coordinates for the vanadium analog. Real and imaginary anomalous dispersion corrections [18] for the vanadium and sulfur atoms were included in the structure factor calculations. Several cycles of a rigid-body least-squares refinement [1] resulted in R_1 6.8% and R_2 8.1%. A difference electron-density map calculated from these parameters contained no peaks of magnitude greater than 0.8 electrons/Å^3. The atomic and rigid-body parameters based on this refinement are presented in Table 4 and the molecular distances and angles in Table 5.

Results and discussion

Description of the structure and bonding implications

Since the crystal structures of $\mathrm{Ti}(h^5\text{-}\mathrm{C_5H_5})_2(\mathrm{SC_6H_5})_2$ and $\mathrm{V}(h^5\text{-}\mathrm{C_5H_5})_2$-$(\mathrm{SC_6H_5})_2$ are isomorphous, in this discussion the molecular parameters of the

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* See NAPS document no. 02761 for 28 pages of supplementary material involving a tabulation of the observed and calculated structure factors for the $\mathrm{M}(h^5\text{-}\mathrm{C_5H_5})_2(\mathrm{SC_6H_5})_2$ (M = Ti, V) compounds. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., N.Y., N.Y. 10017. Remit in advance for each NAPS accession nmuber $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15c for each additional page. Make checks payable to Microfiche Publications.

titanium complex are given followed by the corresponding values in square brackets for the vanadium analog. The molecular configuration together with selected distances and bond angles is given in Fig. 3 which shows that the two phenylmercapto sulfur atoms and both centroids of the two cyclopentadienyl rings constitute a pseudo-tetrahedral arrangement about the central metal atom. The $C_5H_5(1)$—M—$C_5H_5(2)$ angle (determined by the ring centroids) of 132° [135°] and S(1)—M—S(2) bond angle of 99.3(3)° [94.1(1)°] show a considerable angular distortion (expected for nonequivalent ligands) from a regular tetrahedron relative to the variations of the other four $C_5H_5(n)$—M—S angles of range 102—109° [102—108°]. With the assumption of cylindrical symmetry for each of the cyclopentadienyl rings, the coordination polyhedron about the metal atom ideally conforms to C_{2v}-$2mm$ symmetry. Nevertheless, a distinct deformation from this C_{2v} geometry is observed, as indicated by the plane containing the metal and two cyclopentadienyl ring centers being tilted by 5° [4°] from the normal to the MS_2 plane, such that the resulting molecular configuration (including the phenyl rings) conforms closely to the reduced point group symmetry C_2-2. The two cyclopentadienyl rings are not oriented in an exactly eclipsed array but are rotated about their M—(C_5H_5 centroid) vectors from this conformation by only 15.5° relative to one another; the resulting ring positions are consistent with the pseudo C_2 molecular geometry.

Fig. 2 shows an [010] projection depicting the orientations of the eight $M(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ molecules per cell under $C2/c$ monoclinic symmetry. The closest intermolecular contacts are normal, thereby indicating no unusual intermolecular interactions.

The fact that these d^0 titanium(IV) and d^1 vanadium(IV) complexes are crystallographically isomorphous makes it an especially reasonable assumption that the differences in corresponding molecular parameters are predominantly a consequence of intramolecular forces reflecting the change in electronic structure between the two metal atoms. There are two striking differences between $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ and $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ which have major implications with respect to the electronic structure of $M(h^5\text{-}C_5H_5)_2L_2$-type complexes. The first distinction is that the S—V—S bond angle of 94.1(1)° is 5° *less* than the S—Ti—S bond angles of 99.3(3)°. This significant decrease in the L—M—L bond angle in a $M(h^5\text{-}C_5H_5)_2L_2$ molecule upon occupation of a predominantly metal orbital which is empty in the d^0 titanium(IV) molecule is in direct opposition to the qualitative Ballhausen—Dahl model which presumes that the unpaired electron in a $V(h^5\text{-}C_5H_5)_2L_2$ molecule would reside in a metal hybrid orbital which occupies a sterically active position bisecting the V—L bonds. If the Ballhausen—Dahl model were correct, it would be expected from electron—pair repulsion arguments that the L—V—L bond angle should be significantly larger and not smaller than the L—Ti—L bond angle in a given pair of $M(h^5\text{-}C_5H_5)_2L_2$ molecules with identical L ligands. Hence, these crystallographic results were taken as strong evidence [19] for the nonvalidity of the Ballhausen—Dahl model applied to $M(h^5\text{-}C_5H_5)_2L_2$ systems *. The Ballhausen—Dahl

(continued on p. 86)

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* Independent preparative and crystallographic investigations by Green, Prout and co-workers [20] of a number of $M(h^5\text{-}C_5H_5)_2L_2$ complexes for which M = Zr, Nb, Mo have led them to an analogous correlation between the L—M—L bond angle and the number of nonbonding d electrons of the second-row transition metal, which they cite as strong evidence for the Alcock model [21] being valid for $M(h^5\text{-}C_5H_5)_2L_2$-type systems.

TABLE 4

ATOMIC PARAMETERS FOR $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ AND $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ [a]

	A. $Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$				B. $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$			
	x	*y*	*z*	*B*	*x*	*y*	*z*	*B*
M	0.1166(1)	0.0108(5)	−0.0477(2)	1.7(1)	0.1149(1)	−0.0019(2)	−0.0518(1)	*b*
S(1)	0.1799(2)	0.1699(6)	0.0242(3)	2.0(1)	0.1778(1)	0.1710(3)	0.0244(1)	*b*
S(2)	0.0798(1)	0.0087(7)	0.0717(3)	2.4(1)	0.0798(1)	0.0048(3)	0.0739(1)	*b*
C(1)	0.2156(4)	0.0742(21)	0.1191(7)	3.2(5)	0.2130	0.0749	0.1194	3.3(2)
C(2)	0.2600(4)	0.0621(20)	0.1238(7)	3.2(5)	0.2578	0.0663	0.1237	4.4(2)
C(3)	0.2890(3)	0.0073(19)	0.2025(8)	4.5(5)	0.2872	0.0144	0.2019	5.4(2)
C(4)	0.2737(4)	−0.0354(18)	0.2766(6)	4.8(6)	0.2719	−0.0290	0.2759	5.8(2)
C(5)	0.2294(4)	−0.0233(18)	0.2719(7)	4.5(5)	0.2271	−0.0205	0.2716	4.5(2)
C(6)	0.2003(3)	0.0314(20)	0.1932(9)	3.4(5)	0.1797	0.0314	0.1934	3.7(2)
C(7)	0.0662(4)	0.2123(13)	0.1015(8)	1.9(4)	0.0670	0.2138	0.1039	2.6(1)
C(8)	0.0985(3)	0.3319(17)	0.1338(8)	3.1(5)	0.0999	0.3319	0.1393	3.2(2)
C(9)	0.0876(4)	0.4862(15)	0.1645(8)	4.5(5)	0.0890	0.4904	0.1684	3.8(2)
C(10)	0.0444(4)	0.5212(12)	0.1630(8)	4.7(6)	0.0451	0.5309	0.1622	4.6(2)
C(11)	0.0121(3)	0.4017(16)	0.1307(9)	3.8(5)	0.0123	0.4127	0.1268	5.6(2)
C(12)	0.0230(4)	0.2473(14)	0.1000(9)	3.3(5)	0.0232	0.2542	0.0977	4.3(2)
C(13)	0.0921(6)	0.2883(18)	−0.0930(10)	5.4(6)	0.0891	0.2690	−0.0897	5.0(2)
C(14)	0.1185(4)	0.2343(22)	−0.1479(12)	4.9(6)	0.1166	0.2211	−0.1443	6.0(2)
C(15)	0.0975(6)	0.0990(21)	−0.1997(10)	4.7(6)	0.0968	0.0835	−0.1972	5.4(2)
C(16)	0.0581(5)	0.0694(18)	−0.1767(11)	4.8(6)	0.0571	0.0463	−0.1753	5.6(2)
C(17)	0.0548(5)	0.1863(22)	−0.1107(11)	6.1(7)	0.0523	0.1609	−0.1089	4.8(2)
C(18)	0.1720(3)	−0.2008(20)	−0.0297(10)	4.6(6)	0.1720	−0.1972	−0.0309	5.1(2)
C(19)	0.1457(4)	−0.2415(19)	0.0279(7)	3.8(5)	0.1456	−0.2383	0.0270	4.1(2)
C(20)	0.1037(4)	−0.2782(21)	−0.0251(9)	2.9(5)	0.1038	−0.2829	−0.0246	3.8(2)
C(21)	0.1040(4)	−0.2602(20)	−0.1153(8)	2.9(5)	0.1043	−0.2694	−0.1144	4.1(2)
C(22)	0.1462(5)	−0.2123(19)	−0.1183(8)	3.5(5)	0.1464	−0.2164	−0.1184	4.7(2)
H(2)	0.2719	0.0955	0.0659	7.8	0.2698	0.1003	0.0659	8.0
H(3)	0.3237	−0.0021	0.2061	7.8	0.3222	0.0077	0.2053	8.0
H(4)	0.2964	−0.0782	0.3381	7.8	0.2949	−0.0697	0.3371	8.0
H(5)	0.2174	−0.0567	0.3297	7.8	0.2152	−0.0544	0.3295	8.0
H(6)	0.1657	0.0409	0.1895	7.8	0.1627	0.0381	0.1901	8.0
H(8)	0.1323	0.3045	0.1350	7.5	0.1342	0.3004	0.1442	8.0
H(9)	0.1128	0.5796	0.1898	7.5	0.1144	0.5827	0.1961	8.0
H(10)	0.0358	0.6419	0.1871	7.5	0.0365	0.6534	0.1850	8.0
H(11)	−0.0217	0.4290	0.1295	7.5	−0.0220	0.4443	0.1219	8.0

H(12)	−0.0023	0.1540	0.0748	7.5	−0.0024	0.1619	0.0700	8.0
H(13)	0.0993	0.3912	−0.0449	9.2	0.0952	0.3719	−0.0410	8.0
H(14)	0.1498	0.2880	−0.1500	9.2	0.1478	0.2802	−0.1455	8.0
H(15)	0.1096	0.0294	−0.2490	9.2	0.1100	0.0172	−0.2466	8.0
H(16)	0.0343	−0.0273	−0.2051	9.2	0.0340	−0.0540	−0.2047	8.0
H(17)	0.0280	0.1963	−0.0790	9.2	0.0249	0.1649	−0.0778	8.0
H(18)	0.2063	−0.1663	−0.0093	7.5	0.2062	−0.1574	−0.0115	8.0
H(19)	0.1561	−0.2441	0.1008	7.5	0.1557	−0.2361	0.0993	8.0
H(20)	0.0758	−0.3143	−0.0004	7.5	0.0759	−0.3213	0.0007	8.0
H(21)	0.0764	−0.2799	−0.1730	7.5	0.0768	−0.2954	−0.1711	8.0
H(22)	0.1570	−0.1884	−0.1786	7.5	0.1573	−0.1943	−0.1788	8.0

[a] The rigid-group atomic positions [1] are defined relative to an orthonormal axis coordinate system a'', b'', c'' as follows: for a phenyl group, the carbon atom attached to the sulfur atom lies as the origin, a'' passes through the *para*-carbon, and all atoms lie in the $a''b''$ plane; for a cyclopentadienyl group, the centroid of the ring lies at the origin, a'' passes through one atom in the ring, and all atoms lie in the $a''b''$ plane. The rotation angles ϕ, θ, ρ, define the position (apart from translation to the crystallographic origin) of the rigid-group coordinate system with respect to the orthonormal axis system, a', b', c'. The latter is defined in terms of the crystallographic axis system, a, b, c, by the conditions: a' parallel to a, b' parallel to $c' \times a'$, and c' parallel to $a \times b$. The group rotation angles for the two phenyl and two cyclopentadienyl rings are as follows:

	$Ti(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$			$V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$		
	ϕ	θ	ρ	ϕ	θ	ρ
$C_6H_5(1)$	96.4(5)	−154.6(4)	111.1(5)	97.2(2)	−154.2(2)	110.2(2)
$C_6H_5(2)$	106.6(4)	167.9(4)	19.7(4)	105.1(2)	165.0(2)	19.0(2)
$C_5H_5(1)$	100.0	−165.9	42.7	102.3	−166.4	43.8
$C_5H_5(2)$	−68.7	106.3	84.1	−73.7	105.6	90.9

The hydrogen atoms of phenyl and cyclopentadienyl rings lie along vectors extended from the ring centroid through the attached carbon atom. The phenyl ring conforms to C_{2v} symmetry with C—C 1.395, C—H 1.09 Å. The cyclopentadienyl ring conforms to D_{5h} symmetry with C—C 1.405, C—H 1.09 Å.

[b] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were used for, V S(1), and S(2). The resulting thermal coefficients (× 10^4) are as follows:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	97(2)	1097(23)	229(5)	14(7)	42(2)	−14(12)
S(1)	100(3)	1357(42)	352(11)	−59(9)	44(4)	76(17)
S(2)	96(2)	1128(34)	278(8)	− 7(10)	61(4)	− 6(18)

bonding model modified by Alcock [21], which would predict that the unpaired electron in $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ is sterically localized in a hybrid vanadium orbital in the plane formed by the two V—S bonds with equal lobes perpendicular to the line bisecting the two V—S bonds, is not incompatible with the S—M—S angles found in $M(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ (M = Ti, V). However, Alcock's bonding scheme* is also based solely on the arbitrary hybridization of metal orbitals along specified directions to maximize overlap with the ligands, and hence it is not necessarily adequate (without direct evidence) in its qualitative description of the nature of the metal orbital containing the so-called nonbonding electron(s).

The second significant structural variation pertains to the unusual length of the two V—S bonds compared to the Ti—S bonds. A consideration of the covalent radii [22] of 1.32 Å for Ti and 1.22 Å for V leads to the expectation that the titanium-to-(cyclopentadienyl carbon) distances and the Ti—S bond lengths should be 0.1 Å longer than the vanadium-to-(cyclopentadienyl carbon) distances and V—S bond lengths respectively. Whereas the M—C distances of range 2.38—2.40 Å [2.27—2.32 Å] and mean value 2.39 Å [2.305 Å] follow this trend**, the mean Ti—S bond length of 2.41 Å instead is 0.05 Å shorter than the mean V—S bond length of 2.46 Å. This bond-length anomaly involving a relative lengthening of the V—S bonds by 0.15 Å may be rationalized on the basis of a composite of: (1) an electronic effect arising from the presence of the unpaired electron in $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ in a molecular orbital which has significant antibonding V—S orbital character but relatively little cyclopentadienyl character; and (2) intramolecular overcrowding due primarily to nonbonding repulsive forces from the cyclopentadienyl ligands. These results suggest that the size of the L ligands may be a much more important factor in governing the stability of a $V(h^5\text{-}C_5H_5)_2L_2$ complex (relative to dissociation of an L ligand) than of a corresponding titanium complex due to the presumably weaker V—L bonds (as indicated by the M—L bond-length difference).

Bonding implications of the magnetic data

The closeness of the observed ESR spectroscopic splitting factor, $\langle g \rangle = 2.00$, to the spin free $\langle g \rangle$ factor of 2.0023 as well as the closeness of the effective magnetic moment, μ_{eff} 1.78 BM, to the spin only value suggest that there is negligible spin-orbit coupling contributions to the ground state of $V(h^5\text{-}C_5H_5)_2\text{-}(SC_6H_5)_2$. The value of the isotropic hyperfine coupling constant, $\langle a \rangle =$ 62.6(5) G, obtained from the EPR spectrum can arise mainly from two mechanisms [23,24]. (*a*) direct admixture of the $(n + 1)s$ wavefunction into the nd^m configuration, and (*b*) a polarization of the inner filled *s* orbitals by the unpaired *d* electron. The magnitude of the isotropic coupling constant for a 4*s* configuration in the V^{4+} ion has been estimated to be about 4000 G [23]. This value suggests that if an electron were in an orbital with much *s* character, then the

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* This alternative bonding representation was proposed by Alcock [21] in 1967 in connection with his X-ray crystallographic examination of $Re(h^5\text{-}C_5H_5)(h^4\text{-}C_5H_5CH_3)(CH_3)_2$, from which he concluded that the H_3C—Re—CH_3 bond angle of 75.8(1.3)° was too acute to allow placement of an occupied orbital between the two methyl ligands.

** This difference is likewise reflected in the Ti—C_5H_5(centroid) distances of 2.07 Å being 0.10 Å larger than the V—C_5H_5(centroid) distances of 1.97 Å.

isotropic hyperfine constant would be dominated by mechanism (*a*). The similarity of the isotropic hyperfine constant given above for $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ with those of range 60—75 G measured by Doyle and Tobias [25] for other $V(h^5\text{-}C_5H_5)_2L_2$ complexes with widely differing L ligands emphasizes that the unpaired electron must be localized primarily on the vanadium atom in this type of complex. The fact that Davison et al. [23] concluded from a detailed analysis of their EPR measurements of the $[VS_6C_6(CN)_6]^{2-}$ dianion that the observed $\langle a \rangle$ value of 63 G would be inconsistent with any admixture of the 4*s* orbial greater than ≈3% into the ground state electronic configuration lends weight to the premise that the similarly low $\langle a \rangle$ values in the $V(h^5\text{-}C_5H_5)_2L_2$ molecules indicate that the unpaired electron in each of these vanadium(IV) complexes resides in a metal orbital with little 4*s* orbital character. It is noteworthy that this conclusion is in severe disagreement with the Ballhausen—Dahl model which proposed that the electron(s) in a d^1 or d^2 metal(IV) complex $M(h^5\text{-}C_5H_5)_2L_2$ would occupy a hybrid metal orbital with considerable 4*s* character.

Stereochemistry of the $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ *dimer*

The $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ complex, unexpectedly obtained in our attempt to synthesize $V(h^5\text{-}C_5H_5)_2(SC_6H_5)_2$ by the reaction of $V(h^5\text{-}C_5H_5)_2Cl_2$ with C_6H_5SH, is presumably analogous to the corresponding methylmercapto compound, $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCH_3)_4$, prepared by Holm, King, and Stone [26] from the reaction of $V(h^5\text{-}C_5H_5)(CO)_4$ with $(CH_3)_2S_2$ or CH_3SH. The structural equivalence of these two mercapto derivatives is indicated by the similarity of their magnetic moments, viz., μ_{eff}^{300} 1.15 BM for $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SC_6H_5)_4$ vs. μ_{eff}^{298} 0.92 BM for $V_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCH_3)_4$. The geometry proposed by Holm et al. [26] for their methylmercapto compound resembles that determined subsequently by an X-ray diffraction study [27] of both the neutral [28] and oxidized $[Mo_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCH_3)_4]^n$ complexes ($n = 0, +1$), in which two $Mo(h^5\text{-}C_5H_5)$ moieties are linked to each other by four symmetrically positioned bridging mercapto ligands.

Analogous metal dithiolene complexes $M_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCCF_3)_4$ (M = V, Mo) of this type of binuclear metal dimer were prepared and characterized from NMR, IR, and room-temperature magnetic susceptibility data by King [28,29] who proposed the existence of a Mo—Mo single bond to account for the observed diamagnetism of the molybdenum dimer and a V—V bond of partial double-bond character in the vanadium derivative to explain the observed small magnetic moment. Preliminary structural determinations by X-ray diffraction of these two metal dithiolene dimers were performed by Cox and Baird [30] who, in spite of crystallographic problems encountered in unsuccessful attempts to refine the compounds, nevertheless established the molybdenum and vanadium dithiolene dimers to be isostructural and confirmed the gross tetramercapto-bridged configuration proposed by King [28]. The closeness of the determined Mo—Mo distances in $Mo_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCCF_3)_4$ 2.62(2) Å [30] and $Mo_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}SCH_3)_4$ 2.603(2) Å [27] makes it likely that the detailed geometries of these mercaptomethyl and dithiolene metal dimers are closely related to each other.

TABLE 5

SELECTED INTERATOMIC DISTANCES AND BOND ANGLES

	$Ti(h^5\text{-}C_5H_5)_2\text{-}(SC_6H_5)_2$	$V(h^5\text{-}C_5H_5)_2\text{-}(SC_6H_5)_2$
A. Intramolecular distances (Å)		
M—S(1)	2.395(8)	2.448(3)
M—S(2)	2.424(8)	2.470(2)
	2.410 (av)	2.459 (av)
S(1)···S(2)	3.673	3.601
S(1)—C(1)	1.78	1.778
S(2)—C(7)	1.77	1.775
M—C(13)	2.39	2.294
M—C(14)	2.37	2.272
M—C(15)	2.38	2.293
M—C(16)	2.40	2.327
M—C(17)	2.40	2.328
M—C(18)	2.40	2.320
M—C(19)	2.40	2.301
M—C(20)	2.38	2.289
M—C(21)	2.39	2.301
M—C(22)	2.40	2.320
	2.39 (av)	2.305 (av)
$M—C_5H_5(1)$[a]	2.067	1.968
$M—C_5H_5(2)$	2.072	1.971
	2.07 (av)	1.97 (av)
B. Bond angles (degrees)		
S(1)—M—S(2)	99.3(3)	94.1(1)
$C_5H_5(1)—M—C_5H_5(2)$	132.4	134.6
M—S(1)—C(1)	115.4	115.5
M—S(2)—C(7)	112.9	113.6
$S(1)—M—C_5H_5(1)$	101.8	102.4
$S(1)—M—C_5H_5(2)$	108.7	108.2
$S(2)—M—C_5H_5(1)$	108.3	107.6
$S(2)—M—C_5H_5(2)$	101.9	102.9

[a] $C_5H_5(n)$ denotes the centroid of the *n*th cyclopentadienyl ring.

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References

1 S.F. Watkins, Ph.D. Thesis, University of Wisconsin (Madison), 1967.
2 (a) S.A. Giddings, U.S. Patent 3030395 (1962) (c.f., Chem. Abstr., 57 (1962) 9881);

(b) S.A. Giddings, 2nd International Symposium on Organometallic Chemistry, Madison, Wisconsin, 1965; S.A. Gidding, Inorg. Chem., 6 (1967) 819.
3 C.J. Ballhausen and J.P. Dahl, Acta Chem. Scand., 15 (1961) 1333.
4 J.L. Petersen and L.F. Dahl, J. Amer. Chem. Soc., 96 (1974) 2248.
5 E.G. Muller, Ph.D. Thesis, University of Wisconsin (Madison), 1970.
6 J.J. Eisch and R.B. King, Organometallic Synthesis, Vol. 1, Academic Press, New York, 1965.
7 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 280.
8 R. Rogers and G. Pake, J. Chem. Phys., 33 (1960) 1107.
9 D. Kivelson, J. Chem. Phys., 33 (1960) 1094.
10 D.C. Phillips, Acta Crystallogr., 7 (1954) 746.
11 D.L. Stevenson, C.H. Wei, and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 6027; C.H. Wei, L. Markó, G. Bor and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 4840.
12 V.A. Uchtman and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 3756.
13 International Tables for X-Ray Crystallography, Vol. 1, Kynoch Press, Birmingham, England, 1962.
14 H. Hauptman and J. Karle, Solution of the Phase Problem, I. The Centrosymmetric Crystal, American Crystallographic Association Monograph No. 3, Polycrystal Book Service, Pittsburg, Pa., 1953; I.L. Karle and J. Karle, Acta Crystallogr., 16 (1963) 969.
15 (a) H.G. Stout and L.H. Jensen, X-Ray Structure Determination, The Macmillian Co., New York, N.Y., 1968, p. 321;
(b) I.L. Karle, K.S. Dragonette and S.A. Brenner, Acta Crsytallogr., 19 (1965) 713.
16 R.B.K. Dewar and A.L. Stone, Fame and Magic, Fortran Computer Programs For Use in the Symbolic Addition Method, University of Chicago, 1966; cf., E.B. Fleischer, R.B.K. Dewar and A.L. Stone, Abstracts of Papers, American Crystallographic Association Winter Meeting, Atlanta, Georgia, 1967, p. 20.
17 (a) W.C. Hamilton, Statistics in the Physical Sciences, The Ronald Press Company, New York, 1964, p. p. 124;
(b) J. Donohue and A. Caron, Acta Crystallogr., 17 (1964) 663.
18 International Tables for X-Ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1967, p. 215.
19 L.F. Dahl, Plenary Lecture, 4th International Conference on Organometallic Chemistry, Bristol, 1969.
20 (a) J.C. Green, M.L.H. Green and C.K. Prout, J. Chem. Soc., Chem. Commun., (1972) 421, and references cited therein;
(b) M.H.L. Green, Sectional Lecture, 5th International Conference on Organometallic Chemistry, Moscow, 1971 [cf., Pure Appl. Chem., 30 (1972) 373];
(c) K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton and G.V. Rees, Acta Crsytallogr., Sect. B, 30 (1974) 2290.
21 N.W. Alcock, J. Chem. Soc. A, (1967) 2001.
22 L. Pauling, The Nature of the Chemical Bond, Third Ed., Cornell University Press, Ithaca, New York, 1960, p. 256.
23 A. Davison, N. Edelstein, R.H. Holm and A. Maki, J. Amer. Chem. Soc., 86 (1964) 2799.
24 B.R. McGarvey, J. Chem. Phys., 71 (1967) 51.
25 G. Doyle and R.S. Tobias, Inorg. Chem., 7 (1969) 2479.
26 R.H. Holm, R.B. King and F.G.A. Stone, Inorg. Chem., 2 (1963) 219.
27 N.G. Connelly and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 7470.
28 R.B. King, J. Amer. Chem. Soc., 85 (1963) 1587.
29 R.B. King and M.B. Bisnette, Inorg. Chem., 6 (1965) 469.
30 J.W. Cox, Jr., M.S. Thesis, Wake Forest College, 1965; H.W. Baird, private communication to L.F. Dahl, 1965.
31 H. Köpf and M. Schmidt, Z. Anorg. Allg. Chem., 340 (1965) 139.
32 J.A. Weil, J. Magn. Resonance, 5 (1971) 394.