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## SYNTHESIS AND CHARACTERIZATION OF DI- $\pi$ -CYCLOPENTADIENYL-METAL PENTASULFIDES OF TITANIUM(IV) AND VANADIUM(IV): AN OPERATIONAL TEST OF THE INFLUENCE OF AN UNPAIRED ELECTRON ON THE MOLECULAR GEOMETRY

E. GORDON MULLER\*, JEFFREY L. PETERSEN\*\*, and LAWRENCE F. DAHL\*  
 Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

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### Summary

Our preparation of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  by the reaction of elemental sulfur with  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{CO})_2$  in hexane and of  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$  by the reaction of  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{Cl}_2$  with  $\text{Na}_2\text{S}_5$  in THF and structural analyses by single crystal X-ray diffraction (together with infrared, solution EPR, and temperature-dependent magnetic susceptibility measurements) represent an extension of our previous work on  $\text{M}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  ( $\text{M} = \text{Ti}, \text{V}$ ). The crystallographic results provide further support of our previous conclusions that the Ballhausen-Dahl model is not valid for  $\text{M}(h^5\text{-C}_5\text{H}_5)_2\text{L}_2$  systems. The structural features of the chair-like titanium and vanadium pentasulfide molecules are compared to the corresponding phenylmercapto analogs and to the chair-like cyclohexasulfur molecule in rhombohedral sulfur.  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  was isolated as a mixture of monoclinic and orthorhombic crystalline phases which were both characterized by preliminary X-ray data. A complete structural determination and refinement of the monoclinic phase, which contains two independent molecules in a cell of dimensions  $a$  22.843(2),  $b$  7.958(1),  $c$  14.465(1) Å,  $\beta$  90.074(4)° and symmetry  $P2_1/c$ , yielded  $R_1$  5.3% and  $R_2$  5.9% for 2168 independent diffractometry-collected data with  $I \geq 2.5\sigma(I)$ .  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$  contains four  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecules and two water molecules of hydration (of crystallographic site symmetry  $C_2-2$ ) in an orthorhombic unit cell of symmetry  $P2_12_12$  and of dimensions  $a$  13.491(1),  $b$  12.748(1),  $c$  7.715(1) Å. Least-squares refinement of 750 diffractometry data with  $I \geq 2.0\sigma(I)$  gave  $R_1$  2.4% and  $R_2$  3.0%. Both of these compounds were independently synthesized and spectroscopically characterized by Köpf and co-workers, and a complete X-ray diffraction study was performed by Epstein and Bernal on a different monoclinic phase of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  (isolated by Köpf). An extraction of  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  with re-

\* Present address: Colgate-Palmolive Co., 909 River Road, Piscataway, New Jersey 08854 (U.S.A.)

\*\* Present address: West Virginia University, Morgantown, West Virginia 26506 (U.S.A.)

fluxing benzene under nitrogen atmosphere in a Soxhlet apparatus led to the formation of the previously reported  $[V_2(h^5-C_5H_5)_2S_5]_n$  compound which was characterized by physical measurements including a preliminary X-ray diffraction study.

## Introduction

A structural comparison between the isomorphous  $M(h^5-C_5H_5)_2(SC_6H_5)_2$  ( $M = Ti, V$ ) compounds revealed a significant decrease of  $5^\circ$  in the S—M—S bond angle in going from the  $d^0$  titanium(IV) to the  $d^1$  vanadium(IV) complex [1]. This trend was taken as strong evidence [1,2] for the nonvalidity of the Ballhausen—Dahl bonding model [3] employed for  $d^1$  and  $d^2$  metal(IV) complexes ( $M(h^5-C_5H_5)_2L_2$ ) in that this qualitative representation would localize the unpaired electron in the vanadium molecule between the two phenylmercapto ligands, which in turn from electron-pair repulsion arguments would lead to the prediction of an increase in the L—M—L bond angle in going from a  $d^0$  titanium(IV) to a  $d^1$  vanadium(IV) system.

In order to gain further insight into the chemistry and bonding of dicyclopentadienyl complexes of titanium and vanadium, further reactions were carried out. This extended investigation has led to the isolation of two unusual compounds  $Ti(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2S_5$ , which were of particular interest to us from a structural viewpoint in providing an operational test of the above conclusion resulting from our crystallographic analyses of the  $M(h^5-C_5H_5)_2(SC_6H_5)_2$  ( $M = Ti, V$ ) compounds.

At the outset of this investigation, the only other known species having a pentasulfide ligand related to a transition metal was the octahedrally coordinated  $[Pt(S_5)_3]^{2-}$  dianion which was characterized in  $(NH_4)_2Pt(S_5)_3 \cdot 2H_2O$  from an X-ray diffraction study by Jones and Katz [4]; this compound had been originally prepared by Hofmann and Höchtlen [5] in 1903. Subsequently, the preparation of  $Ti(h^5-C_5H_5)_2S_5$ , obtained by different synthetic routes, was reported by Köpf et al. [6] followed by an X-ray diffraction study by Epstein and Bernal [7] on one crystalline phase of this compound. Köpf [8] later reported the synthesis of both  $V(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2Se_5$  by the reaction of  $V(h^5-C_5H_5)_2Cl_2$  with  $(NH_4)_2S_5$  and  $Na_2Se_5$ , respectively, in acetone. We present here our preparation and stereochemical characterization of these compounds including X-ray diffraction data on a different crystalline phase of  $Ti(h^5-C_5H_5)_2S_5$  and on  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ . These results (communicated earlier [2]) have provided further convincing evidence of our previous interpretation concerning the distribution of the unpaired electron in a  $V(h^5-C_5H_5)_2L_2$  molecule. We also give here a synthesis and properties including preliminary X-ray data for the previously reported [9]  $[V_2(h^5-C_5H_5)_2S_5]_n$  compound.

## Experimental

### Reagents

Dicyclopentadienylvanadium dichloride and dicyclopentadienyltitanium

dichloride were obtained from Alfa Inorganics, Inc. Reagent grade solvents, when necessary, were dried by normal techniques, distilled, and flushed with nitrogen before use.

#### Analyses

Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

#### Preparation of $Ti(h^5-C_5H_5)_2S_5$ and $V(h^5-C_5H_5)_2S_5$

Dicyclopentadienyltitanium pentasulfide was prepared by the reaction of elemental sulfur with  $Ti(h^5-C_5H_5)_2(CO)_2$  in hexane. Refluxing of the brown solution under nitrogen for several days resulted in the formation of a brownish-red precipitate. Slow evaporation of a benzene solution of this solid yielded two crystalline phases of  $Ti(h^5-C_5H_5)_2S_5$  (vide infra), which were established to be chemically equivalent by melting point, IR, NMR, and X-ray diffraction techniques.

The  $Ti(h^5-C_5H_5)_2(CO)_2$  was prepared from the reaction of  $Ti(h^5-C_5H_5)_2Cl_2$  with excess  $NaC_5H_5$  and carbon monoxide in a high pressure autoclave by a modification of the method described by Murray [10].

Dicyclopentadienylvanadium pentasulfide was prepared in an analogous fashion to that independently reported by Köpf et al. [8] by the reaction of  $V(h^5-C_5H_5)_2Cl_2$  and  $Na_2S_5$  in THF. All operations were carried out under an atmosphere of nitrogen unless stated explicitly otherwise.  $Na_2S_5$  was prepared by the addition of Na (16 mmol) to approximately 75 ml of liquid ammonia followed by slow addition of elemental sulfur (40 mmol). After about one-half of the sulfur was added, the blue solution turned yellow. The excess  $NH_3$  was allowed to thoroughly evaporate overnight, and the resulting  $Na_2S_5$  was dissolved in 20 ml of  $H_2O$ . This solution was placed in a dropping funnel and added slowly to a slurry of  $V(h^5-C_5H_5)_2Cl_2$  (8 mmol) in 300 ml of THF. The resulting red mixture was stirred ca.  $\frac{1}{2}$  h, and the volume of the solution then reduced under vacuum with heating until crystallization had begun. The mixture was allowed to cool for a short period, after which the  $V(h^5-C_5H_5)_2S_5$  was collected on a Büchner funnel, exposed to the atmosphere, and washed with  $H_2O$ , ethanol, and hexane. The compound was then dried under vacuum. Well-formed dark red crystals of  $V(h^5-C_5H_5)_2S_5$  (1.24 g) were obtained in 45% yield based upon  $V(h^5-C_5H_5)_2Cl_2$ . This compound is air-stable and decomposes at ca.  $150^\circ C$ . (Found: C, 35.1; H, 3.0; V, 14.6; S, 46.6.  $C_{10}H_{10}VS_5$  calcd.: C, 35.2; H, 3.0; V, 14.9; S, 47.0%.)

#### Preparation and identification of $[V_2(h^5-C_5H_5)_2S_5]_n$ \*

$[V_2(h^5-C_5H_5)_2S_5]_n$  was prepared by an extraction of  $V(h^5-C_5H_5)_2S_5$  with refluxing benzene under a  $N_2$  atmosphere in a Soxhlet apparatus for two days.

\*  $[V_2(h^5-C_5H_5)_2S_5]_n$  was first reported by Schunn, Fritchie, and Prewitt [9] from the reaction of  $V(h^5-C_5H_5)(CO)_4$  with either elemental sulfur or cyclohexene sulfide in a refluxing toluene solution. The low solubility of this air- and water-stable solid precluded a solution molecular weight determination. The compound was shown to be diamagnetic from a magnetic susceptibility measurement.

The resulting dark red benzene solution was then reduced in volume and placed on an alumina chromatographic column prepared with benzene. A black diffuse band was developed and eluted with benzene. The burgundy colored eluent was reduced in volume with a rotary evaporator and allowed to slowly evaporate until dark crystals formed; the crystals were collected on a filter and washed with pentane. The compound sublimes at ca. 150°C ( $\approx 0.1$  torr) with slight decomposition. (Found: C, 30.70; H, 2.65; V, 25.97; S, 40.82.  $C_{10}H_{10}V_2S_5$  calcd.: C, 30.61; H, 2.57; V, 25.98; S, 40.84%.)

An infrared spectrum (KBr disc) showed bands at 3098m, 1440m, 1426m, 1362w, 1260w, 1100w(br), 1059m, 1011m, 917w(br), 838(sh), 810s, 560m, and 528m  $cm^{-1}$ .

Preliminary X-ray diffraction studies involving oscillation and Weissenberg photographs indicated that the crystals of  $[V_2(h^5-C_5H_5)_2S_5]_n$  are orthorhombic. The measured lattice constants are  $a$  19.5,  $b$  20.0,  $c$  7.03 Å; unit cell volume 2742 Å<sup>3</sup>. The experimental density of 1.89 g/cm<sup>3</sup> (flotation method) agrees well with the value 1.90 g/cm<sup>3</sup> calculated on the basis of eight  $V_2(h^5-C_5H_5)_2S_5$  monomers per unit cell.

Weissenberg photographs showed systematic absences of  $\{hkl\}$  for  $h+k$  odd and  $\{hk0\}$  for  $h$  odd, which suggests the probable space group to be either the centrosymmetric  $Cmma$  ( $D_{2h}^{21}$ , No. 67) or the noncentrosymmetric  $Cm2a$  ( $C_{2v}^{15}$ , No. 39). These crystals were judged to be unsuitable for further X-ray investigation due not only to indications of twinning from split spots on upper level Weissenberg photographs but also to diffuse streaking characteristic of a crystal order-disorder phenomena. The crystal data are in accord with  $n$  being only 1 or 2.

#### Physical properties of $M(h^5-C_5H_5)_2S_5$ ( $M = Ti, V$ )

Infrared spectra (calibrated with polystyrene film) were obtained with a Beckman IR-8 spectrometer from KBr discs containing the compound. For  $Ti(h^5-C_5H_5)_2S_5$ : 3105w, 1432w, 1366vw, 1125w, 1021m, 1011m, 923w(br), 859m, and 824s  $cm^{-1}$ ; for  $V(h^5-C_5H_5)_2S_5$ : 3098w, 1436m, 1428m, 1366w, 1123vw, 1019m, 1006m, 928vw(br), 871w, and 825s  $cm^{-1}$ . The IR spectra of  $Ti(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2S_5$  are nearly identical except that for the vanadium compound the band at ca. 1430  $cm^{-1}$  appears as a doublet.

TABLE 1

MAGNETIC SUSCEPTIBILITY DATA FOR  $V(h^5-C_5H_5)_2S_5$ 

$T$ (°K)	$10^6 \chi_g$ (cgsu/gm)	$10^6 \chi_M^{corr}$ (cgsu/mol)
94.66	9.50	3438
110.38	8.53	3107
126.10	7.52	2762
141.82	6.76	2502
157.54	6.09	2274
173.26	5.59	2103
188.98	5.13	1946
204.70	4.66	1786
220.42	4.24	1642
296.50	3.15	1270

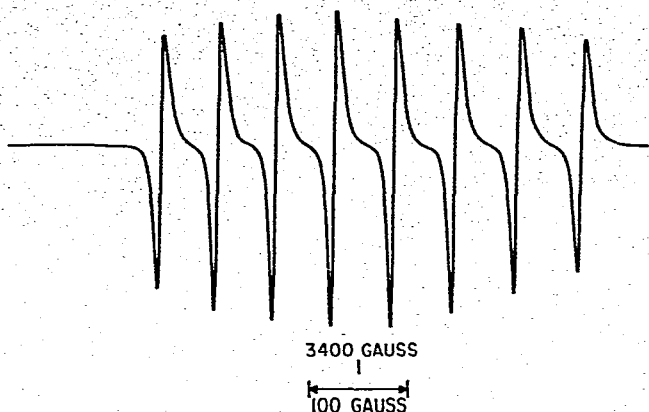


Fig. 1. An EPR spectrum of a benzene solution of  $V(h^5-C_5H_5)_2S_5$  centered about 3400 G.

A  $CS_2$  solution of  $Ti(h^5-C_5H_5)_2S_5$  at  $35^\circ$  gives two sharp  $^1H$  NMR resonances at  $\tau$  3.63 and  $\tau$  3.96 ppm (TMS as internal standard). The resonances are of equal integrated intensity and separated by 19.1 Hz. These values are in good agreement with the results obtained by Köpf et al. [6a] of  $\tau$  3.58 and 3.90 ppm at  $30^\circ C$ . Köpf et al. [6a] also reported the spectra of  $Ti(h^5-C_5H_5)_2S_5$  at higher temperatures and showed that the two resonances broaden at higher temperatures and finally coalesce to a single sharp peak at  $120^\circ C$ .

Magnetic susceptibility data for  $V(h^5-C_5H_5)_2S_5$  were obtained over a temperature range of 95–297 K via a Faraday apparatus [11] (Table 1). A diamagnetic correction of  $-195 \times 10^{-6}$  cgsu/mol was applied to the molar susceptibility. Within this temperature range the compound follows a Curie–Weiss dependence,  $\chi_M^{corr} = C/(T - \theta)$ . From a least-squares analysis of the plot of  $1/\chi_M^{corr}$  vs.  $T$  (K), the values  $C$  and  $\theta$  were determined to be  $0.393 \pm 0.014$  (estimated error at 95% CL) and  $-19.07$ , respectively, giving an effective magnetic moment,  $\mu_{eff} = 2.828[\chi_M^{corr}(T - \theta)]^{1/2}$ , of  $1.77 \pm 0.03$  BM.

A solution EPR spectrum of  $V(h^5-C_5H_5)_2S_5$  dissolved in benzene is shown in Fig. 1. The eight-line spectrum, which was recorded on a Varian E-3 spectrometer at room temperature, is characteristic of the hyperfine interaction of the unpaired electron with the  $^{51}V$  nucleus (99.8% abundance,  $I$  7/2). The isotropic EPR parameters, calculated from a procedure described elsewhere [1], are  $g_{iso}$  2.00(1) and  $A_{iso}$  61.4(5) G.

#### Single crystal data and data collection for $M(h^5-C_5H_5)_2S_5$ ( $M = Ti, V$ )

Of the two isolated crystal phases of  $Ti(h^5-C_5H_5)_2S_5$ , the most predominant form crystallized as well-formed dark-red orthorhombic bipyramids, m.p.  $194$ – $198^\circ C$ . Photographic X-ray examination indicated the Laue symmetry to be  $D_{2h}-2/m2/m2/m$ , consistent with the crystal habit. Systematic absences of  $\{h00\}$  for  $h \neq 2n$ ,  $\{0k0\}$  for  $k \neq 2n$ , and  $\{00l\}$  for  $l \neq 2n$  indicated the probable space group to be  $P2_12_12_1$ . The lattice constants obtained from Weissenberg and oscillation photographs are  $a$  20.40,  $b$  7.93,  $c$  8.02 Å, Vol.  $1298 \text{ \AA}^3$ . The observed density of  $1.69 \text{ g/cm}^3$ , obtained by the flotation technique in a mixture of 2-iodopropane and ethyliodide, compares well with a calculated

density of 1.73 g/cm<sup>3</sup> for four Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> per cell. However, the splitting of the intensity maxima observed on the X-ray photographs indicated that the crystals were not suitable for further crystallographic analysis. The other crystalline form of Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> was obtained in a very small amount as light-red plates, m.p. 192–200°C. Oscillation and Weissenberg photographs of rod-shaped crystals cut to suitable size from large plates indicated the Laue symmetry to be monoclinic *C*<sub>2*h*</sub>-2/*m*. Since the X-ray photographs indicated these crystals to be suitable for a complete crystallographic analysis, a rod-shaped crystal with dimensions of 0.11 × 0.15 × 0.40 mm along the [100], [010], and [001] directions, respectively, was used to collect the intensity data. This crystal was mounted with epoxy cement on the end of a thin-glass fiber such that the needle axis was approximately parallel to the spindle axis of the goniometer. Systematic absences for {*h*0*l*} of *l* = 2*n* + 1 and {0*k*0} of *k* = 2*n* + 1 uniquely define the space group to be *P*2<sub>1</sub>/*c*(*C*<sub>2*h*</sub><sup>5</sup>, No. 14) which results in two independent Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> molecules comprising the crystallographically independent unit.

For V(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub>, a brownish-red rhombic-shaped crystal of dimensions 0.13 × 0.20 × 0.33 mm along the [100], [010], and [001] directions, respectively, was used to collect the X-ray data. Preliminary oscillation and Weissenberg photographs taken with Cu-*K*<sub>α</sub> radiation showed the Laue symmetry to be orthorhombic *D*<sub>2*h*</sub>-2/*m*2/*m*2/*m*. Systematic absences of {*h*00} for *h* = 2*n* + 1 and {0*k*0} for *k* = 2*n* + 1 uniquely indicate the noncentrosymmetric space group as *P*2<sub>1</sub>2<sub>1</sub>2(*D*<sub>2</sub><sup>2</sup>, No. 18), which necessitates the location of one independent V(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> molecule.

Each of the above crystals was aligned about the rotation axis (along the crystal's longest dimension) on a General Electric—Datex card-controlled diffractometer (with an E and A full circle), and 25 reflections were carefully centered in each case. The angular coordinates (2θ, χ, φ) were least-squares refined to yield the respective lattice parameters given in Table 2 for Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> and V(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub>. All intensity data were collected with a take-off angle of 3.0° by the θ–2θ scan technique with symmetric 2θ scans at a rate of 2.0 degrees/min over a range of 1.0° for Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> and 1.0 degrees/min over a range of 1.2° for V(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub>. A (stationary-crystal)—(stationary counter) background measurement for one-half of the total scan time was

TABLE 2  
CRYSTAL DATA FOR Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> AND V(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> · ½H<sub>2</sub>O

System	Ti( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub> Monoclinic	V( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub> · ½H <sub>2</sub> O Orthorhombic
<i>a</i> (Å)	22.843(2)	13.491(1)
<i>b</i> (Å)	7.958(1)	12.748(1)
<i>c</i> (Å)	14.465(1)	7.715(1)
β (deg.)	90.074(4)	
Volume (Å <sup>3</sup> )	2630	1327
Density (obsd.)	1.70	1.71
Density (calcd.)	1.71	1.71
<i>Z</i>	8	4
μ (cm <sup>-1</sup> )	13.99	15.08
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2

made on each side of a peak. The counter aperture of 2 mm diameter was placed 31 mm from the crystal. Zr-filtered Mo- $K_{\alpha}$  radiation [ $\lambda(K_{\alpha_1})$  0.70926 Å,  $\lambda(K_{\alpha_2})$  0.71354 Å] was used with a scintillation counter with the pulse-height analyzer adjusted to admit 90% of the Mo- $K_{\alpha}$  peak. In both cases intensity data ( $hkl$ ,  $hkl$ ) were collected out to  $2\theta = 40^\circ$  with four standard reflections measured every 100 reflections to monitor the instrument's stability as well as crystal alignment and decay. For  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  no significant changes ( $> 3\%$ ) in the intensities of these standard reflections were observed during the entire data collection, while for  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  the intensities of each of the four standard reflections were observed to decrease uniformly in a linear fashion (indicative of crystal decay) such that the intensities of the final set of standard reflections were ca. 65% of their original values. Correction for crystal decay was accomplished by multiplying each set of 100 reflections by an appropriate scale factor obtained from the standards. After correction of the data for background and Lorentz-polarization effects, structure amplitudes and corresponding standard deviations were obtained in a manner described elsewhere [1,12]\*. This treatment included the correction of the  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  data for absorption effects due to the calculated transmission coefficients varying from 0.73 to 0.83 (based on a  $\mu$  value of  $15.1 \text{ cm}^{-1}$  for Mo- $K_{\alpha}$  radiation). No absorption correction was necessary for the  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  data in that the calculated transmission coefficients ranged from only 0.82 to 0.86 (based on a  $\mu$  value of  $14.0 \text{ cm}^{-1}$  for Mo- $K_{\alpha}$  radiation). Of the 2168 independent reflections that were sampled for  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ , 1712 possessed  $I \geq 2.5\sigma(I)$ . For  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ , 750 reflections were considered above background with the criterion  $I \geq 2.0\sigma(I)$ . The structural determinations and refinements are based on the data with  $I \geq 2.0\sigma(I)$ .

#### *Solution and refinement of the structures*

(a).  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ . The structure of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  with space group  $P2_1/c$  was solved by application of the symbolic addition method of Hauptman and Karle [13] with the computer programs FAME and MAGIC [14]. A total of 289 symbolic signs with probabilities of correctness greater than or equal to 0.98, were determined from a set of 300 largest  $|E|$ 's (for which each  $|E|$  was  $\geq 1.38$ ). A resulting  $E$ -map gave the location of the two independent titanium and ten independent sulfur atoms; the coordinates for the rest of the non-hydrogen atoms were revealed from subsequent Fourier syntheses. Full-matrix least-squares refinement with rigid-body constraints on the cyclopentadienyl rings (viz.,  $D_{5h}$  symmetry with C—C 1.405 Å and C—H 1.09 Å), isotropic temperature factors for the carbon and hydrogen atoms, and isotropic temperature factors for the titanium and sulfur atoms resulted in discrepancy factors of  $R_1$  7.0% and  $R_2$  7.7%\*\* . Further least-squares refinement with no rigid-body constraints on the cyclopentadienyl carbon atoms and anisotropic temperature factors for all nonhydrogen atoms gave final discrepancy factors of  $R_1$  5.3%

\* The programs utilized for the data collection and reduction, the structural determination and refinement, and error analysis are given elsewhere [1,12], if not otherwise referenced.

\*\*  $R_1 = (\sum |F_o| - |F_c| / \sum |F_o|) \times 100$  and  $R_2 = (\sum w_i |F_o| - |F_c|^2 / \sum w_i |F_o|^2)^{1/2} \times 100$ . All least-squares refinements were based on the minimization of  $\sum w_i |F_o| - |F_c|^2$  with individual weights  $w_i = 1/\sigma(|F_o|)^2$ .

and  $R_2$  5.9%. A difference Fourier map calculated from the output of the last cycle revealed no anomalous features with no peaks of magnitude greater than 0.8 electron/Å<sup>3</sup>.

(b).  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ . The location of the approximate positions of the vanadium and five sulfur atoms was accomplished by an interpretation of a sharpened Patterson map; the coordinates for the cyclopentadienyl carbon atoms were obtained from subsequent Fourier syntheses. Full-matrix, anisotropic least-squares refinement with rigid-body group parameters (vide supra) for the cyclopentadienyl rings resulted in  $R_1$  5.9% and  $R_2$  7.5% at convergence. A difference Fourier map calculated from these parameters gave no peaks of magnitude greater than 0.6 electron/Å<sup>3</sup> except for one peak located on a two-fold axis with 1.7 electrons/Å<sup>3</sup>. Since the crystal used for data collection was crystallized from a THF/H<sub>2</sub>O solution, it was apparent from an examination of appropriate distances (vide infra) that this extra peak must be due to a water molecule of hydration which was confirmed by further least-squares refinement. Initially all positional and thermal parameters for the independent  $V(h^5-C_5H_5)_2S_5$  molecule were fixed, while the one positional parameter of the crystallographically independent oxygen atom and its isotropic thermal parameter were varied; this refinement led to a reasonable value of 9.6 Å<sup>2</sup> for the thermal parameter of the oxygen atom as well as a significant lowering of the discrepancy factors to  $R_1$  3.9% and  $R_2$  4.8%. Two additional cycles of least-squares refinement, performed with the positional and thermal parameters of all atoms being varied and with anisotropic thermal motion allowed for the oxygen atom, further decreased the discrepancy factors to  $R_1$  2.4% and  $R_2$  3.0%. The addition of the water molecule of hydration into the refinement also resulted in a remarkable lowering of the standard deviation of an average observation of unit weight,  $[\sum w_i \|F_o - |F_c|^2 / (n - m)]^{1/2}$ , where  $n$  is the number of independent data and  $m$  the number of parameters varied, from 2.4 to 0.8 as well as a drastic decrease of the esd's of the atomic positional and thermal parameters to values of approximately one-third those of the previous esd's. Furthermore, the C—C bond lengths of the cyclopentadienyl rings became more uniform in length as demonstrated by the change in the range from 1.35–1.51 Å before inclusion of the oxygen atom in the refinement to a more reasonable range of 1.38–1.43 Å. The fact that the unit cell contains two symmetry-related H<sub>2</sub>O molecules corresponds to the hydrated compound being  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ .

The final positional and thermal parameters for  $Ti(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  are presented in Tables 3 and 4, respectively\*. Interatomic distances and angles (with estimated standard deviations calculated from the variance-covariance matrix) are provided in Table 5 for  $Ti(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ . The least-squares planes defined by specific atoms along with perpendicular displacements of these and other atoms from these planes and the angles between the normals to these planes are presented in Table 6.

\* See NAPS document no. 02761 for 28 pages of supplementary material involving a listing of the observed and calculated structure factors for  $Ti(h^5-C_5H_5)_2S_5$  and  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ . Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y., 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.



TABLE 3

ATOMIC PARAMETERS FOR  $Ti(h^5-C_5H_5)_2S_5$ A. Positional parameters <sup>a-c</sup>

	x	y	z
Ti	0.1213(1)	0.6725(2)	0.3366(1)
Ti'	0.3780(1)	0.6898(2)	0.6125(1)
S(1)	0.0746(2)	0.6299(4)	0.1864(2)
S(1')	0.2821(1)	0.6195(4)	0.5490(2)
S(2)	0.0773(2)	0.3752(5)	0.1544(2)
S(2')	0.2829(1)	0.3675(4)	0.5200(2)
S(3)	0.1633(2)	0.3244(4)	0.1302(2)
S(3')	0.3353(1)	0.3419(4)	0.4071(2)
S(4)	0.2031(1)	0.3116(4)	0.2562(2)
S(4')	0.4206(1)	0.3558(4)	0.4527(2)
S(5)	0.2143(1)	0.5580(4)	0.2921(2)
S(5')	0.4312(1)	0.6073(4)	0.4755(2)
C(1-1)	0.0791(6)	0.4125(17)	0.3823(9)
C(1-1')	0.3881(6)	0.4154(16)	0.6760(8)
C(1-2)	0.0369(6)	0.5364(20)	0.3944(9)
C(1-2')	0.3406(6)	0.4981(18)	0.7297(9)
C(1-3)	0.0570(6)	0.6427(16)	0.4632(9)
C(1-3')	0.3748(6)	0.6314(18)	0.7724(9)
C(1-4)	0.1129(6)	0.5896(18)	0.4913(8)
C(1-4')	0.4350(6)	0.6289(16)	0.7465(9)
C(1-5)	0.1265(6)	0.4436(18)	0.4420(9)
C(1-5')	0.4424(6)	0.4961(17)	0.6859(8)
C(2-1)	0.1707(7)	0.9033(17)	0.2666(10)
C(2-1')	0.3586(7)	0.9365(17)	0.5259(10)
C(2-2)	0.1113(7)	0.9444(16)	0.2659(10)
C(2-2')	0.3300(7)	0.9541(21)	0.6084(14)
C(2-3)	0.0933(8)	0.9571(20)	0.3561(14)
C(2-3')	0.3731(8)	0.9640(19)	0.6747(11)
C(2-4)	0.1410(8)	0.9276(20)	0.4151(11)
C(2-4')	0.4290(8)	0.9513(19)	0.6315(12)
C(2-5)	0.1898(7)	0.8974(18)	0.3567(11)
C(2-5')	0.4165(7)	0.9385(17)	0.5387(11)
H(1-1)	0.0766	0.3072	0.3318
H(1-1')	0.3792	0.3027	0.6324
H(1-2)	-0.0052	0.5440	0.3591
H(1-2')	0.2999	0.4656	0.7364
H(1-3)	0.0340	0.7537	0.4911
H(1-3')	0.3543	0.7223	0.8208
H(1-4)	0.1401	0.6458	0.5452
H(1-4')	0.4673	0.7185	0.7691
H(1-5)	0.1664	0.3701	0.4468
H(1-5')	0.4827	0.4595	0.6529
H(2-1)	0.1972	0.8871	0.2036
H(2-1')	0.3354	0.9270	0.4578
H(2-2)	0.0826	0.9635	0.2052
H(2-2')	0.2832	0.9586	0.6233
H(2-3)	0.0486	0.9900	0.3822
H(2-3')	0.3674	0.9784	0.7529
H(2-4)	0.1422	0.9300	0.4902
H(2-4')	0.4714	0.9590	0.6675
H(2-5)	0.1896	0.8955	0.3570
H(2-5')	0.4517	0.9272	0.4851

continued

TABLE 3 (continued)

B. Anisotropic thermal coefficients <sup>d</sup>

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ti	17(1)	126(5)	44(1)	-1(1)	1(1)	8(2)
Ti'	18(1)	118(5)	42(1)	1(1)	3(1)	3(2)
S(1)	31(1)	203(10)	51(2)	-3(3)	-5(1)	20(4)
S(1')	19(1)	186(9)	62(2)	6(2)	-2(1)	-2(4)
S(2)	33(1)	245(11)	70(3)	-18(3)	-13(2)	-12(4)
S(2')	23(1)	198(10)	68(3)	-15(2)	-1(1)	1(4)
S(3)	40(1)	226(11)	59(3)	-1(3)	10(1)	-24(4)
S(3')	30(1)	176(10)	53(2)	-5(2)	-7(1)	-6(4)
S(4)	28(1)	151(9)	72(3)	9(2)	2(1)	3(4)
S(4')	25(1)	132(9)	63(2)	13(2)	3(1)	-9(3)
S(5)	20(1)	157(9)	64(3)	4(2)	4(2)	-3(4)
S(5')	21(1)	158(9)	48(2)	6(2)	7(1)	9(3)
C(1-1)	37(4)	163(34)	50(9)	-14(10)	9(5)	21(14)
C(1-1')	41(4)	113(30)	44(9)	26(9)	-6(5)	36(13)
C(1-2)	32(4)	201(36)	66(10)	-6(10)	9(5)	42(15)
C(1-2')	33(4)	232(34)	49(9)	-3(9)	-4(5)	26(14)
C(1-3)	25(4)	174(31)	65(8)	-5(8)	8(4)	6(13)
C(1-3')	52(5)	200(38)	41(10)	8(9)	0(6)	-9(15)
C(1-4)	32(4)	275(35)	37(9)	-11(9)	-1(5)	0(15)
C(1-4')	26(4)	240(34)	67(8)	11(8)	-10(4)	18(14)
C(1-5)	20(4)	218(33)	63(8)	1(8)	2(5)	42(14)
C(1-5')	23(4)	237(30)	49(8)	5(8)	-5(4)	34(13)
C(2-1)	38(5)	118(35)	93(11)	-6(9)	10(5)	29(15)
C(2-1')	43(5)	187(35)	69(11)	-8(9)	-2(6)	14(15)
C(2-2)	38(4)	120(33)	79(10)	6(8)	-10(5)	23(14)
C(2-2')	36(5)	123(48)	145(13)	3(11)	6(8)	30(19)
C(2-3)	40(6)	99(47)	151(14)	21(22)	10(8)	-33(20)
C(2-3')	77(5)	37(42)	46(12)	2(11)	1(7)	-54(16)
C(2-4)	40(5)	245(41)	71(12)	-17(11)	10(7)	-10(17)
C(2-4')	38(5)	145(43)	146(13)	-10(10)	-28(7)	-14(17)
C(2-5)	37(5)	160(39)	90(11)	-50(9)	-14(6)	16(16)
C(2-5')	37(5)	154(36)	93(11)	-6(9)	2(5)	0(15)

<sup>a</sup> Estimated deviations of the last significant figures in this and the following tables are enclosed in parentheses. <sup>b</sup> The unprimed and primed atoms correspond to the two independent molecules A and B, respectively. <sup>c</sup> The positional and isotropic temperature factors (arbitrarily assigned at values of  $8.0 \text{ \AA}^2$ ) of the hydrogen atoms were not varied. <sup>d</sup> Anisotropic temperature factors utilized for the nonhydrogen atoms in this and the following table are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

The scattering factors utilized in all structure factor calculations were those of Hanson et al. [15] for the nonhydrogen atoms and those of Stewart et al. [16] for the hydrogen atoms with corrections applied for real and imaginary dispersion effects [17] for the titanium (or vanadium) and sulfur atoms.

## Results and discussion

### General description of the structures

The crystal structures of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$  are both composed of discrete  $\text{M}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecules with an analogous overall configuration shown in Fig. 2. Although the two crystal structures possess different space group symmetry, the molecular packing is similar as can be seen

(continued on p. 104)

TABLE 4

ATOMIC PARAMETERS FOR  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  <sup>a, b</sup>

## A. Positional parameters

	x	y	z
V	0.08099(6)	0.17398(7)	0.09871(12)
S(1)	-0.07272(11)	0.26997(12)	0.16640(20)
S(2)	-0.11561(11)	0.25854(14)	0.42068(22)
S(3)	-0.16749(12)	0.10730(17)	0.44819(26)
S(4)	-0.04207(14)	0.01589(15)	0.44413(23)
S(5)	0.00071(13)	0.01078(12)	0.19022(21)
C(1-1)	0.1239(5)	0.2204(8)	0.3743(10)
C(1-2)	0.1544(5)	0.3007(6)	0.2625(12)
C(1-3)	0.2274(4)	0.2607(6)	0.1549(10)
C(1-4)	0.2399(4)	0.1536(6)	0.1968(9)
C(1-5)	0.1774(5)	0.1288(7)	0.3349(9)
C(2-1)	-0.0058(4)	0.1260(5)	-0.1437(8)
C(2-2)	0.0166(5)	0.2330(5)	-0.1615(8)
C(2-3)	0.1186(6)	0.2435(5)	-0.1703(8)
C(2-4)	0.1613(5)	0.1412(6)	-0.1603(8)
C(2-5)	0.0830(5)	0.0688(5)	-0.1439(7)
H(1-1)	0.0676	0.2253	0.4772
H(1-2)	0.1287	0.3807	0.2670
H(1-3)	0.2682	0.3027	0.0552
H(1-4)	0.2936	0.0991	0.1340
H(1-5)	0.1698	0.0513	0.3946
H(2-1)	-0.0815	0.0935	-0.1352
H(2-2)	-0.0378	0.2983	-0.1612
H(2-3)	0.1604	0.3171	-0.1807
H(2-4)	0.2390	0.1239	-0.1666
H(2-5)	0.0896	-0.0146	-0.1385
O(H <sub>2</sub> O)	0.2500	0.5000	0.9642(12)

## B. Anisotropic temperature factors

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
V	31(1)	44(1)	94(2)	1(1)	1(1)	-11(1)
S(1)	42(1)	62(1)	127(3)	17(1)	1(2)	-7(2)
S(2)	52(1)	86(1)	138(3)	17(1)	13(2)	-28(2)
S(3)	57(1)	113(2)	182(4)	-17(1)	37(2)	-9(2)
S(4)	89(1)	78(2)	146(4)	-1(1)	29(2)	24(2)
S(5)	70(1)	43(1)	137(3)	-6(1)	19(2)	-1(2)
C(1-1)	39(4)	154(8)	134(14)	-1(5)	-20(7)	-74(10)
C(1-2)	60(4)	79(6)	291(22)	-8(5)	-57(9)	-75(10)
C(1-3)	45(4)	89(6)	219(16)	-21(4)	-4(7)	-39(9)
C(1-4)	33(3)	99(7)	190(14)	14(4)	-23(7)	-51(8)
C(1-5)	45(4)	125(7)	141(15)	-5(5)	-31(7)	11(9)
C(2-1)	54(4)	70(5)	85(12)	-3(4)	-11(6)	-8(6)
C(2-2)	71(5)	71(5)	91(12)	6(4)	-1(6)	3(7)
C(2-3)	91(6)	59(5)	95(12)	-18(5)	30(7)	-2(8)
C(2-4)	48(4)	97(6)	126(14)	-5(4)	29(6)	-16(7)
C(2-5)	75(4)	56(4)	89(11)	7(4)	4(7)	-15(6)
O(H <sub>2</sub> O)	125(7)	127(7)	342(22)	4(6)	0	0

<sup>a</sup> These coordinates are based on the origin being arbitrarily chosen at  $1, 2_1, 1$  in the plane of  $2_1 2_1$  such that the coordinates of the fourfold set (4c) of general positions are:  $x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \bar{z}; \frac{1}{2} - x, \bar{y}, z$ . This origin and hence the coordinates of equivalent positions are not the same as those given in the International Tables for X-Ray Crystallography, Vol. I, 1952, p. 104 for  $P2_1 2_1 2$  ( $D_2^3$ , No. 18); the two origins differ from each other by a translation of  $a/4, 0b, 0c$ . <sup>b</sup> The positional and isotropic temperature factors (arbitrarily assigned at values of  $8.0 \text{ \AA}^2$ ) of the hydrogen atoms were not varied in the least-squares refinement.

TABLE 5  
INTERATOMIC DISTANCES AND BOND ANGLES <sup>a</sup>

## A. Intramolecular distances (Å)

	Ti( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub>		V( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub> · $\frac{1}{2}$ H <sub>2</sub> O
	Molecule A	Molecule B	
M—S(1)	2.443(2)	2.438(3)	2.464(2)
M—S(5)	2.400(4)	2.419(4)	2.450(2)
S(1)—S(2)	2.080(5)	2.049(4)	2.051(2)
S(2)—S(3)	2.036(5)	2.035(5)	2.062(3)
S(3)—S(4)	2.038(4)	2.059(5)	2.055(3)
S(4)—S(5)	2.045(4)	2.043(4)	2.043(3)
M—C(1-1)	2.377	2.381	2.282
M—C(1-2)	2.364	2.390	2.277
M—C(1-3)	2.361	2.360	2.305
M—C(1-4)	2.341	2.383	2.288
M—C(1-5)	2.378	2.380	2.312
M—C(2-1)	2.382	2.370	2.290
M—C(2-2)	2.404	2.372	2.313
M—C(2-3)	2.371	2.362	2.313
M—C(2-4)	2.369	2.401	2.311
M—C(2-5)	2.395	2.415	2.302
M...S(2)	3.68	3.62	3.79
M...S(4)	3.62	3.66	3.73
S(1)...S(5)	3.58	3.57	3.45
S(2)...S(4)	3.27	3.29	3.25
S(1)...S(3)	3.27	3.25	3.26
S(3)...S(5)	3.21	3.20	3.26
S(1)...C(1-1)	3.32	3.45	3.17
S(1)...C(1-2)	3.22	3.15	3.22
S(1)...C(2-1)	3.30	3.09	3.15
S(1)...C(2-2)	2.88	3.00	2.82
S(5)...C(1-1)	3.55	3.42	3.41
S(5)...C(1-5)	3.09	3.18	3.03
S(5)...C(2-1)	2.95	3.19	2.98
S(5)...C(2-5)	2.91	2.81	2.90
S(2)...C(1-1)	3.31	3.32	3.28
S(4)...C(1-1)	3.46	3.35	3.42
S(4)...C(1-5)	3.38	3.59	3.40

## B. Bond angles (degrees)

	Ti( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub>		V( <i>h</i> <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub> · $\frac{1}{2}$ H <sub>2</sub> O
	Molecule A	Molecule B	
S(1)—M—S(5)	95.4(1)	94.6(1)	89.3(1)
M—S(1)—S(2)	108.7(2)	107.1(1)	113.9(1)
S(1)—S(2)—S(3)	105.1(2)	105.5(2)	105.1(1)
S(2)—S(3)—S(4)	106.6(2)	107.1(2)	104.4(1)
S(3)—S(4)—S(5)	103.6(2)	102.5(2)	105.4(1)
S(4)—S(5)—M	108.8(2)	109.8(2)	112.0(1)
S(1)—M—C <sub>5</sub> H <sub>5</sub> (1) <sup>b</sup>	110.4	110.1	109.6
S(1)—M—C <sub>5</sub> H <sub>5</sub> (2)	101.7	102.6	102.6
S(5)—M—C <sub>5</sub> H <sub>5</sub> (1)	110.7	111.1	110.0
S(5)—M—C <sub>5</sub> H <sub>5</sub> (2)	99.6	98.9	102.0
C <sub>5</sub> H <sub>5</sub> (1)—M—C <sub>5</sub> H <sub>5</sub> (2)	132.6	132.7	134.1

<sup>a</sup> The unprimed atoms correspond in the case of Ti(*h*<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> to either molecule A or B. <sup>b</sup> C<sub>5</sub>H<sub>5</sub>(1) and C<sub>5</sub>H<sub>5</sub>(2) denote the cyclopentadienyl centroids for rings 1 and 2, respectively.

TABLE 6

LEAST-SQUARES MOLECULAR PLANES FOR  $Ti(h^5-C_5H_5)_2S_5$  AND  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  <sup>a,b</sup>

## I. Equations of least-squares planes and perpendicular distances (Å) of atoms from these planes

A. Molecules A and B of  $Ti(h^5-C_5H_5)_2S_5$ 

1. Plane through  $C_5H_5(1)$ , Ti, and  $C_5H_5(2)$ <sup>c</sup>. A,  $-0.8949X + 0.1889Y - 0.4044Z + 3.4317 = 0$ ;  
B,  $0.9441X - 0.0742Y - 0.3213Z - 4.8863 = 0$ .

	A	B		A	B
S(1)	1.77	-1.73	C(1-4)	-0.86	0.64
S(2)	1.51	-1.43	C(1-5)	-1.07	1.16
S(3)	-0.18	0.24	C(2-1)	-0.25	-0.16
S(4)	-1.75	1.86	C(2-2)	1.03	-1.17
S(5)	-1.81	1.84	C(2-3)	0.89	-0.57
C(1-1)	0.20	0.08	C(2-4)	-0.48	0.86
C(1-2)	1.18	-1.11	C(2-5)	-1.18	1.03
C(1-3)	0.53	-0.78			

2. Plane through S(1), Ti, S(5). A,  $0.3018X + 0.9084Y - 0.2895Z - 4.286 = 0$ ; B,  $-0.0863X + 0.9287Y - 0.3606Z - 1.1600 = 0$ .

	A	B		A	B
S(2)	-1.69	-1.71	C(2-1)	2.30	2.31
S(3)	-1.36	-1.42	C(2-2)	2.19	2.07
S(4)	-1.71	-1.72	C(2-3)	1.78	1.71
C(1-1)	-2.36	-2.38	C(2-4)	1.65	1.73
C(1-2)	-1.81	-1.97	C(2-5)	2.01	2.15
C(1-3)	-1.19	-1.26	$C_5H_5(1)$	-1.74	-1.76
C(1-4)	-1.31	-1.26	$C_5H_5(2)$	1.99	2.00
C(1-5)	-2.06	-1.94			

3. Plane through C(1-1), C(1-2), C(1-3), C(1-4), C(1-5). A,  $0.4322X + 0.5634Y - 0.7042Z + 1.2631 = 0$ ; B,  $-0.2151X + 0.5948Y - 0.7746Z + 7.5125 = 0$ .

	A	B		A	B
C(1-1)	-0.004	0.000	C(1-4)	0.012	-0.008
C(1-2)	0.012	-0.005	C(1-5)	-0.005	0.005
C(1-3)	-0.015	0.009	Ti	2.04	2.06

4. Plane through C(2-1), C(2-2), C(2-3), C(2-4), C(2-5). A,  $0.2173X + 0.9760Y - 0.0157Z - 7.8161 = 0$ ; B,  $0.0183X + 0.9951Y - 0.0970Z - 6.8377 = 0$ .

	A	B		A	B
C(2-1)	-0.015	-0.010	C(2-4)	-0.007	-0.011
C(2-2)	0.010	0.002	C(2-5)	0.014	0.013
C(2-3)	-0.001	0.005	Ti	-2.07	-2.08

B.  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  <sup>b,c</sup>

1. Plane through  $C_5H_5(1)$ , V,  $C_5H_5(2)$ .  $-0.2784X + 0.9589Y - 0.0545Z - 1.7837 = 0$ .

S(1)	1.72	C(1-4)	-0.90
S(2)	1.63	C(1-5)	-1.05
S(3)	-0.02	C(2-1)	-0.14
S(4)	-1.61	C(2-2)	1.06
S(5)	-1.73	C(2-3)	0.85
C(1-1)	0.23	C(2-4)	-0.57
C(1-2)	1.21	C(2-5)	-0.19
C(1-3)	0.50		

continued

TABLE 6 (continued)

2. Plane through  $S(1)$ ,  $V$ ,  $S(5)$ .  $-0.3232X - 0.1478Y - 0.9347Z + 1.3941 = 0$ .

S(2)	-1.63	C(2-1)	2.24
S(3)	-1.31	C(2-2)	2.03
S(4)	-1.66	C(2-3)	1.62
C(1-1)	-2.26	C(2-4)	1.61
C(1-2)	-1.71	C(2-5)	1.96
C(1-3)	-1.20	C <sub>5</sub> H <sub>5</sub> (1)	-1.72
C(1-4)	-1.37	C <sub>5</sub> H <sub>5</sub> (2)	1.89
C(1-5)	-2.04		

3. Plane through  $C(1-1)$ ,  $C(1-2)$ ,  $C(1-3)$ ,  $C(1-4)$ ,  $C(1-5)$ .  $-0.7018X - 0.2585Y - 0.6638Z + 3.8086 = 0$ .

C(1-1)	0.008	C(1-4)	0.015
C(1-2)	0.002	C(1-5)	-0.014
C(1-3)	-0.010	V	1.96

4. Plane through  $C(2-1)$ ,  $C(2-2)$ ,  $C(2-3)$ ,  $C(2-4)$ ,  $C(2-5)$ .  $-0.0504X - 0.0641Y - 0.9967Z - 1.0167 = 0$ .

C(2-1)	0.006	C(2-4)	0.013
C(2-2)	0.002	C(2-5)	-0.011
C(2-3)	-0.009	V	-1.98

## II. Angles (degrees) between normals to planes

### A. Molecules A and B of $Ti(h^5-C_5H_5)_2S_5$

	A	B		A	B
1 and 2	88.9	92.0	2 and 3	32.2	31.8
1 and 3	89.7	89.9	2 and 4	16.9	16.8
1 and 4	90.2	91.5	3 and 4	49.1	48.5

### B. $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$

1 and 2	90.0	2 and 3	27.7
1 and 3	90.9	2 and 4	16.8
1 and 4	89.6	3 and 4	44.5

<sup>a</sup> The equations of the planes are given in an orthogonal Ångström coordinate system ( $X, Y, Z$ ) which is related to the fractional unit cell coordinate system ( $x, y, z$ ) as follows:  $Ti(h^5-C_5H_5)_2S_5$  (monoclinic):  $X = ax + cz \cos\beta$ ,  $Y = by$ ,  $Z = cz \sin\beta$ .  $V(h^5-C_5H_5)_2S_5$  (orthorhombic):  $X = ax$ ,  $Y = by$ ,  $Z = cz$ . <sup>b</sup> Unit weights were used for all atoms in all plane calculations. <sup>c</sup>  $C_5H_5(n)$  denotes the centroid of the  $n$ th ring.

from a comparison of Fig. 3 for  $Ti(h^5-C_5H_5)_2S_5$  with Fig. 4 for  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ . The closest intermolecular contacts for both compounds are normal thereby suggesting no unusual intermolecular interactions. There is no indication of hydrogen bonding involving the water molecules in the crystalline lattice of  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  (Fig. 5) in that the nearest water oxygen contacts to non-hydrogen atoms are  $\geq 3.40$  Å. In addition to the monoclinic and orthorhombic crystalline phases isolated by us for  $Ti(h^5-C_5H_5)_2S_5$  (vide supra), a different monoclinic phase was prepared by Köpf et al. [6] and structurally characterized by Epstein and Bernal [7]. The crystal data for this second monoclinic phase

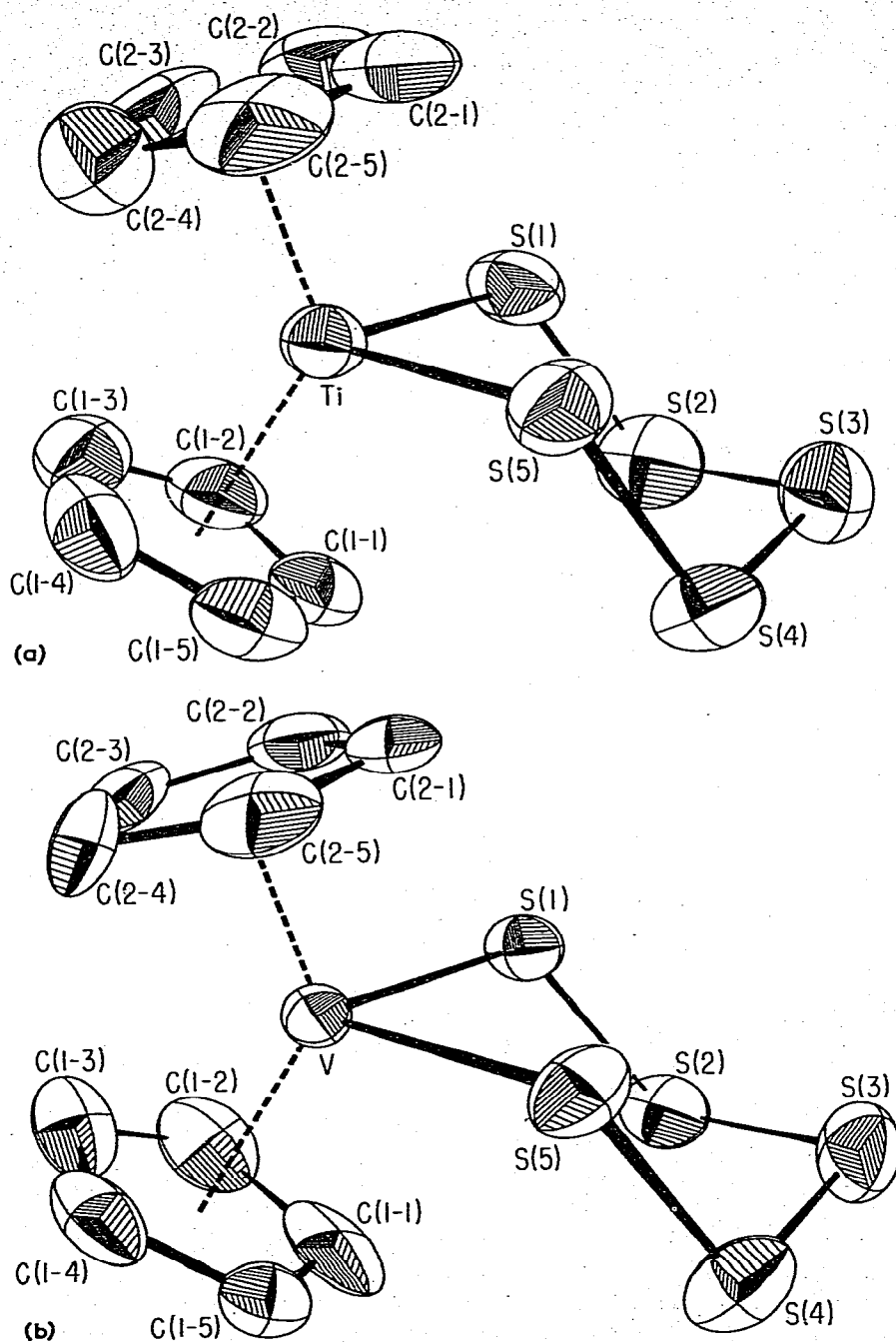


Fig. 2. Molecular configuration of (a)  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and (b)  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  drawn with 50% probability thermal ellipsoids.

are given in Table 7 (footnote b) which also compares the molecular parameters for the two monoclinic phases of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  with those of the orthorhombic phase of  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Since the corresponding distances and

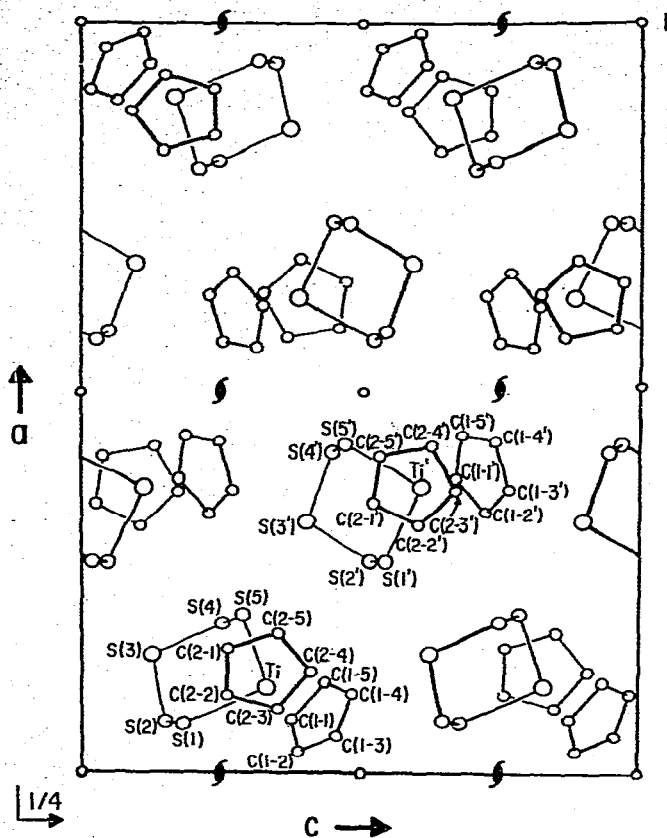


Fig. 3. An [010] projection of the monoclinic unit cell containing eight  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecules. There are two crystallographically independent molecules in this centrosymmetric cell of  $P2_1/c$  symmetry.

bond angles for the two independent  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecules in our monoclinic phase agree closely with each other as well as with the values from the Epstein-Bernal structural analysis of the one independent  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecule in the Köpf monoclinic phase, this discussion will deal with the values obtained in our work unless otherwise stated.

*Stereochemical relationship of  $M(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  ( $M = \text{Ti}, \text{V}$ ) with  $M(h^5\text{-C}_5\text{H}_5)_2\text{-}(\text{SC}_6\text{H}_5)_2$  ( $M = \text{Ti}, \text{V}$ ) and with cyclohexasulfur*

The molecular configuration of both  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  shown in Fig. 2 consists of a six-membered heterocyclic sulfur ring in a chair conformation with the dicyclopentadienylmetal moiety as the heterospecies. The pentasulfide fragment functions as a bidentate ligand in occupying two metal coordination sites with the centroids of the two cyclopentadienyl rings completing a distorted tetrahedral-like coordination around the metal atom. Each molecule ideally conforms to  $C_s-m$  point group symmetry with the mirror plane passing through the ring centroids, the metal atom, and the sulfur atom, S(3), at the foot of the chair.

The disposition of the two cyclopentadienyl rings relative to the six-membered  $\text{MS}_5$  ring system is of particular interest for each molecule, especially



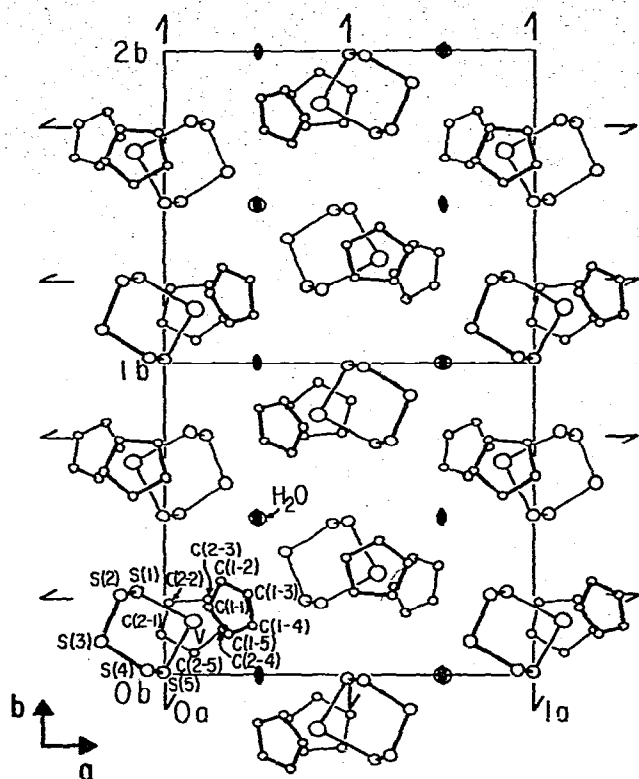


Fig. 4. An [001] projection of two orthorhombic unit cells of  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$  with each cell of nonsymmorphic  $P2_12_12$  symmetry containing four  $V(h^5-C_5H_5)_2S_5$  molecules and two water molecules of hydration. The two symmetry-related water molecules each possess crystallographic  $C_2-2$  site symmetry with one water oxygen atom located on a  $2_c$  at  $a/4, b/2$  and the other water oxygen atom on a  $2_c$  at  $3a/4, 0b$  (relative to a nonstandard origin at  $12_11$ ).

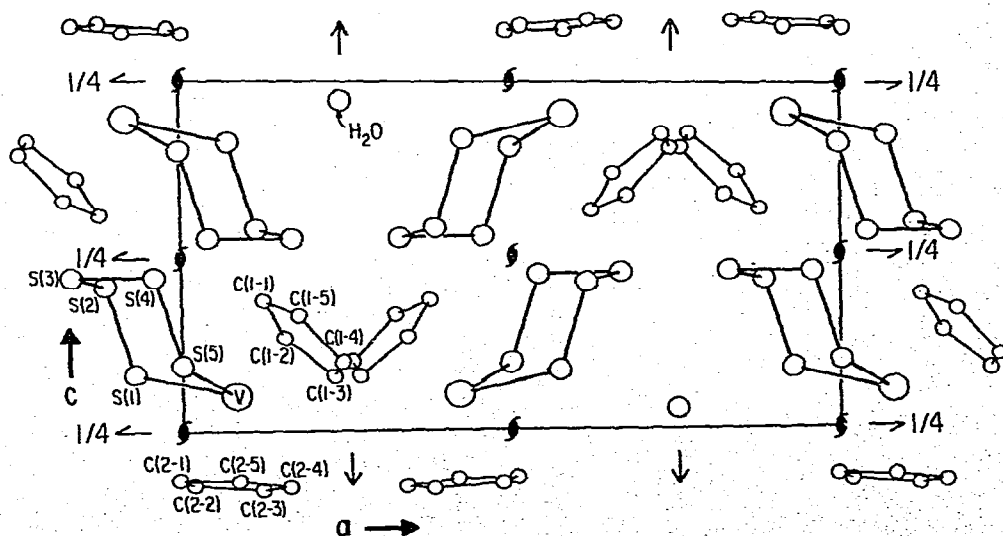


Fig. 5. An [010] projection of the unit cell of  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$ .

TABLE 7

COMPARISON OF MOLECULAR PARAMETERS OF THE TWO MONOCLINIC PHASES OF  $Ti(h^5-C_5H_5)_2S_5$  AND OF THE ORTHORHOMBIC PHASE OF  $V(h^5-C_5H_5)_2S_5 \cdot \frac{1}{2}H_2O$

## A. Distances (Å)

	Ti(MPD) <sup>a</sup>	Ti(EB) <sup>b</sup>	V
M—S(1)	2.441(2)	2.448(1)	2.464(2)
M—S(5)	2.410(3)	2.422(1)	2.450(2)
M—S(av)	2.425	2.435	2.457
S(1)···S(5)	3.576	3.580	3.454
M—C(1-n)(av) <sup>c</sup>	2.371	2.381	2.293
M—C(2-n)(av)	2.384	2.366	2.306
M—C <sub>5</sub> H <sub>5</sub> (1) <sup>d</sup>	2.052	2.066	1.959
M—C <sub>5</sub> H <sub>5</sub> (2)	2.073	2.071	1.972
S(1)—S(2)	2.065(3)	2.059(2)	2.051(2)
S(2)—S(3)	2.036(3)	2.056(2)	2.062(3)
S(3)—S(4)	2.049(3)	2.067(2)	2.055(3)
S(4)—S(5)	2.044(3)	2.059(2)	2.043(2)
S—S(av)	2.049	2.060	2.053

## B. Angles (degrees)

	Ti(MPD) <sup>a</sup>	Ti(EB) <sup>b</sup>	V
S(1)—M—S(5)	95.0(1)	94.6(1)	89.4(1)
C <sub>5</sub> H <sub>5</sub> (1)—M—C <sub>5</sub> H <sub>5</sub> (2)	132.7	133.7	134.1
M—S(1)—S(2)	107.9(1)	107.4(1)	113.9(1)
M—S(5)—S(4)	109.3(1)	108.6(1)	112.0(1)
S(1)—S(2)—S(3)	105.3(1)	105.2(1)	105.1(1)
S(2)—S(3)—S(4)	106.9(1)	106.7(1)	104.4(1)
S(3)—S(4)—S(5)	103.1(1)	102.7(1)	105.4(1)
S—S—S(av)	105.1	104.9	105.0

## C. Torsional angles (degrees)

	Ti(h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub> <sup>a</sup>		V(h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>5</sub>
	Molecule A	Molecule B	
M,S(1);S(2)/S(1),S(2),S(3)	69.3	72.2	73.2
S(1),S(2),S(3)/S(2),S(3),S(4)	76.8	78.2	73.5
S(2),S(3),S(4)/S(3),S(4),S(5)	78.8	76.3	75.8
S(3),S(4),S(5)/S(4),S(5),M	74.3	72.7	76.2
S(4),S(5),M/S(5),M,S(1)	61.9	63.4	60.7
S(5),M,S(1)/M,S(1),S(3)	59.0	61.0	60.1

<sup>a</sup> This work. <sup>b</sup> Taken from the highly precise structural determination by Epstein and Bernal [7] of a different monoclinic phase of  $Ti(h^5-C_5H_5)_2S_5$  (prepared by Köpf et al. [6]) which has the following crystal data:  $P2_1/n$ ;  $a$  9.019(3),  $b$  13.089(6),  $c$  11.294(3) Å,  $\beta$  93.62(4)°;  $V$  1330.6 Å<sup>3</sup>;  $\rho_{obsd}$  1.69(1) vs.  $\rho_{calcd}$  1.69 g cm<sup>-3</sup> for  $Z$  4. <sup>c</sup>  $C(1-n)$  and  $C(2-n)$  denote the  $n$ th carbon atom ( $n = 1-5$ ) of cyclopentadienyl ring 1 and 2, respectively. <sup>d</sup>  $C_5H_5(1)$  and  $C_5H_5(2)$  designate the centroids of rings 1 and 2, respectively.

in light of the nonequivalent sites of the two cyclopentadienyl rings in the  $Ti(h^5-C_5H_5)_2S_5$  molecule being manifested in solution by the detection at room temperature of two sharp NMR peaks (whose observed broadening and then coalescence at high temperatures [6a] can be attributed to fluxional character involving a conformational averaging in solution of two chair forms). Within

experimental error there is no evidence for any unusual steric effects involving a pronounced tilting or skewing of a given ring. The cyclopentadienyl carbon atoms in each ring of the titanium and vanadium molecules are all coplanar within 0.02 Å. Table 5 reveals that the five M—C bond lengths in each ring show a reasonably small variation ( $\leq 0.05$  Å) with the average M—C bond lengths of 2.38 Å in  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and of 2.30 Å in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  being virtually unchanged from those of 2.39 Å in  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  and 2.305 Å in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$ , respectively. This relative constancy of the molecular parameters of the  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2$  fragment (and likewise of the  $\text{V}(h^5\text{-C}_5\text{H}_5)_2$  fragment) upon substitution of a pentasulfide bidentate ligand in place of two phenylmercapto monodentate ligands is also apparent from the experimental equivalence of the metal-to-(ring centroid) distances and  $\text{C}_5\text{H}_5(1)\text{—M—C}_5\text{H}_5(2)$  angles\*, viz., 2.06 Å and  $133^\circ$  for  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  vs. 2.07 Å and  $132^\circ$  for  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$ ; 1.97 Å and  $134^\circ$  for  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  vs. 1.97 Å and  $135^\circ$  for  $\text{V}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$ . In contrast to the  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  molecules in each of which the two cyclopentadienyl ring centroids are symmetrically disposed relative to the  $\text{MS}_2$  fragment, the corresponding perpendicular displacements of the two ring centroids from the  $\text{MS}_2$  plane instead differ by 0.24 Å for  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and 0.17 Å for  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ . This unsymmetrical positioning of the  $\text{M}(h^5\text{-C}_5\text{H}_5)_2$  fragment relative to the  $\text{MS}_2$  part of the  $\text{MS}_5$  ring is also observed in  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  since the normal to the  $\text{MS}_2$  plane makes an angle of  $32^\circ$  with the  $\text{Ti—C}_5\text{H}_5(1)$  line compared to  $17^\circ$  with the  $\text{Ti—C}_5\text{H}_5(2)$  line while in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  the corresponding angles are  $28^\circ$  compared to  $17^\circ$ . This structural difference signifies primarily an angular distortion in which the entire  $\text{M}(h^5\text{-C}_5\text{H}_5)_2$  fragment is tipped in an upward direction relative to the  $\text{MS}_2$  part of the  $\text{MS}_5$  ring (Fig. 2) in order to increase the otherwise too close nonbonding separations (Table 5) between the bottom  $\text{C}_5\text{H}_5(1)$  ring and the two sulfur atoms S(2) and S(4) which are each bonded to a sulfur atom coordinated to the metal. This angular tipping can be readily shown to correspond to a rotation of the  $\text{M}(h^5\text{-C}_5\text{H}_5)_2$  fragment about an axis passing through the metal atom and perpendicular to the plane formed from the metal and two cyclopentadienyl ring centroids; this rotational distortion amounts to ca.  $7.5^\circ$  for a  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecule and to ca.  $5.5^\circ$  for a  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecule from a symmetrical positioning of the  $\text{M}(h^5\text{-C}_5\text{H}_5)_2$  fragment with respect to the  $\text{MS}_2$  plane. It is important to note in each of the titanium and vanadium pentasulfide molecules that the asymmetrical disposition of the  $\text{M}(h^5\text{-C}_5\text{H}_5)_2$  fragment has not noticeably affected its geometry which is essentially unchanged from that in the corresponding phenylmercapto molecule.

Of obvious interest is a comparison of the molecular parameters of these heteroatom ring systems with those of cyclohexasulfur,  $\text{S}_6$ . An X-ray diffraction study by Donohue, Caron, and Goldish [18] of this sulfur allotrope, commonly referred to as rhombohedral sulfur, yielded for the chair-like molecules a S—S bond length of 2.057(18) Å, a S—S—S bond angle of  $102.2(1.6)^\circ$ , and a S—S—S—S torsional angle of  $74.5(2.5)^\circ$ . The formal substitution of either a

\*  $\text{C}_5\text{H}_5(1)$  and  $\text{C}_5\text{H}_5(2)$  are used to designate the ring centroids.

$\text{Ti}(h^5\text{-C}_5\text{H}_5)_2$  or  $\text{V}(h^5\text{-C}_5\text{H}_5)_2$  fragment in place of one sulfur atom produces a similar deformation on the ring parameters. The much longer M—S distances (2.40–2.46 Å) compared to the S—S bond lengths are compensated to a large extent by the smaller S—M—S bond angle (89–95°) such that the geometry of the resultant  $\text{S}_5$  ligand is not appreciably altered from that of  $\text{S}_6$ . The greatest deformation expectedly involves the two sulfur atoms, S(1) and S(5), directly bonded to the metal atom, as seen by the S(1)···S(5) separation of 3.58 Å (av) in the titanium molecule and 3.45 Å in the vanadium molecule\* being considerably larger than the other corresponding S···S ring contacts of 3.20–3.29 Å range in the titanium molecule and of 3.25–3.26 Å range in the vanadium molecule (which are comparable to the corresponding value of 3.20 Å in  $\text{S}_6$ ). Although the S—S—S bond angles and S—S—S—S torsion angles (Table 7) in the metal complexes also reflect this trend, the variations in the S—S bond lengths are expectedly small with the average S—S bond length in each metal complex being essentially identical with that of  $\text{S}_6$ .

It is also apparent from an examination not only of the molecular parameters but also of appropriate least-squares planes (Table 6) that whereas the  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecule closely adheres to a  $C_5\text{-}m$  geometry (with the inherent assumption of cylindrical symmetry for each cyclopentadienyl ring), the  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  molecule displays a considerable deviation from bilateral symmetry. With respect to the mirror plane being defined by the metal atom and two cyclopentadienyl ring centroids, the perpendicular displacement of S(3) is only 0.02 Å in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  but 0.18 and 0.24 Å in molecules A and B of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ , while the two differences obtained from the perpendicular distances between each of the two pairs of mirror-related sulfur atoms (i.e., the difference between the S(1), S(5) pair and that between the S(2), S(4) pair) are only 0.01 and 0.02 Å in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  in contrast to corresponding values of 0.04 and 0.24 Å in molecule A and 0.11 and 0.43 Å in molecule B of  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ . This distinct skewing of only the titanium pentasulfide geometry from mirror plane symmetry may be rationalized on the basis of a much larger distortion of the regular cyclohexasulfur ring occurring upon substitution of a  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2$  fragment (rather than of a  $\text{V}(h^5\text{-C}_5\text{H}_5)_2$  fragment) in place of a sulfur atom, as indicated by the resulting increase in S(1)···S(5) separation being 0.13 Å greater in the titanium molecule than in the vanadium molecule.

#### *Comparison of the molecular structures of $M(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$ ( $M = \text{Ti}, \text{V}$ ) and resulting bonding implications*

The important differences between  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  in the S—M—S bond angle and in the M—S bond lengths and metal-to-(ring centroid) distances (Fig. 6 and Table 7) closely parallel those between  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$ .

The most striking difference between  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(h^5\text{-C}_5\text{H}_5)_2\text{S}_5$  is that the S—V—S bond angle of 89.4(1)° is ca. 6° less than the corresponding

\* The corresponding unconstrained S—M—S' bond angle and S···S' separation are 99.3(3)° and 3.67 Å in  $\text{Ti}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  and 94.1(1)° and 3.60 Å in  $\text{V}(h^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  [1].

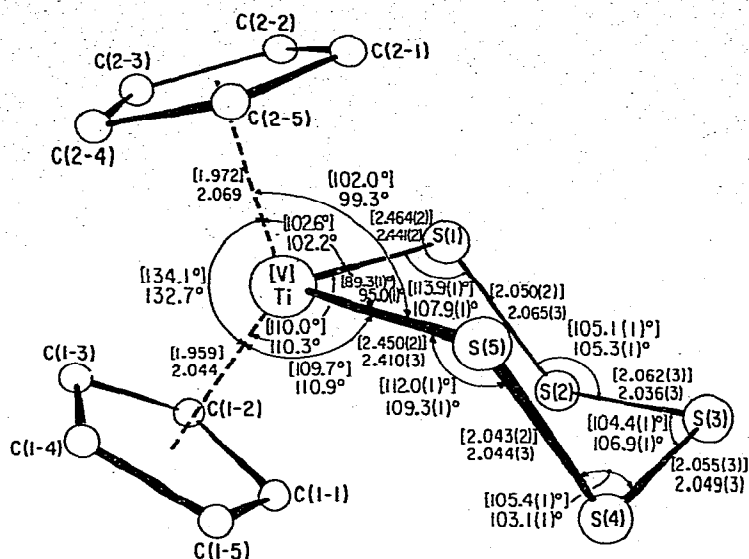


Fig. 6. Comparison of selected molecular parameters between  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$ . The values for these titanium and vanadium species are given without and with square brackets, respectively.

S—Ti—S bond angle of  $95.0(1)^\circ$ . This reduction in the S—V—S bond angle, which is in accord with the corresponding  $5^\circ$  decrease from  $99.3(3)^\circ$  to  $94.1(1)^\circ$  found in  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$  ( $\text{M} = \text{Ti}, \text{V}$ ), provides further support for our rejection [1,2] of the qualitative Ballhausen—Dahl representation [3] as an adequate bonding model for  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2$  systems. A similar correlation involving a decrease in L—M—L bond angle with an increase in the number of so-called nonbonding  $d$  electrons has been independently made by Green, Prout, and their co-workers [19] from X-ray diffraction studies of a number of  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2$  complexes with second-row transition metals.

The other prominent structural difference between  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  concerns the metal-to-ligand distances. Although the metal-to-(cyclopentadienyl ring centroid) distances of 2.06 and 1.97 Å for  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  and  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$ , respectively, reflect the 0.10 Å smaller covalent radius of vanadium, an opposite effect is found for the metal—sulfur distances which are 0.02–0.03 Å greater for  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  than for  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$ . This reverse bond-length trend [1,19], may be rationalized on the basis of two composite effects — one being a consequence of the unpaired electron in  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$  occupying a molecular orbital which is antibonding with respect to the V—S bonds and the other being due to increased intramolecular repulsive forces arising from the shorter metal—cyclopentadienyl distances in  $\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}_5$ .

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