

THE CRYSTAL AND MOLECULAR STRUCTURES OF DI- π -CYCLOPENTADIENYL TITANIUM PENTACHALCOGENIDES $(C_5H_5)_2TiS_{5-x}Se_x$

I. THE STRUCTURAL PROPERTIES OF π -(h^5 - C_5H_5) $_2TiS_5$

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SUMMARY

The crystal and molecular structure of $(C_5H_5)_2TiS_5$ has been determined from diffractometry data. The cell constants are $a = 9.019(3)$ Å, $b = 13.089(6)$ Å, $c = 11.294(3)$ Å, $\beta = 93.62(4)^\circ$; the space group is $P2_1/n$, and $Z = 4$. The molecule consists of a titanium atom which is part of a six-membered ring whose other members are the five sulfur atoms of the polysulfide chain. This ring has a cyclohexane-like chair configuration. The coordination polyhedron about the titanium comprises the two terminal sulfur atoms of the pentasulfide chain and the centroids of the π -cyclopentadienyl rings and is in the form of a distorted tetrahedron. The S-Ti-S angle is 94.6° while the (centroid)-Ti-(centroid) angle is 133.7° . The Ti-S distances are $2.422(1)$ Å and $2.448(1)$ Å. The four S-S distances range from 2.056 to 2.067 Å (average e.s.d. 0.002 Å) with an average value of 2.060 Å. This average S-S distance is very close to the values found in the polysulfide chain S_4^{2-} and in various allotropes of elementary sulfur. The narrow range of titanium-carbon distances, 2.341 to 2.398 Å (average e.s.d. 0.005 Å), establish a distinct *pentahapto* coordination mode for the five-membered rings with respect to the titanium atom. The titanium-ring centroid distances of 2.066 and 2.071 Å are among the longest thus far found for cyclopentadienyl rings coordinated to transition metals.

INTRODUCTION

In 1903 Hofman and Höchtlen¹ reported the synthesis of a Pt-S compound of composition $(NH_4)_2PtS_{15}$ whose structure, recently determined by Jones and Katz², showed that the PtS_{15}^{2-} ion consists of an octahedrally coordinated Pt^{IV} ion whose ligands are three bidentate S_5^{2-} ions. Recently, Köpf³ reported that the reaction of $(C_5H_5)_2MX_2$ (where $M = Ti, Mo, W$, and $X = Cl, Br$) with ammonium or alkali metal pentachalcogenides (S, Se, or mixtures of these two) yields as one product the compound $(C_5H_5)_2TiS_5$. A six-membered ring structure was predicted for the TiS_5 fragment on the basis of its reactions and its IR and NMR spectra. At room temperature, the 1H NMR spectrum shows *two* singlets of the π - C_5H_5 ligands while at 120° only one sharp singlet is obtained in those cases where the complexes are stable against the solvent $(CH_3)_2S_2$ ⁴. These spectra were taken to indicate that at room temperature

the MX_5 rings are fixed in conformation whereas at elevated temperatures rapid conformational changes take place.

The crystal structure of $(\text{C}_5\text{H}_5)_2\text{TiS}_5$ has been carried out in order to establish the precise geometry of the TiS_5 moiety and to determine its relationship to the PtS_{15}^{2-} anion. The geometry of the polysulfide chain was of interest for comparison with chains found in complexes which do not contain transition metals. Finally, the presence of two distinct cyclopentadienyl rings in different electron environments, as indicated by the NMR spectra, suggested that it would be possible to obtain a considerable amount of structural information about these important species.

EXPERIMENTAL

The compound $(\text{C}_5\text{H}_5)_2\text{TiS}_5$ was prepared by Dr. H. Köpf (Würzburg) who provided crystalline samples which are in the form of beautiful red parallelepipeds. The crystal selected for X-ray work was mounted at the end of a glass fiber. Preliminary precession photographs ($h0l$, $h1l$, $hk0$, $hk1$) indicate that the space group is $P2_1/n$, whose fourfold set of general positions is: $\pm(x, y, z; 1/2-x, 1/2+y, 1/2-z)$. The observed density of $1.69 \pm 0.01 \text{ g/cm}^3$, obtained by flotation in a zinc bromide solution agrees well with the calculated value of 1.69 g/cm^3 for a formula weight of 338.41 g/mole and four molecules in a unit cell of volume 1330.6 \AA^3 . The unit cell parameters of $a=9.019(3) \text{ \AA}$, $b=13.089(6) \text{ \AA}$, $c=11.294(3) \text{ \AA}$, $\beta=93.62(4)^\circ$ were obtained from a least-squares refinement of twenty sets of setting angles for reflections which were centered, at 22° , on a Picker automated diffractometer equipped with a graphite monochromator and using Mo $K\bar{\alpha}$ radiation ($\lambda=0.71069 \text{ \AA}$).

Data collection was carried out with the Picker diffractometer controlled by the Brookhaven Multiple Spectrometer Control System. The scintillation counter system included a pulse-height analyzer and pulse shape discriminator and was set to accept approximately 90% of the diffracted intensity. The c^* axis of the crystal coincided with the Φ axis of the instrument and the data were collected using a $\theta-2\theta$ step scan technique. A reflection was scanned in steps of $\Delta(2\theta)=0.03^\circ$, with a counting time of two seconds for each step. The total scan range of 1.80 ($1.0+1.0 \tan\theta$) was centered about the Bragg angle which corresponds to the unweighted average wavelength of 0.7104 \AA for Mo $K\alpha_1$ and Mo $K\alpha_2$ radiation. Since complete resolution of the α_1 and α_2 peaks occurred when 2θ was about 45° , background was taken to be the total count for the five points at each end of the scan and no attempt was made to fit the data points to a polynomial. The intensities of 4710 reflections with $2\theta \leq 52^\circ$, comprising two asymmetric forms of data were measured. Periodic checks of two standard reflections indicated that no crystal decomposition occurred. Individual measurements were within 3% of the average values of the two standard reflections.

For $(\text{C}_5\text{H}_5)_2\text{TiS}_5$, the linear absorption coefficient, μ , for Mo $K\bar{\alpha}$ radiation is estimated from atomic absorption coefficients⁵ to be 13.54 cm^{-1} . The size and the shape of the crystal (a parallelepiped with pairs of faces separated by 0.105, 0.105, and 0.208 mm) suggested that absorption corrections would be desirable if hydrogen atoms were to be located and refined. Therefore a correction for absorption was made based on the equations of these crystal faces: (011), (01 $\bar{1}$), (0 $\bar{1}$ 1), (0 $\bar{1}\bar{1}$), (100), and ($\bar{1}$ 00). The transmission factors were in the range 0.74 to 0.79. The data were corrected for the usual Lorentz polarization effects. No correction was made for the use of partially

polarized X-rays. The data were averaged and placed on a single scale. This procedure gave 1642 reflections for which $F^2 \geq 2\sigma(F^2)$, with $\sigma(F^2) = [\sigma_{\text{counting}}^2 + 0.05 F_o^2]^{\frac{1}{2}}$, where σ_{counting} was obtained from Poisson counting statistics⁶.

SOLUTION AND REFINEMENT OF THE STRUCTURE

One form of data, which was corrected for Lorentz and polarization effects but not for absorption, was used to solve and refine the structure initially. An unsharpened, origin-containing Patterson function gave the approximate coordinates of the titanium atom and the five sulfur atoms. These atoms provided phases for a difference synthesis which yielded the approximate coordinates of the ten carbon atoms. Full-matrix isotropic, least-squares refinement of the positions of the titanium, of the five sulfur atoms and of group parameters of the cyclopentadienyl rings was carried out. For the two planar rigid groups the values of the C-C and C-H bond lengths were taken initially as 1.419 and 0.98 Å, respectively. This C-C bond length is the average value found by Wheatley in his survey of cyclopentadienyl complexes of transition metals.⁷ The scattering factors of Cromer⁸ were used for the Ti, S, C, and H atoms. Anomalous dispersion corrections⁹ to the scattering factors for Ti ($\Delta f' = 0.3$, $\Delta f'' = 0.6$) and S ($\Delta f' = 0.1$, $\Delta f'' = 0.2$) were included in the calculation. The function minimized in the least-squares refinement was $\sum \omega \cdot (|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively and $\omega = [\sigma(|F_o|)]^{-2}$.

Three cycles of isotropic full-matrix least-squares refinement of the scale factor, the positional parameters of the titanium, the five sulfur atoms and of the rigid group parameters gave discrepancy indices of $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.081$ and $R_2 = \{\sum \omega \cdot (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2\}^{\frac{1}{2}} = 0.107$. Refinement was continued with anisotropic thermal parameters of the form $\exp[-(h^2 \cdot \beta_{11} + k^2 \cdot \beta_{22} + l^2 \cdot \beta_{33} + 2h \cdot k \cdot \beta_{12} + 2h \cdot l \cdot \beta_{13} + 2k \cdot l \cdot \beta_{23})]$ for the titanium and five sulfur atoms. Three cycles of refinement brought the discrepancy factors to $R_1 = 0.077$ and $R_2 = 0.103$ with an error of fit $[\sum \omega \cdot \Delta^2 / (N_o - N_v)]^{\frac{1}{2}}$ of 2.94, where N_o is the number of observations and N_v is the number of variables.

At this point the second form of data was reduced to $|F_o|$'s, the complete set was corrected for absorption, and *then* averaged. Full-matrix least-squares refinement was continued initially constraining the cyclopentadienyl rings to be rigid planar groups with individual, isotropic, thermal motion for the carbon atoms while the titanium and five sulfur atoms had anisotropic thermal parameters. This refinement converged to values of $R_1 = 0.071$ and $R_2 = 0.099$. The isotropic thermal parameters for the carbon atoms of the rigid groups were converted to anisotropic form and these parameters were refined along with the positional and anisotropic thermal parameters of the titanium and the five sulfur atoms, while the positional parameters of the carbon and hydrogen atoms were held fixed. This refinement converged to the values $R_1 = 0.048$ and $R_2 = 0.061$. The positions of *all* atoms were then refined along with the anisotropic thermal parameters of non-hydrogen atoms. The positional and isotropic thermal parameters for all of the hydrogen atoms were also varied. This refinement converged to give the final values of $R_1 = 0.037$, $R_2 = 0.043$ and an error of fit of 1.28 for the 1642 structure amplitudes with $F_o^2 \geq 2\sigma(F_o^2)$.

The positional and thermal parameters from the final cycle of refinement are given in Table 1. Table 2 gives a list of the observed and calculated structure factors

based on these parameters. Interatomic distances and angles with estimated standard deviations (which include the effect of the estimated error in lattice parameters) are given in Table 3. The equations of planes determined by a least-squares procedure and the distances of atoms from these planes are given in Table 4. The following programs were used: PROCH (initial processing of data); DATAPH (Lorentz-polarization and absorption corrections); ESORTH (sorting and averaging); JIMDAP (local version of the Zalkin Fourier summation program); LINUS (modification of the Busing, Martin, and Levy ORFLS least-squares program)¹⁰; ORFFE (function and error)¹¹; RBANG (rigid group parameters)¹²; PLANET (least-squares planes)¹³; ORTEP (molecular plotting)¹⁴.

DISCUSSION

The molecular configuration of $(C_5H_5)_2TiS_5$, which appears in Fig. 1, consists of two cyclopentadienyl rings coordinated to a formally Ti^{4+} ($3d^0$) ion which is part of a six-membered hetero-atom ring, whose other five members are sulfur atoms. This six-membered ring has a cyclohexane-like chair configuration. If the five-membered

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TABLE 1

POSITIONAL AND THERMAL PARAMETERS

A. FRACTION COORDINATES

Atom	x	y	z
Ti	0.49565(7)	0.30390(5)	0.27416(5)
S1	0.73890(12)	0.23218(8)	0.23541(9)
S2	0.88618(13)	0.35208(10)	0.23049(10)
S3	0.91839(12)	0.40066(10)	0.40328(10)
S4	0.73350(13)	0.48555(8)	0.43964(9)
S5	0.57641(11)	0.37481(7)	0.46455(7)
C1-1	0.5201(7)	0.3838(4)	0.0865(4)
C1-2	0.3724(7)	0.3581(4)	0.0920(4)
C1-3	0.3175(6)	0.4172(4)	0.1834(5)
C1-4	0.4295(6)	0.4774(3)	0.2312(4)
C1-5	0.5543(6)	0.4579(4)	0.1711(4)
C2-1	0.4714(10)	0.1634(6)	0.4059(8)
C2-2	0.4805(9)	0.1240(4)	0.3005(11)
C2-3	0.3648(11)	0.1590(6)	0.2300(5)
C2-4	0.2760(8)	0.2129(6)	0.2970(11)
C2-5	0.3478(12)	0.2186(6)	0.4086(7)
H1-1	0.577(6)	0.365(4)	0.042(4)
H1-2	0.317(7)	0.315(5)	0.044(6)
H1-3	0.231(5)	0.412(3)	0.205(4)
H1-4	0.434(5)	0.531(4)	0.293(4)
H1-5	0.643(6)	0.478(4)	0.189(4)
H2-1	0.556(8)	0.163(5)	0.485(6)
H2-2	0.552(9)	0.086(6)	0.264(7)
H2-3	0.333(7)	0.129(5)	0.153(6)
H2-4	0.222(7)	0.221(5)	0.270(5)
H2-5	0.342(7)	0.249(5)	0.455(6)

(Continued)

TABLE 1 (continued)

B. THERMAL PARAMETERS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti ^a	669(11)	331(4)	361(5)	- 23(5)	3(5)	- 28(3)
S1 ^a	953(16)	486(6)	702(9)	159(8)	89(9)	- 91(6)
S2 ^a	866(17)	882(9)	733(10)	- 119(9)	212(10)	- 32(8)
S3 ^a	905(17)	903(10)	776(10)	- 247(10)	- 149(10)	- 8(8)
S4 ^a	1434(19)	466(7)	717(9)	- 258(9)	- 75(10)	- 110(6)
S5 ^a	1031(16)	434(6)	401(7)	- 43(7)	0(8)	- 90(5)
C1-1 ^b	183(11)	81(4)	50(4)	44(5)	25(5)	29(3)
C1-2 ^b	177(10)	63(4)	68(4)	8(4)	- 58(5)	3(3)
C1-3 ^b	76(8)	74(4)	117(5)	23(4)	- 12(5)	23(4)
C1-4 ^b	169(9)	39(3)	70(4)	24(4)	- 12(5)	- 1(3)
C1-5 ^b	131(9)	56(3)	84(5)	- 11(4)	- 24(5)	32(3)
C2-1 ^b	220(13)	85(5)	143(8)	- 73(7)	- 50(9)	59(5)
C2-2 ^b	209(14)	38(3)	28(15)	- 20(5)	100(13)	- 14(6)
C2-3 ^b	276(15)	92(5)	71(5)	- 109(8)	15(7)	- 22(4)
C2-4 ^b	70(10)	98(6)	285(17)	- 25(6)	- 19(10)	80(8)
C2-5 ^b	332(21)	89(6)	106(7)	- 96(9)	121(11)	- 38(5)
H1-1 ^c	2.2(1.2)					
H1-2 ^c	6.0(1.7)					
H1-3 ^c	1.0(1.0)					
H1-4 ^c	3.4(1.2)					
H1-5 ^c	2.1(1.1)					
H2-1 ^c	7.8(1.9)					
H2-2 ^c	8.4(2.2)					
H2-3 ^c	6.5(1.7)					
H2-4 ^c	2.4(1.7)					
H2-5 ^c	4.8(2.0)					

C. R.M.S. AMPLITUDES OF VIBRATION ALONG THE THREE PRINCIPAL AXES OF THE THERMAL ELLIPSOID (Å)

Atom	Axis 1	Axis 2	Axis 3
Ti	0.148	0.167	0.173
S1	0.169	0.211	0.331
S2	0.173	0.224	0.279
S3	0.169	0.234	0.289
S4	0.163	0.227	0.261
S5	0.150	0.200	0.208
C1-1	0.148	0.222	0.323
C1-2	0.151	0.235	0.311
C1-3	0.151	0.248	0.297
C1-4	0.169	0.207	0.279
C1-5	0.162	0.216	0.292
C2-1	0.172	0.249	0.410
C2-2	0.174	0.260	0.442
C2-3	0.158	0.222	0.406
C2-4	0.154	0.232	0.461
C2-5	0.179	0.215	0.444

^{a,b} Multiplied by 10^5 and 10^4 , respectively. The form of the thermal ellipsoid is $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot h \cdot k + 2\beta_{13} \cdot h \cdot l + 2\beta_{23} \cdot k \cdot l)]$. ^c Isotropic temperature factor in Å².

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES)

A. BOND DISTANCES

Ti...S1	2.4483(14)	C1-1...C1-2	1.379(8)
Ti...S5	2.4219(11)	C1-2...C1-3	1.405(7)
Ti...(centroid, ring 1)	2.066(-)	C1-3...C1-4	1.365(7)
Ti...(centroid, ring 2)	2.071(-)	C1-4...C1-5	1.375(7)
		C1-5...C1-1	1.382(7)
Ti...C1-1	2.376(4)		
Ti...C1-2	2.374(4)	C2-1...C2-2	1.305(10)
Ti...C1-3	2.367(4)	C2-2...C2-3	1.324(10)
Ti...C1-4	2.388(4)	C2-3...C2-4	1.389(12)
Ti...C1-5	2.398(4)	C2-4...C2-5	1.381(12)
		C2-5...C2-1	1.332(11)
Ti...C2-1	2.392(5)		
Ti...C2-2	2.380(6)	C1-1...H1-1	0.78(5)
Ti...C2-3	2.348(5)	C1-2...H1-2	0.91(7)
Ti...C2-4	2.341(6)	C1-3...H1-3	0.84(4)
Ti...C2-5	2.370(6)	C1-4...H1-4	0.98(5)
		C1-5...H1-5	0.86(5)
S1...S2	2.0590(17)		
S2...S3	2.0556(16)	C2-1...H2-1	1.14(8)
S3...S4	2.0665(18)	C2-2...H2-2	0.93(8)
S4...S5	2.0586(15)	C2-3...H2-3	0.95(7)
		C2-4...H2-4	0.57(5)
		C2-5...H2-5	0.66(6)

B. BOND ANGLES

S1 Ti S5	94.59(4)	H1-1 C1-1 C1-2	129(3)
R1 Ti R2	133.7(-)	H1-1 C1-1 C1-5	122(3)
R1 Ti S1	110.7(-)	H1-2 C1-2 C1-1	128(4)
R1 Ti S5	110.7(-)	H1-2 C1-2 C1-3	125(4)
R2 Ti S1	100.5(-)	H1-3 C1-3 C1-2	123(3)
R2 Ti S5	99.6(-)	H1-3 C1-3 C1-4	128(3)
		H1-4 C1-4 C1-3	133(3)
Ti S1 S2	107.41(6)	H1-4 C1-4 C1-5	119(3)
Ti S5 S4	108.58(5)	H1-5 C1-5 C1-4	128(3)
S1 S2 S3	105.24(6)	H1-5 C1-5 C1-1	123(3)
S5 S4 S3	102.68(7)		
S2 S3 S4	106.71(7)	H2-1 C2-1 C2-2	129(4)
		H2-1 C2-1 C2-5	121(4)
C1-2 C1-1 C1-5	108.3(5)	H2-2 C2-2 C2-1	135(5)
C1-1 C1-5 C1-4	108.5(5)	H2-2 C2-2 C2-3	114(5)
C1-5 C1-4 C1-3	107.8(4)	H2-3 C2-3 C2-2	130(4)
C1-4 C1-3 C1-2	108.8(5)	H2-3 C2-3 C2-4	122(4)
C1-3 C1-2 C1-1	106.5(5)	H2-4 C2-4 C2-3	108(7)
		H2-4 C2-4 C2-5	145(7)
C2-2 C2-1 C2-5	109.6(7)	H2-5 C2-5 C2-4	134(6)
C2-1 C2-2 C2-3	110.3(6)	H2-5 C2-5 C2-1	117(6)
C2-2 C2-3 C2-4	106.9(7)		
C2-3 C2-4 C2-5	105.9(7)		
C2-4 C2-5 C2-1	107.2(6)		

(Continued)

TABLE 3 (continued)

C. NON-BONDED INTRAMOLECULAR CONTACTS LESS THAN 3.50 Å^a

Ti...H2-5	2.65	C1-3...H2-4	2.90
Ti...H2-4	2.70	C1-3...C2-4	3.00
Ti...H1-5	2.83	C2-3...H1-2	3.01
Ti...H1-3	2.84	C2-4...H1-3	2.82
Ti...H1-1	2.88	S1...S3	3.27
Ti...H2-2	2.90	S1...C2-1	3.31
Ti...H1-2	2.97	S1...H1-5	3.36
Ti...H2-3	3.00	S1...C1-5	3.45
Ti...H1-4	3.03	S1...H2-1	3.47
Ti...H2-1	3.04	S2...H1-3	3.24
S1...H2-2	2.58	S2...H2-1	3.26
S1...C2-2	2.86	S2...S4	3.31
S1...H1-1	3.09	S2...C1-5	3.33
S1...C1-1	3.20	S2...H1-1	3.40
S2...H1-5	2.76	S2...H2-4	3.48
S4...H1-5	2.90	S3...S5	3.22
S4...H1-4	3.14	S4...C1-5	3.36
S5...H2-5	2.68	S5...H1-5	3.48
S5...H2-1	2.79	S5...C1-5	3.48
S5...C2-5	2.94	C1-2...H1-4	3.22
S5...C2-1	2.98	C2-3...H2-1	3.26
S5...H1-4	3.04	C2-3...H1-3	3.35
S5...C1-4	3.17	C2-4...H1-2	3.20
C1-2...H2-4	3.07	C2-4...H2-1	3.26
C1-2...H2-3	3.10		
C1-2...C2-3	3.12		
C1-2...C2-4	3.16		

D. INTERMOLECULAR CONTACTS LESS THAN 3.5 Å

S1...H2-5	3.37	00 $\bar{1}$	3 ^b	C1-2...H2-1	3.04	$\bar{1}0\bar{1}$	3
S2...H2-2	3.11	100	4	C1-3...H2-1	3.22	$\bar{1}0\bar{1}$	3
S2...H2-1	3.26	00 $\bar{1}$	3	C1-4...H2-3	3.41	000	4
S2...H2-5	3.39	00 $\bar{1}$	3	C1-4...H2-4	3.47	000	4
S3...H2-3	3.00	000	3	C1-5...H1-1	3.49	110	2
S3...H2-2	3.10	100	4	C2-1...H1-2	3.40	000	3
S3...H1-2	3.39	000	3	C2-2...H1-3	3.36	0 $\bar{1}0$	4
S4...H2-3	2.93	000	3	C2-3...H1-4	3.12	0 $\bar{1}0$	4
S4...H2-2	3.36	100	4	C2-3...H1-3	3.35	0 $\bar{1}0$	4
S4...H1-4	3.47	111	2	C2-4...H1-4	3.17	0 $\bar{1}0$	4
S5...H1-4	3.01	111	2	C2-5...H1-1	3.14	$\bar{1}00$	3
S5...H2-3	3.04	000	3				
S5...H1-2	3.38	000	3				

^a Contacts between carbon and hydrogen atoms of the same cyclopentadienyl ring are not included.

^b The notation 00 $\bar{1}$ 3 indicates that the second atom is in the symmetry position 3 with a cell translation in the $-c$ direction. The symmetry positions 2, 3, and 4 are: $1/2-x, 1/2+y, 1/2-z$; $-x, -y, -z$; $1/2+x, 1/2-y, 1/2+z$.

TABLE 4

PLANES^a

A. EQUATIONS OF PLANES AND DISTANCES (Å) FROM THESE PLANES

(a). Plane containing Ti, S1 and S5

$$0.2758X + 0.8532Y - 0.4427Z = 3.2100$$

Centroid, Ring 1 1.76

Centroid, Ring 2 -2.00

(b). Plane containing C1-1, C1-2, C1-3, C1-4, C1-5

$$-0.2186X + 0.7177Y - 0.6611Z = 1.9552$$

C1-1	-0.01	H1-1	0.04
C1-2	0.00	H1-2	0.06
C1-3	0.00	H1-3	-0.03
C1-4	0.00	H1-4	0.04
C1-5	0.01	H1-5	-0.11
Ti	-2.07		

(c). Plane containing C2-1, C2-2, C2-3, C2-4, C2-5

C2-1	0.00	H2-1	0.12
C2-2	0.00	H2-2	0.06
C2-3	0.00	H2-3	-0.12
C2-4	0.00	H2-4	-0.07
Ti	2.07	H2-5	0.13

(d). Plane containing S1, S2, S3, S4

$$0.5703X - 0.4457Y + 0.6900Z = 4.19$$

S1	0.01	Ti	1.40
S2	-0.01	Centroid, Ring 1	3.25
S3	0.01	Centroid, Ring 2	0.80
S4	-0.01		

(e). Plane containing S2, S3, S4

$$0.4679X + 0.8275Y - 0.3103Z = 6.67$$

Ti	2.33	Centroid, Ring 1	0.87
S1	1.94	Centroid, Ring 2	4.40
S5	1.96		

(f). Plane containing Ti and the centroids of the two rings

S1	1.78	S4	-1.73
S2	1.57	S5	-1.80
S3	-0.11		

B. ANGLES (DEGREES) BETWEEN THE NORMALS TO PLANES

a	b	32.4	b	f	89.6
a	c	17.0	c	d	75.0
a	d	58.1	c	e	3.5
a	e	13.5	c	f	89.8
a	f	90.4	d	e	71.6
b	c	49.3	d	f	89.0
b	d	25.8	e	f	90.4
b	e	45.8			

(Continued)

TABLE 4 (continued)

C. ANGLES (DEGREES) BETWEEN INTERATOMIC VECTORS AND THE NORMALS TO PLANES

Vector	Plane	Angle
Ti-Centroid, Ring 1	a	31.4
Ti-Centroid, Ring 1	b	1.0
Ti-Centroid, Ring 2	a	14.9
Ti-Centroid, Ring 2	c	2.0
S1-S5	f	1.1

^a The equations of the planes and distances and angles were obtained with the Smith plane program. Unit weights were used in the calculations. The equation of the plane is expressed in orthogonal coordinates which are related to the fractional coordinates x , y , z by the transformation:

$$X = a \cdot x + c \cdot z \cdot \cos \beta$$

$$Y = b \cdot y$$

$$Z = c \cdot z \cdot \sin \beta$$

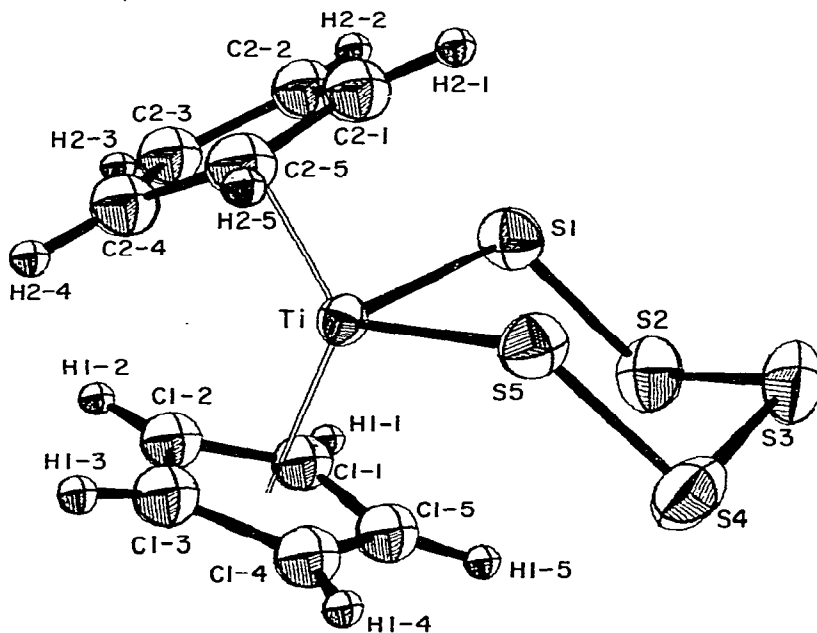


Fig. 1. The molecular configuration of $(C_5H_5)_2TiS_5$. For the sake of illustrative convenience, the thermal parameters of the carbon and hydrogen atoms are isotropic and of arbitrary magnitude. See Fig. 2.

rings are each considered to occupy a single titanium coordination site, then the terminal atoms of the bidentate pentasulfide chain complete a distorted tetrahedral coordination geometry for the metal ion. The extent of the distortion is indicated by the two angles (ring 1 centroid)-Ti-(ring 2 centroid) and S1-Ti-S5 which are 133.7° and 94.6° , respectively. The chair conformation for the TiS_5 moiety results in an electronic environment which is different for the two cyclopentadienyl rings. One result of this asymmetric environment is that the two cyclopentadienyl rings are disposed such that the bisector of the (centroid)-Ti-(centroid) angle does not lie in the S1-Ti-S5 plane, thereby reducing the idealized point group symmetry for the

coordination polyhedron at the titanium atom from C_{2v} to m . The compound is diamagnetic and monomeric in the solid state. The Ti^{4+} ($3d^0$) ion achieves the 18 electron rare gas configuration by the formal contribution of six electrons from each cyclopentadienyl group and three electrons from each coordinated sulfur atom of the bidentate polysulfide chain. This formalism suggests that there is a degree of multiple character to the titanium-sulfur bond via the overlap of a lone pair of electrons on the sulfur atom with the unfilled d orbitals of the metal.

The ten titanium-carbon distances range from 2.341 to 2.398 Å (average e.s.d. 0.005 Å). The average value of 2.374 (5) Å is close to the average titanium-carbon distance of 2.38 Å found in the phenylthio complex $(C_5H_5)Ti(SC_6H_5)_2$ ¹⁵. A structural determination of the dimeric complex $(C_5H_5)_2TiAl(C_2H_5)_2Cl_2$ ¹⁶ has yielded an average Ti-C distance of 2.38 Å for one of the two independent five-membered rings (the second ring is distorted due to interactions which appear not to involve the titanium atom). The narrow range for the ten titanium-carbon distances in $(C_5H_5)_2TiS_5$ establish a distinct *pentahapto* coordination mode¹⁷ for the five-membered rings with respect to the titanium atom. The titanium-(ring centroid) distances are 2.066 Å (ring 1) and 2.071 Å (ring 2) and are typical of the values found for complexes of titanium which are bound to π -cyclopentadienyl groups⁷. The titanium-ring distances for these compounds are significantly longer than for any transition metal-cyclopentadienyl ring distances except for those of molybdenum¹⁸. For $(\pi-C_5H_5)Mo(CO)_3-C_2H_5$ ¹⁹ and $[(\pi-C_5H_5)Mo(CO)_2]_2(H)[P(CH_3)_2]$ ²⁰ the metal to ring distances are 2.04 Å and 2.00 Å, respectively. The vanadium complexes differ from those of titanium by the formal addition of a single electron. For the vanadium compound $(\pi-C_5H_5)_2V^{21}$ and for $(\pi-C_5H_5)(\pi-C_7H_7)V^{22}$ the metal-cyclopentadienyl ring distances are 1.96 and 1.90 Å, respectively. The substantial decrease in metal-ring distance as one d electron is added to the system when the central ion changes from Ti^{4+} ($3d^0$) to V^{4+} ($3d^1$) is to be contrasted with the insignificant change in the metal-ring distance which occurs when Mo^{4+} ($4d^2$) is substituted for the titanium ion. The survey of cyclopentadienyl complexes by Wheatley⁷ indicates that no simple correlation exists between the number of d electrons and the metal-ring distance. On the other hand, there is no uniform set of compounds having the same composition (except for the central metal ion) whose structural characteristics are known. Therefore, one must conclude that the wide variation in metal-ring distances is a product of both the electronic configuration of the ion and the effect of the other ligands present.

The two Ti-S bond lengths are 2.422(1) and 2.448(1) Å. The difference of 0.026 (2) Å is considered to be significant. The average value of 2.435 Å is close to the average value of 2.41 Å found for the Ti-S bond lengths in $(C_5H_5)_2Ti(SC_6H_5)_2$ ¹². The "bite" of the S_5 fragment is 3.58 Å, a value which is longer than the Van der Waals contact distance of 3.40 Å²³ for a pair of sulfur atoms, but close to the value of 3.67 Å found for this contact in $(C_5H_5)_2Ti(SC_6H_5)_2$ ¹². In the phenylthio complex, the $(C_5H_5)_2TiS_2$ moiety has a geometry which is similar to that found in $(C_5H_5)_2TiS_5$ and the titanium-sulfur distances in both of these compounds are greater than the titanium-sulfur distance (2.32 Å) found for TiS^{24} but less than the distance 2.45 Å found in the non-stoichiometric phase $Ti_{2+x}S_4$ ($0.2 < x \leq 1$)²⁵. It is of interest to note that the Ti-S distances in $(C_5H_5)_2TiS_5$ and $(C_5H_5)_2Ti(SC_6H_5)_2$ are quite close to the average Mo-S distance of 2.433(5) Å found by X-ray diffraction for di- π -cyclopentadienyl(3,4-toluenedithiolato)molybdenum¹⁸. The average molybdenum-carbon distance of

2.33(2) Å is also quite close to the values found for the metal-carbon distances in the closely related titanium compounds. However, the S-Mo-S angle of 82.4(2)° is significantly less than the values 94.6(1)° and 99.3(3)° found for (C₅H₅)₂TiS₅ and (C₅H₅)₂Ti(SC₆H₅)₂, respectively. Despite the difference in S-M-S angle, the (ring centroid)-Mo-(ring centroid) angle of 132.5° is very close to the values 133.7° and 132.4° for the similar angles in the titanium compounds. It should be noted that the S-Mo-S angle depends upon the ligand "bite". The molybdenum atom has two more valence electrons for bonding to the π -cyclopentadienyl rings and the sulfur atoms than does the titanium atom in these compounds. Ballhausen and Dahl²⁶ have studied the compounds of the type (π -C₅H₅)₂MX₂ and suggest that the lowest energy molecular orbital is one which lies in the plane of the metal atom and the two X ligands. If in the 3,4-toluenedithiolate (C₅H₅)₂Mo(S₂C₇H₆) this orbital is occupied by the two additional electrons, then repulsions between these electrons and those of the ligand should force the "bite" of the dithiolate ligand to open. This appears to be the case since the S...S "bite" distance for the dithiolate ligand²⁷ in Mo(S₂C₂H₂)₃, which contains the formally Mo⁶⁺ (*d*⁰) ion, is 3.10 while that in dicyclopentadienyl(3,4-toluenedithiolato)-molybdenum which contains the formally Mo⁴⁺, is 3.205 Å. The S-M-S angles in these two molybdenum dithiolate complexes are identical. The average Mo-S bond distance in the toluedithiolate of 2.433(5) Å is approximately 0.1 Å longer than the value 2.33(2) Å for this distance in Mo(S₂C₂H₂)₃²⁷. This increase in Mo-S bond distance is consistent with the change in the S...S "bite" distance and with the identity of the S-Mo-S bond angle for the two compounds.

The four S-S distances within the S₅ fragment are the same, within the accuracy of this determination, with values which range from 2.056(2) Å to 2.067(2) Å [average value 2.060(2) Å]. The bond angles at the sulfur atoms are close to, but less than, the tetrahedral angles which would be expected for *sp*³ orbitals. The Ti-S1-S2 and Ti-S5-S4 angles are 107.4(1)° and 108.6(1)°, respectively, while the S-S-S angles at S2, S3, and S4 are 105.2(1), 106.7(1), and 102.7(1)°, respectively. Recently Abrahams and Bernstein²⁸ have redetermined the structure of BaS₄·H₂O from diffractometry data and found that the three S-S bond lengths are the same [average value 2.062(2) Å]. Donohue²⁹ has redetermined the structures of three allotropes of elementary sulfur and found that the S-S bond lengths are the same within each allotrope and have the average values 2.060(2), 2.063(17), and 2.057(18) Å for the α -S₈, β -S₈, and ρ -S₆ forms, respectively. The bond angles within the S₄²⁻ anion have an average value of 104.2(1)°, a value which agrees well with those found for the formally S₅²⁻ chain in (C₅H₅)₂TiS₅. The dihedral angles for the pairs of planes TiS1S5/S1S2S4S5 and S1S2S4S5/S2S3S4 are 58° and 72°, respectively. The latter dihedral angle is similar to the dihedral angles 76.2(2) and 76.5(2)° for the sulfur containing planes in the S₄²⁻ chain²⁸. The identity of S-S bond lengths and the similarity of bond angles for the formally S₅²⁻, S₄²⁻ chains and the various allotropes of elementary sulfur indicate a similar mode of bonding for these species. The average bond length of 2.06 Å for all these species is somewhat shorter than the value of 2.08–2.09 Å for a S-S single bond^{30,31}. This suggests that there is a degree of multiple character to the S-S bonds in these chains, probably involving sulfur *d* orbitals. The nearly tetrahedral geometry at the sulfur atoms in these chains leads to a minimization of repulsion between lone pairs of electrons centered at each of the sulfur atoms in the chain.

The geometry of the cyclopentadienyl rings is of particular interest because of

the asymmetry of the field in which the two groups lie. Cyclopentadienyl ring 1 is an exact pentagon whose atoms, including the hydrogens, lie in a plane. The C–C bond lengths are the same and the bond angles at the carbon atoms are all within 1.4° of the 108° angle for a pentagon. The range of C–C distances is from 1.365 Å to 1.405 Å (average e.s.d. 0.007 Å) with an average value of 1.381 Å. The range of C–H distances is from 0.78 Å to 0.98 Å (average e.s.d. 0.06 Å) with an average value of 0.87 Å. The largest displacement of a *carbon* atom from the mean plane of the five carbon atoms is 0.006 Å for cyclopentadienyl group 1. The largest displacement of a *hydrogen* atom from this plane is 0.11 Å (H1–5), the displacement from the mean plane being towards the TiS_5 moiety. All other hydrogen displacements are less than 0.06 Å. The displacement of H1–5 results in the short hydrogen–sulfur *intramolecular* contacts of 2.76 and 2.90 Å to S2 and S4, respectively. For the carbon atoms of this group the r.m.s. amplitudes of vibration for motion along the two shortest of the three principal axes of the thermal ellipsoid are 0.15 ± 0.02 and 0.22 ± 0.02 Å. These values are not significantly larger than the amplitudes found for the sulfur atoms. The largest amplitude of vibration for each of the carbon atoms of cyclopentadienyl group 1 has an average value of 0.30 Å. An analysis of the motion of this group as a rigid body using the method of Schomaker and Trueblood³² indicates that there is a small degree of libration about the normal to the plane containing the rigid group. This libration has been estimated to correspond to an oscillation of approximately $\pm 5^\circ$ about the equilibrium position. A rigid body motion of approximately $8\text{--}16^\circ$ has been estimated by McCullough^{33,34} to result in an apparent shortening of the chlorine–oxygen bond of 0.04 Å for perchlorate groups.

Cyclopentadienyl ring 2 also has a strictly planar geometry. The largest deviation of a carbon atom from the mean plane is less than 0.002 Å while the largest deviation of a hydrogen atom from the mean plane of the five carbon atoms is 0.12 Å. The ten titanium–hydrogen intramolecular distances are all in the range 2.65 to 3.04 Å with the shortest distance involving H2–5. There is no indication that the hydrogen atoms of either ring are systematically displaced towards the titanium atom. This type of displacement has been observed in $(\text{C}_5\text{H}_5)\text{CuP}(\text{C}_6\text{H}_5)_3$ ³⁵ whose structure has been carefully determined with the intent of studying the geometry of the five-membered ring. This copper complex has a planar pentagonal carbon ring with an average carbon–carbon bond length of 1.399(4) Å. In $(\text{C}_5\text{H}_5)_2\text{TiS}_5$ there is a variation in the carbon–carbon bond lengths in cyclopentadienyl group 2. The distances C2–1...C2–5, C2–1...C2–2, and C2–2...C2–3 are 1.33(1), 1.31(1), and 1.32(1) Å, respectively, while the distances C2–4...C2–5 and C2–3...C2–4 are 1.39(1) and 1.39(1) Å, respectively. The non-parallel disposition of the two cyclopentadienyl rings and their orientation (they are neither staggered or eclipsed but approximately midway between these configurations) is such that C2–4 has the closest contact of a carbon atom of ring 2 to atoms of ring 1. The distances C2–4...C1–2 and C2–4...C1–3 are 3.16 and 3.00 Å, respectively. These carbon–carbon distances and the C2–3...C1–2 distance of 3.12 Å are the shortest inter-ring distances within the molecule which do not involve hydrogen atoms. The Van der Waals contacts for carbon atoms are estimated to be 3.14 and 2.94 Å for sp^3 and sp^2 hybridized atoms³⁵. These distances suggest the possibility of a bonding overlap of the π -densities of the two rings and may account for the longer C–C bond lengths between C2–4 and C2–3 and C2–5. Cyclopentadienyl ring 2, however, is subject to a considerable degree of libration. Although the typical r.m.s. amplitudes of

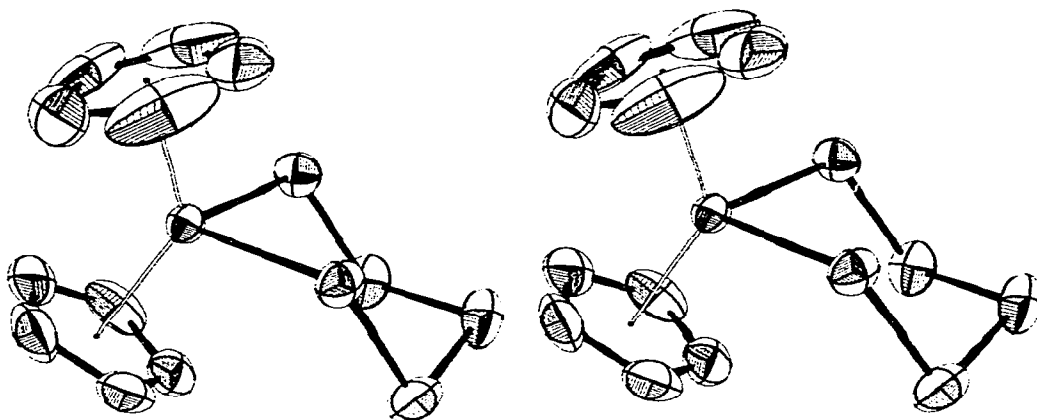


Fig. 2. Thermal motion in $(C_5H_5)_2TiS_5$. The surfaces correspond to 50% probability envelopes.

vibration along the two shortest principal axes of the thermal ellipsoids are 0.17 ± 0.02 Å and 0.23 ± 0.02 Å, the largest amplitude is typically 0.43 Å. The principal axis of the thermal ellipsoid which corresponds to this large amplitude is essentially in the plane of the cyclopentadienyl ring. The thermal motion of the molecule can be seen in Fig. 2. An analysis of this libration³² indicates that the ring undergoes oscillations of approximately $\pm 20^\circ$ about the equilibrium configuration.

The two cyclopentadienyl rings are asymmetrically disposed with respect to the TiS_5 fragment. For the $(C_5H_5)_2Ti(SC_6H_5)_2$ ¹⁵ and $(C_5H_5)_2Mo(S_2C_7H_6)$ (3,4-toluenedithiolate)¹⁸ molecules the sulfur-metal-sulfur plane is the approximate bisector of the (centroid)-metal-(centroid) angle which is typically 132° . In $(C_5H_5)_2TiS_5$ the rings are disposed such that this angle is essentially preserved. However, the normal to the sulfur-titanium-sulfur plane makes an angle of 17° with respect to the

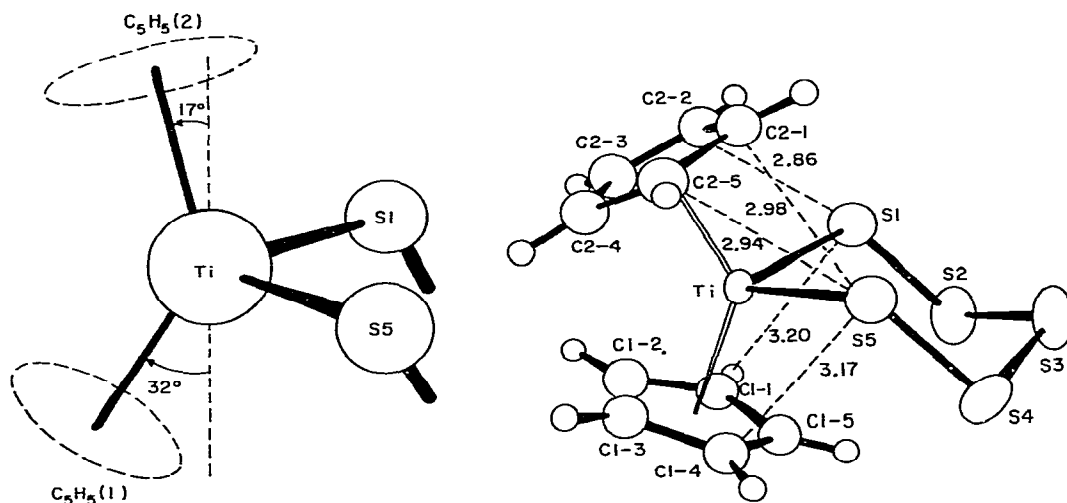


Fig. 3. The coordination geometry about the titanium atom.

Fig. 4. Intramolecular sulfur-carbon contacts which are less than the sum of Van der Waals radii for these atoms (3.20 Å).

titanium–(ring 2 centroid) vector while the angle with respect to the titanium–(ring 1 centroid) vector is 32° . This geometry is illustrated in Fig. 3. Presumably repulsions between ring 1 and the sulfur chain are responsible for this orientation as well as bonding interactions between atoms in ring 2 and various sulfur atoms (*vide supra*). Intramolecular sulfur–carbon contacts which are less than the sum of Van der Waals radii (3.20 \AA)³⁶ for these atoms are illustrated in Fig. 4. These intramolecular contacts do not serve to explain the difference in the thermal models for the two cyclopentadienyl rings. The sulfur–carbon contacts between atoms of ring 2 and the sulfur chain [*i.e.*, C2–5...S5 (2.94 \AA), C2–2...S1 (2.86 \AA), and C2–1...S5 (2.98 \AA)] are essentially the same as found in the constrained $(C_5H_5)_2MoS_2C_7H_6$ ¹⁸.

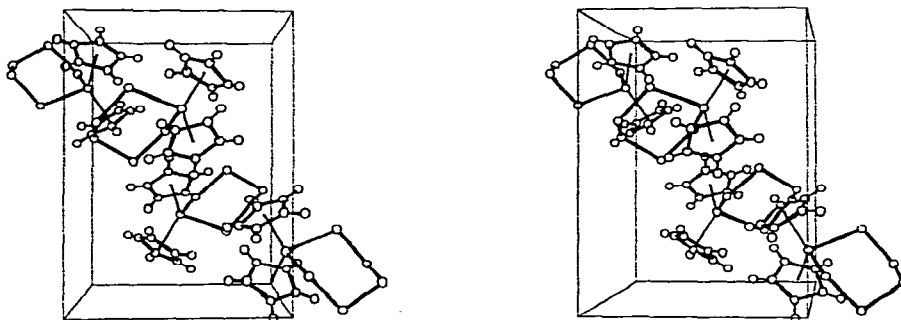


Fig. 5. The packing of the molecules in the monoclinic unit cell.

The packing of the molecules in the unit cell is shown in Fig. 5. The intermolecular contacts are less important than intramolecular contacts. The shortest intermolecular distances which do not involve hydrogens exclusively are between hydrogen and sulfur atoms. These distances are no shorter than 2.93 \AA while there are five *intramolecular* hydrogen–sulfur distances considerably less than 2.90 \AA . The shortest of these distances are S1...H2–2 (2.58 \AA) and S5...H2–5 (2.73 \AA). The geometry of this molecule appears to be dominated by sizable intramolecular interactions.

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REFERENCES

- 1 K. A. HOFMAN AND F. HÖCHTLEN, *Ber. Deut. Chem. Ges.*, 36 (1903) 3090.
- 2 P. E. JONES AND L. KATZ, *Acta Crystallogr. Sect. B*, 25 (1969) 745.
- 3 H. KÖPF AND B. BLOCK, in M. CAIS (Ed.), *Progress in Coordination Chemistry*, Elsevier, Amsterdam, 1968, p. 337.
- 4 H. KÖPF, B. BLOCK AND M. SCHMIDT, *Chem. Ber.*, 101 (1968) 272.
- 5 *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1967, p. 162.
- 6 P. W. R. CORFIELD, R. J. DOEDENS AND J. A. IBERS, *Inorg. Chem.*, 6 (1967) 197.

- 7 P. J. WHEATLEY, in J. D. DUNITZ AND J. A. IBERS (Eds.), *Perspectives in Structural Chemistry*, Vol. I, Wiley, New York, 1967, p. 1.
- 8 D. T. CROMER, *International Tables for X-Ray Crystallography*, new edition to be published.
- 9 Ref. 5, p.215.
- 10 W. R. BUSING, K. O. MARTIN AND H. LEVY, "ORFLS", *A Fortran Crystallographic Least Squares Program*, ORNL-TM-305, Oak Ridge National Laboratory, 1962.
- 11 W. R. BUSING, K. O. MARTIN AND H. LEVY, "ORFFE", *A Fortran Crystallographic Function and Error Program*, ORNL-TM-306, Oak Ridge National Laboratory, 1962.
- 12 S. F. WATKINS, Ph.D. Thesis, University of Wisconsin, 1967.
- 13 D. L. SMITH, Ph.D. Thesis, University of Wisconsin, 1962.
- 14 C. K. JOHNSON, "ORTEP", *A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-3794-Revised, Oak Ridge National Laboratory, 1965.
- 15 S. F. WATKINS AND L. F. DAHL, to be published.
- 16 G. NATTA, P. CORRADINI AND I. W. BASSI, *J. Amer. Chem. Soc.*, 80 (1958) 755.
- 17 F. A. COTTON, *J. Amer. Chem. Soc.*, 90 (1968) 6230.
- 18 J. R. KNOX AND C. K. PROUT, *Acta Crystallogr., Sect. B*, 25 (1969) 2013; see also ref. 7 for other examples.
- 19 M. J. BENNETT AND R. MASON, *Proc. Chem. Soc. (London)*, (1963) 273.
- 20 R. J. DOEDENS AND L. F. DAHL, *J. Amer. Chem. Soc.*, 87 (1965) 2576.
- 21 E. WEISS AND E. O. FISCHER, *Z. Anorg. Allg. Chem.*, 278 (1955) 219.
- 22 G. ENGBRETSON AND R. E. RUNDLE, *J. Amer. Chem. Soc.*, 85 (1963) 481.
- 23 L. D. VAN DER HELM, A. E. LESSOR AND L. L. MERRITT, JR., *Acta Crystallogr.*, 13 (1960) 1050.
- 24 H. HAHN AND B. HARDER, *Z. Anorg. Allg. Chem.*, 288 (1956) 241.
- 25 A. D. WADSLEY, *Acta Crystallogr.*, 10 (1957) 715.
- 26 C. J. BALLHAUSEN AND J. P. DAHL, *Acta Chem. Scand.*, 15 (1961) 1333.
- 27 A. E. SMITH, G. N. SCHRAUZER, V. P. MAYWEG AND W. HEINRICH, *J. Amer. Chem. Soc.*, 87 (1965) 5798.
- 28 S. C. ABRAHAMS AND J. L. BERNSTEIN, *Acta Crystallogr., Sect. B*, 25 (1969) 2365.
- 29 J. DONOHUE, in B. MEYER (Ed.), *Elemental Sulfur*, Interscience Publishers, New York, 1965, chapter 2.
- 30 S. C. ABRAHAMS AND E. GRISON, *Acta Crystallogr.*, 6 (1953) 206.
- 31 O. FOSS, in H. J. EMELEUS AND A. G. SHARPE (Eds.), *Advances in Inorganic Chemistry and Radiochemistry*, Vol. II, Academic Press, New York, 1960, p. 237.
- 32 V. SCHOMAKER AND K. N. TRUEBLOOD, *Acta Crystallogr., Sect. B*, 24 (1968) 63.
- 33 J. D. McCULLOUGH, *Acta Crystallogr., Sect. B*, 17 (1964) 1067.
- 34 C. L. COLTER, P. K. GANTZEL AND J. D. McCULLOUGH, *Acta Crystallogr., Sect. B*, 16 (1963) 676.
- 35 F. A. COTTON AND J. TAKATS, *J. Amer. Chem. Soc.*, 92 (1970) 2353.
- 36 L. PAULING, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, pp. 224, 263.

J. Organometal. Chem., 26 (1971) 229-245