Dilute Single-Crystal Electron Paramagnetic Resonance Study of Bis(cyclopentadienyl)vanadium Pentasulfide, $V(\eta^5\text{-}C_5H_5)_2S_5$. The Coup de Grace to the Ballhausen–Dahl Bonding Model Applied to $M(\eta^5\text{-}C_5H_5)_2L_2$-Type Complexes[1]

Jeffrey L. Petersen and Lawrence F. Dahl*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received February 24, 1975

Abstract: A dilute single-crystal EPR investigation of $V(\eta^5\text{-}C_5H_5)_2S_5$ doped in the crystal lattice of the diamagnetic $Ti(\eta^5\text{-}C_5H_5)_2S_5$ host has provided the first *quantitative* determination of the *relative* metal orbital character and the directional properties of the unpaired electron in a V(IV) $V(\eta^5\text{-}C_5H_5)_2L_2$ complex. Based upon the principal orthogonal coordinate system of the hyperfine coupling tensor being oriented within experimental error with respect to the pseudo-C_{2v} geometry of the $V(\eta^5\text{-}C_5H_5)_2S_2$ fragment such that the x axis lies along the S–V–S bisector with the y axis perpendicular to the VS_2 plane and the z axis perpendicular to the plane bisecting the VS_2 part, a detailed analysis of the anisotropy of the hyperfine interaction of the unpaired electron with the ^{51}V nucleus shows clearly that the unpaired electron resides primarily on the vanadium atom in an a_1-type MO mainly composed of $3d_{z^2}$ with a small but significant amount of $3d_{x^2-y^2}$ and virtually no 4s character. These EPR results thereby provide convincing evidence that the widely utilized Ballhausen–Dahl (qualitative) model is not valid for d^1 and d^2 M(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$ compounds and additionally indicate that the subsequent alternative Alcock (qualitative) model (which arbitrarily assumes the d^1 and d^2 electrons to occupy solely a d_{z^2} AO) is not an adequate representation of this MO. The directional properties of the metal components of the MO are compatible with the observed decrease in the L–M–L bond angle upon its occupation. The average principal values of the g tensor and hyperfine tensor for the two nonequivalent magnetic sites are $g_x = 1.9964$, $g_y = 1.9997$, and $g_z = 1.9689$ and $T_x = (-)66.6$ G, $T_y = (-)111.3$ G, and $T_z = (-)23.5$ G; these two tensors were determined to be noncoincident (presumably due at least in part to significant deviations of the vanadium molecule of crystallographic site symmetry C_1 from C_{2v} symmetry). The small spin-orbit coupling λ (estimated to be only 30 cm^{-1}) is in accord with the principal components of g not differing appreciably from the free-electron value. The calculated value of 93.2 G for P expectedly compares favorably with that between a V^0 and V^+ system.

Two qualitative representations have been proposed to represent the bonding in $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes. Based solely on NMR results[2] Ballhausen and Dahl[3] in 1961 formulated a (back-of-the-envelope) representation involving the use of hybrid metal orbitals to describe the bonding in protonated sandwich compounds. For $Mo(\eta^5\text{-}C_5H_5)_2H_2$ this model suggested that the d^2 Mo(IV) electrons are located in a sterically active orbital directed between the two metal-coordinated hydrogens. This B-D representation has been widely accepted[4] and generalized to other d^1 and d^2 M(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes containing nonhydridic L ligands. An alternative description which retains the basic hybrid orbital features of the B-D approach was proposed in 1967 by Alcock[5] on the basis of his concluding from an X-ray diffraction study of $Re(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5CH_3)(CH_3)_2$ that the acute H_3C–Re–CH_3 bond angle of 75.8 (1.3)° indicated the nonvalidity of the B-D model in its placement of an occupied orbital between the methyl ligands. Instead, Alcock[5] suggested with the rather bulky methyl groups that it is more satisfactory to have the lone pair in a metal orbital primarily directed normal to the plane bisecting the H_3C–Re–CH_3 bond angle. Alcock[5] also proposed that $Mo(\eta^5\text{-}C_5H_5)_2H_2$ might have an analogous electronic structure, although he pointed out that from repulsion considerations the smaller hydrogen atoms might make the B-D structure more stable. The major difference in these two bonding models lies in the directional character of this presumed sterically active "ninth" orbital which for $Mo(\eta^5\text{-}C_5H_5)_2H_2$ contains the d^2 electrons.

The outcome of the X-ray diffraction studies on several $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes (i.e., $M(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$ and $M(\eta^5\text{-}C_5H_5)_2S_5$ where M = Ti, V), carried out as operational tests of the B-D description, has been previously reported.[6-8] These results together with those obtained by Green, Prout, and coworkers[9] for second-row transition metals reveal that the L–M–L bond angle *decreases* in going from a d^0 (Ti, Zr) to a d^1 (V, Nb) to a d^2 (Mo) system. This opposite trend in the behavior of the L–M–L bond angles with that necessitated from electron-pair repulsion arguments via the B-D model was taken as strong evidence for its invalidity when applied to $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes. In addition, Green et al.[9a] concluded that their crystallographic data supported the Alcock model for $M(\eta^5\text{-}C_5H_5)_2L_2$ molecules; they also formulated a qualitative MO bonding description (incorporating features of both the B-D and Alcock models) for $M(\eta^5\text{-}C_5H_5)_2H_n$ (n = 1, 2, 3) and $(\eta^5\text{-}C_5H_5)_2M\text{-}(\mu_2\text{-}L)_2\text{-}M'L_n'$ systems. Although considerable structural data have been obtained for $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes, the metal orbital character and spatial arrangement of the "ninth" orbital in these complexes remained without any quantitative foundation. Both of the Ballhausen–Dahl and Alcock bonding schemes are based solely on the hybridization of the metal orbitals along specific directions to maximize overlap with the ligands.

The main objective of the work presented here was to ascertain the specific nature of the "ninth" metal orbital from dilute single-crystal EPR measurements conducted on an appropriate paramagentic d^1 V(IV) $V(\eta^5\text{-}C_5H_5)_2L_2$ molecule. In this particular paper,[10,11] we describe the results and interpretation of an EPR investigation of $V(\eta^5\text{-}C_5H_5)_2S_5$ (containing the bidentate S_5^{2-} ligand) doped in the crystal lattice of the diamagnetic host $Ti(\eta^5\text{-}C_5H_5)_2S_5$. A detailed analysis of the principal values and directions of the hyperfine coupling tensor (T), made possible from the

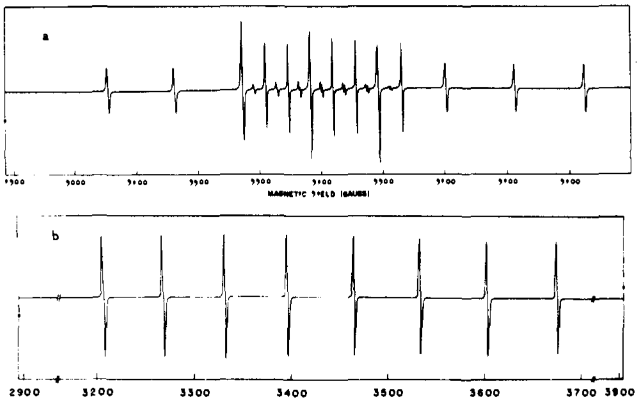

Figure 1. EPR spectra of $V(\eta^5\text{-}C_5H_5)_2S_5$ diluted in the crystal lattice of $Ti(\eta^5\text{-}C_5H_5)_2S_5$ with (a) the *a* axis perpendicular to the direction of the magnetic field, and (b) the *b* axis perpendicular to the direction of the magnetic field.

hyperfine interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$ for ^{51}V, 99.8%), has been utilized to extract the metal orbital character and directional properties of the MO containing the unpaired electron.

Experimental Section

In order to reduce effectively the exchange interaction between paramagnetic sites in a single-crystal EPR study, it is necessary to dilute the paramagnetic species into the crystal lattice of an isostructural diamagnetic host material. An appropriate pair of complexes for such an experiment is $V(\eta^5\text{-}C_5H_5)_2S_5$ and $Ti(\eta^5\text{-}C_5H_5)_2S_5$, which have been shown by X-ray diffraction[8,12] to possess nearly identical molecular structures.

Single crystals of ca. 0.2% $V(\eta^5\text{-}C_5H_5)_2S_5$ diluted in the crystal lattice of $Ti(\eta^5\text{-}C_5H_5)_2S_5$ were grown from a DMF solution by slow evaporation of the solvent. The EPR measurements were made on several of these deep-red crystals which were found from X-ray oscillation and Weissenberg photographs to possess monoclinic Laue symmetry $C_{2h}\text{-}2/m$ with $\beta = 93°$. From the X-ray photographs it was also determined that the lattice parameters of the doped crystals did not vary by more than 1% from those reported by Epstein, Bernal, and Köpf[12] for single crystals of monoclinic $Ti(\eta^5\text{-}C_5H_5)_2S_5$, which were also grown from a DMF solution.

These parallelepiped crystals were mounted with a water-soluble glue on the end of 0.5-mm Lindemann capillary tubes, which in turn were each glued to a larger 5-mm quartz tube that fit into the holder of a Varian single-crystal goniometer. The crystals were oriented along the *a*, *b*, and *c* crystallographic axes[13] to within 0.5°, 0.2°, and 2.0°, respectively. The doped crystals were placed individually in a Varian cylindrical microwave cavity between the pole faces of a Varian 15-in. rotating magnet such that the spindle axis of the goniometer was perpendicular to the direction of the magnetic field and the plane of rotation. The orientation of the crystal with respect to the magnetic field direction was changed by a counterclockwise rotation of the magnet. A 1000-G scan of 1-hr duration was obtained for every 10° rotation about each of the three crystallographic directions. For particular orientations where the two observed overlapping spectra (due to the two magnetically nonequivalent sites in the host lattice) were nearly equivalent, spectra were obtained at 5° intervals.

From symmetry considerations of the crystal structure of the host monoclinic $Ti(\eta^5\text{-}C_5H_5)_2S_5$ lattice, two magnetically nonequivalent orientations of the $V(\eta^5\text{-}C_5H_5)_2S_5$ molecules are present. Two overlapping eight-line spectra were observed except when the *b* axis was perpendicular to or parallel with the direction of the magnetic field. For each of these particular orientations only one eight-line spectrum was observed. Figure 1 shows two representative EPR spectra obtained for the dilute single-crystals of $V(\eta^5\text{-}C_5H_5)_2S_5$; Figure 1a shows the presence of two overlapping eight-line spectra taken with the *a* axis perpendicular to the magnetic field, while Figure 1b has only one eight-line spectrum obtained with the *b* axis perpendicular to the direction of the magnetic field.

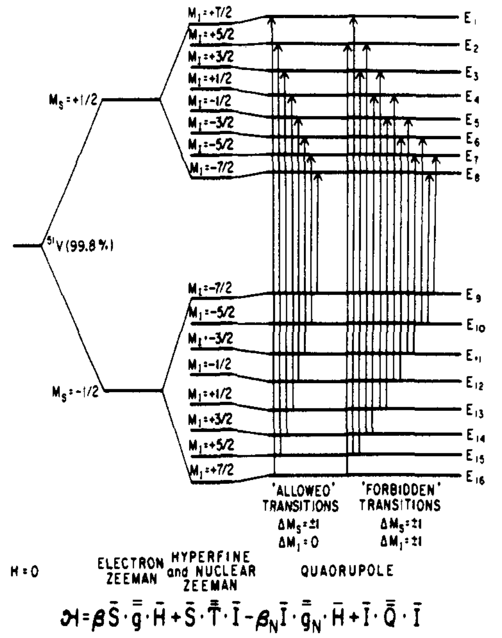

Figure 2. Energy-level diagrams of spin states $|m_sm_I\rangle$ for $S = 1/2$, $I = 7/2$.

A closer look at Figure 1a reveals that between the eight more intense "allowed" resonance lines there are seven pairs of weaker resonance lines which represent "forbidden" transitions. These 14 lines are a consequence of the anisotropic part of the hyperfine coupling interaction which provides a mechanism for the mixing of nuclear spin states.[14] This effect leads to transitions in the EPR spectra where both the electron and nuclear spin may change simultaneously (i.e., $\Delta m_s = \pm 1$, $\Delta m_I = \pm 1$). An examination of the spectra containing these weaker resonance lines shows that the spacing between two "forbidden" transitions comprising a "forbidden pair" increases slightly with the magnetic field strength. This variation has been used to estimate the magnitude of the nuclear quadrupole interaction.[15] For nuclei such as ^{51}V where the nuclear spin quantum number $I > 1/2$, a nuclear quadrupole interaction described by $I{\cdot}\mathbf{Q}{\cdot}I$ is possible. However, since the variation in spacing between pairs of "forbidden" lines ranges from ca. 1 to 3 G, the quadrupole interaction for $V(\eta^5\text{-}C_5H_5)_2S_5$ is reasonably small (estimated to be ca. $|Q| = 0.1\text{-}0.2$ G). Figure 2 represents the energy-level diagram for a $S = 1/2$, $I = 7/2$ system and illustrates the origin of the eight "allowed" transitions and the 14 "forbidden" transitions. Compared to the electron Zeeman and hyperfine interactions, the nuclear Zeeman and nuclear quadrupole terms are several orders of magnitude smaller for $V(\eta^5\text{-}C_5H_5)_2S_5$.

Data Analysis

The initial *g* value for each spectrum was calculated from the average of the magnetic fields of the eight hyperfine lines, H_{av}, from the relationship $g_{av} = h\nu/\beta H_{av}$. Since second-order effects make the smallest contributions to the two inner-most hyperfine lines, the experimental hyperfine splitting value for each $V(\eta^5\text{-}C_5H_5)_2S_5$ spectrum was calculated from the difference between the magnetic field strengths for these two hyperfine lines. Least-square fits to the experimental data were made with a three-parameter equation

$$y_i = P\cos^2\theta_i + Q\sin^2\theta_i - 2R\sin\theta_i\cos\theta_i$$

where $y_i = g^2$ or g^2T^2 and θ_i is the angle of rotation. From the "best" values of *P*, *Q*, and *R* obtained for the three (nearly) orthogonal sets of crystal orientations, the matrix elements of the g^2 and $K^2 = g^2T^2$ matrices were determined.[16] The g^2 matrix was diagonalized to obtain the principal directions and principal components of the g tensor.

$$\Lambda_g{}^2 = \tilde{C}_g g^2 C_g$$

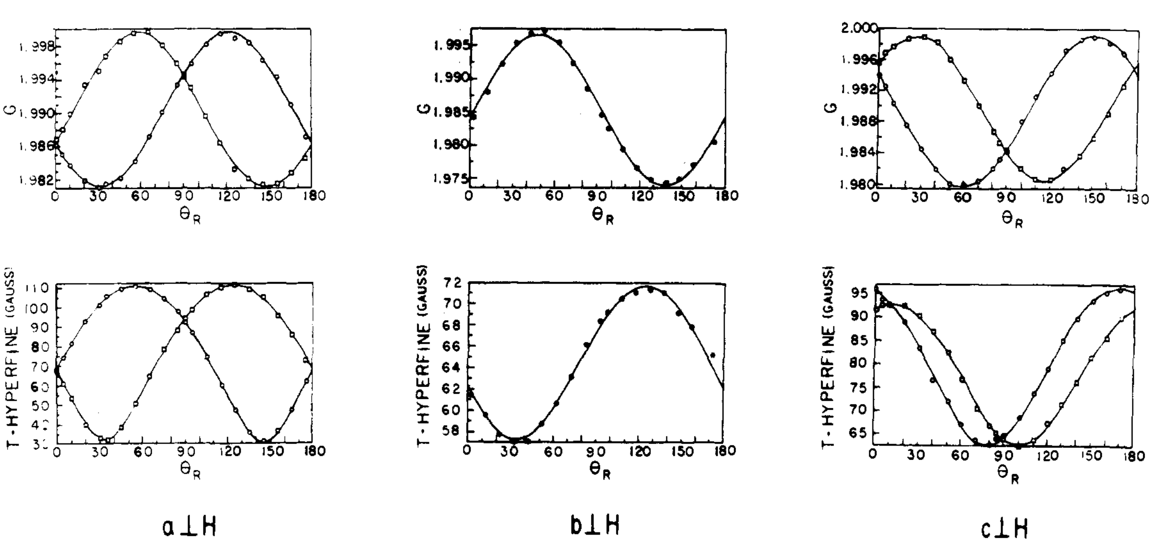

Figure 3. Plots of experimental g values and hyperfine coupling constants, T, vs. the angle of rotation, θ_R, for the three nearly orthogonal sets[13] of EPR data obtained for $V(\eta^5\text{-}C_5H_5)_2S_5$ diluted in the crystal lattice of $Ti(\eta^5\text{-}C_5H_5)_2S_5$. The solid lines represent the best fit of the experimental data (open symbols) to a three-parameter equation, $P \cos^2 \theta_i + Q \sin^2 \theta_i - 2R \sin \theta_i \cos \theta_i$.

The diagonal elements of Λ_g, which are the principal values of $\mathbf{g}$, are simply the square roots of the diagonal elements of the $\Lambda_g{}^2$ matrix. All of the diagonal elements of Λ_g were assumed to be positive. The inverse of g was then determined and used to calculate the T^2 matrix from the relationship, $T^2 = g^{-1}K^2g^{-1}$. The T^2 matrix was then diagonalized to determine the principal values and directions of T.

$$\Lambda_{T}{}^2 = \tilde{C}_T T^2 C_T$$

Since the diagonal elements of Λ_T are equal to the square roots of the diagonal elements of $\Lambda_T{}^2$, the principal values of T are known to within a sign. The orientations of the principal axes of $\mathbf{g}$ and T with respect to the laboratory-fixed crystallographic axial system were extracted from the transformation matrices C_g and C_T, respectively, and reexpressed in terms of the Eulerian angles Φ, θ, and Ψ.[17] A second-order correction to the initial g values was performed for each spectrum. For the spin Hamiltonian $\mathcal{H} = \beta S\cdot g\cdot H + S\cdot T\cdot I$, which contains the two principal magnetic interactions observed for $V(\eta^5\text{-}C_5H_5)_2S_5$, the energies through second-order have been found by the solution for the eigenvalues of $\mathcal{H}$ via the usual perturbation theory techniques. Weil et al.[18] have derived the following expression for the "allowed" transition energies for a $S = ½$, $I = n/2$ system.

$$h\nu = E(1/2, m_1) - E(-1/2, m_1) =$$

$$g\beta H + (t_{33})^{1/2}m_1 + \frac{1}{2g\beta H}\left\{ \left[Trt - \left(\sum_{i=1}^{3} t_{3i}{}^2 / t_{33} \right) \right] \times \right.$$

$$\left. [(I(I+1) - m_1{}^2)/2] + [(t_{31}{}^2 + t_{32}{}^2)/t_{33}]\, m_1{}^2 \right\}$$

where $\mathbf{t} = \mathrm{T}^2$. If C is set equal to the contents in brackets, the resulting quadratic expression in g can be obtained.

$$0 = g^2 + ((t_{33})^{1/2}m_1 - \nu)(h/\beta H)g + 1/2(h/\beta H)^2C$$

From the components of T at the appropriate crystal orientation and the values of the corresponding experimental hyperfine line positions, a set of eight g values was computed for each spectrum. The final g value was designated as the average of the corrected g values calculated for the two inner-most hyperfine lines. The previously described (least-squares fit)-routine was then repeated. The final components of the g^2 and the K^2 matrices for both molecules of $V(\eta^5\text{-}C_5H_5)_2S_5$ are listed in Table I. The results of the least-squares fits of the EPR data are illustrated in Figure 3, which presents plots of g_{exptl} vs. θ_R and T_{exptl} vs. θ_R.

Table I. Final Analysis of Single-Crystal EPR Data Obtained for the Two Magnetically Nonequivalent $V(\eta^5\text{-}C_5H_5)_2S_5$ Molecules Doped in the Diamagnetic $Ti(\eta^5\text{-}C_5H_5)_2S_5$ Host[a]

	Molecule 1		Molecule 2	
	g^2	K^2	g^2	K^2
P_a	3.94562	17960.6	3.94543	18129.3
Q_a	3.97809	34821.4	3.97810	34813.1
R_a	0.0327681	−20887.7	−0.0326216	20654.0
σ_g	0.00032		0.00034	
σ_T	0.62		0.78	
P_b	3.93655	15231.1	3.93655	15231.0
Q_b	3.94565	17860.2	3.94565	17860.2
R_b	−0.0447060	3231.37	−0.0447060	3231.37
σ_g	0.00056		0.00056	
σ_T	0.45		0.45	
P_c	3.97719	36126.5	3.98135	33400.9
Q_c	3.93821	16180.3	3.93733	16126.1
R_c	0.0331762	4059.55	−0.029703	−3743.20
σ_g	0.00019		0.00022	
σ_T	0.30		0.32	
g_x	1.9965		1.9963	
g_y	1.9998		1.9999	
g_z	1.9686		1.9691	
g_{av}	1.9883		1.9884	
ϕ	58.15		−59.47	
θ	51.81		128.97	
ψ	−61.58		125.83	
T_x	(−)66.7 G		(−)66.4 G	
T_y	(−)112.0 G		(−)110.7 G	
T_z	(−)23.6 G		(−)23.4 G	
T_{av}	(−)67.4 G		(−)66.8 G	
ϕ	33.04		−31.77	
θ	140.79		39.45	
ψ	28.81		207.12	

[a] The estimated standard deviations, σ_g and σ_T, were calculated from $\sigma_g = [\Sigma_{i=1}(g_{\text{calcd}} - g_{\text{exptl}})^2/(n-1)]^{1/2}$ and $\sigma_T = [\Sigma_{i=1}(T_{\text{calcd}} - T_{\text{exptl}})^2/(n-1)]^{1/2}$ for each least-squares curve with n observations.

Once the principal values and the orientation of the electron Zeeman and the hyperfine coupling tensors were determined, the theoretical magnetic field was computed for the hyperfine lines of each spectrum. This calculation was performed in order to check the correctness of the data-analysis procedure. Rather than performing an exact calculation which involves the diagonalization of a 16 × 16 matrix, a second-order perturbation treatment incorporating a partitioning technique[19] was utilized which requires the diagonalization of two 8 × 8 matrices. A comparison of the experimental line positions with those calculated by this sec-

Table II. Experimental g and T Tensors with Best-Fit Parameters (av) from the Single-Crystal EPR Study of $V(\eta^5\text{-}C_5H_5)_2S_5$ Doped in $Ti(\eta^5\text{-}C_5H_5)_2S_5$

g_x = 1.9964	ϕ = 59.05
g_y = 1.9997	θ = 51.50
g_z = 1.9689	ψ = −59.52
T_x = (−)66.6 G	ϕ = 32.41
T_y = (−)111.3 G	θ = 140.68
T_z = (−)23.5 G	ψ = 27.97
For a = −0.963 and b = 0.270, where $\lvert\psi_0\rangle = a\lvert d_{z^2}\rangle + b\lvert d_{x^2-y^2}\rangle$	
T_x = (−)66.6 G	P = 87.1 × 10^{-4} cm^{-1}
T_y = (−)111.3 G	$\langle r^{-3}\rangle$ = 1.86 au
T_z = (−)23.5 G	χ = −1.97
K = 61.5 × 10^{-4} cm^{-1}	λ = 30 cm^{-1}
per cent character of $3d_{z^2}$ to $3d_{x^2-y^2}$, a^2/b^2 = $(-0.963)^2/(0.270)^2$ = 12.7/1	

ond-order perturbation computation indicated agreement for most resonance lines for $V(\eta^5\text{-}C_5H_5)_2S_5$ to within 2 G for spectra collected about the a and b axes. Since this calculation was performed for orientations about three orthogonal directions, the discrepancies between the observed and calculated line positions were expectedly larger (as high as 15 G for some of the outermost hyperfine lines) for the spectra recorded about the c axis.[13]

Interpretation of the EPR Data

The experimental results obtained for $V(\eta^5\text{-}C_5H_5)_2S_5$, which have been averaged for the two magnetically nonequivalent sites, are presented in Table II. An examination of the Euler angles shows that the principal directions for **g** and T are *not* coincident, which is consistent with the observation that the dilute powder EPR spectra of $V(\eta^5\text{-}C_5H_5)_2S_5$ shown in Figure 4 could not be simulated[20a,b] from a second-order expression[20c] derived with the assumption of their coincidence. For molecules of low symmetry (i.e., less than twofold or mirror symmetry about the paramagnetic site), the principal axial systems for **g** and T are generally quite different.[21] The dipolar hyperfine nteraction is a *magnetic* dipolar interaction between the ^{51}V nucleus and the total unpaired electron distribution. The **g** tensor reflects a changing electron magnetic moment due to changing orbital angular momentum which in turn is determined by the surrounding *electrical* charge distribution. While the anisotropic ^{51}V hyperfine interaction is determined only by the unpaired electron distribution, the **g** tensor is influenced by the total electron distribution. Hence, an asymmetric ligand environment may have a pronounced effect on the principal components and directions of **g**, and therefore the noncoincidence of the **g** and T tensors in $V(\eta^5\text{-}C_5H_5)_2S_5$ is presumed to be at least partially a consequence of the significant deviation of the molecule (of crystallographic site symmetry C_1-1) from C_2-2 or C_s-m symmetry.

The interpretation of the EPR data for $V(\eta^5\text{-}C_5H_5)_2S_5$ is considerably complicated by the noncoincidence of **g** and T. However, since the spin density of the unpaired electron is located primarily on the vanadium atom (as previously indicated from the solution EPR spectra[22] of a number of $V(\eta^5\text{-}C_5H_5)_2L_2$ complexes), the information of prime importance—viz., the metal orbital character—can be extracted from the anisotropy in the hyperfine coupling components. Consequently, our interpretation focuses mainly on the principal values of T.

The orientation of the principal directions of the hyperfine tensor with respect to the $V(\eta^5\text{-}C_5H_5)_2S_2$ fragment in $V(\eta^5\text{-}C_5H_5)_2S_5$ is shown in Figure 5. Within experimental error T_x lies along the S–V–S bisector, T_y is perpendicular to the VS_2 plane, and T_z is normal to the plane which bisects the S–V–S angle. This principal axial system for T is compatible with an idealized C_{2v}-$2mm$ geometry for the $V(\eta^5\text{-}C_5H_5)_2S_2$ moiety. From energetic considerations the d orbitals of the vanadium are expected to make the dominant contributions to the metal character of the unpaired electron. Hence, we concluded that the anisotropic nature of the hyperfine coupling interaction must be the consequence of the admixture of two or more d orbitals into the electronic ground state. Under C_{2v} symmetry the a_1 irreducible representation is the only one which contains more

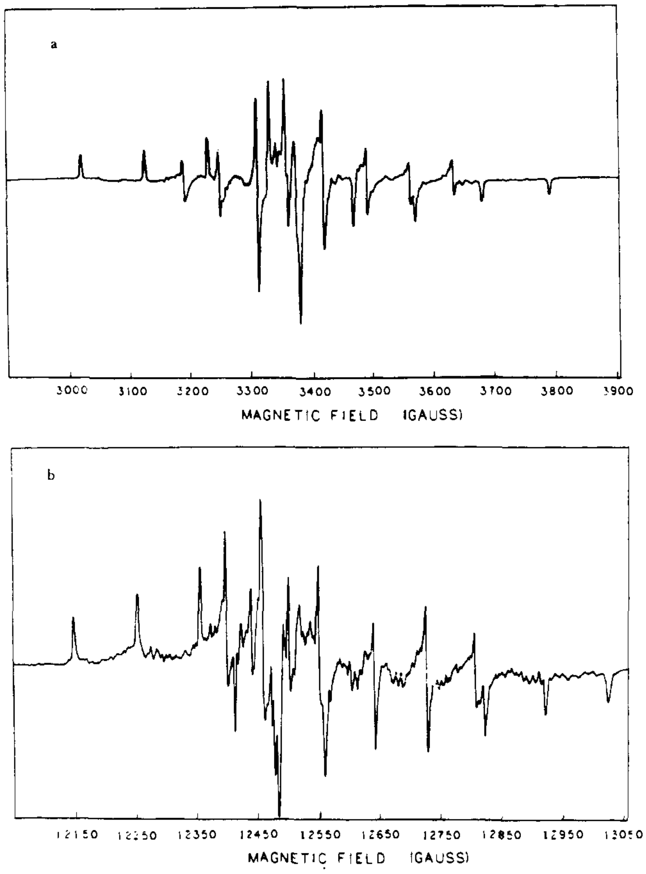

Figure 4. Powder EPR spectra of $V(\eta^5\text{-}C_5H_5)_2S_5$ diluted in $Ti(\eta^5\text{-}C_5H_5)_2S_5$ recorded at room temperature: (a) X-band, ν_0 = 9.5216 GHz; and (b) Q-band, ν_0 = 35.010 GHz.

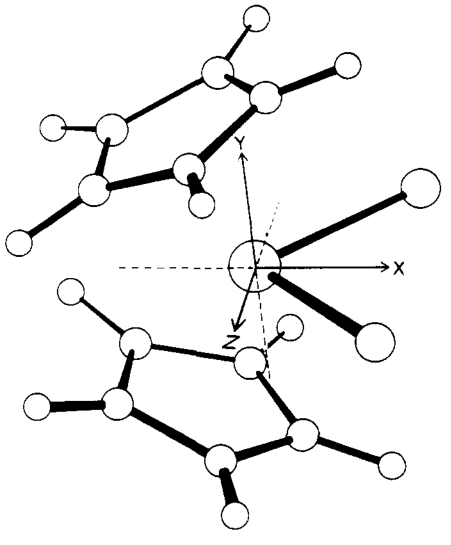

Figure 5. Orientation of the principal axes of the hyperfine coupling tensor with respect to the idealized C_{2v} geometry of the $V(\eta^5\text{-}C_5H_5)_2S_2$ fragment of the $V(\eta^5\text{-}C_5H_5)_2S_5$ molecule.

than one d orbital of the same character (viz., the d_{z^2} and the $d_{x^2-y^2}$) in addition to the s and p_x AO's. On the basis of the computed χ value[23] of -1.97 which is nearly identical with that of -2.08 reported[24] for $V(\eta^5\text{-}C_5H_5)_2Cl_2$, we concur that the direct 4s vanadium contribution to the MO containing the unpaired electron must be sufficiently small to be neglected.[24] The omission of both the $4p_x$ and 4s AO's as primary contributors to the metal orbital character of the unpaired electron is completely consistent with our molecular orbital calculations[11,25] on several d^1 V(IV) molecules via the Fenske–Hall model which shows that for these molecules the vanadium 4s and 4p character is $\leq 0.02\%$ and $\leq 1.0\%$, respectively. Hence, from an assumed ligand-field model (by which the electron is assumed to be localized completely on the vanadium), the electronic ground state is represented by

$$|\Psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$$

with a and b the mixing coefficients. Although the ligand-field model assumes the principal axes of **g** and **T** are coincident, this approach can still be used to calculate the *relative* metal orbital character of the d_{z^2} and $d_{x^2-y^2}$ AO's in the MO. From the application of second-order perturbation theory, the relationships given in Table III for the principal components of **g** and **T** have been derived[26] in terms of a and b. The expressions for the principal components of **g** are generated from the relationship

$$g_i = g_0 - 2\lambda \sum_{n=1}^{3} \frac{\langle\psi_0|l_i|\psi_n\rangle\langle\psi_n|l_i|\psi_0\rangle}{E_n - E_0}$$

where $i = x, y, z$, and λ is the spin–orbit coupling constant for vanadium. The three excited states, ψ_1, ψ_2, and ψ_3, represent the individual atomic d orbitals, d_{yz}, d_{xz}, and d_{xy}, respectively, which have not been included in the electronic ground-state wave function. The dipolar contributions to the anisotropic part of the hyperfine coupling components are derived with the operator

$$\alpha_i = 1/7(4s_i - (l_is_i + 1/2(l_+s_- + l_-s_+))l_i - l_i(l_is_i + 1/2(l_+s_- + l_-s_+))$$

where $i = x, y, z, +,$ or $-$. The matrix element for α_z and α_- can be found elsewhere.[27]

From an inspection of the analytical expressions for the hyperfine coupling components in Table III, the second-order contributions to the anisotropic part (i.e., α_i's) are of the order $g_0 - g_i$ and $\lambda/\Delta E_{ij}$. For systems in which g is ca. 2 and the spin–orbit coupling is small ($\lambda < 100$ cm^{-1}), which is certainly the situation here, these two terms are negligible in comparison to the remaining ones. This fact is especially important with regard to the interpretation of the hyperfine coupling data for $V(\eta^5\text{-}C_5H_5)_2S_5$ in that the values of $\lambda/\Delta E_{ij}$ cannot be accurately determined due to the noncoincidence of **g** and **T**. Hence, the errors introduced by these second-order terms do not appreciably affect the "best" values calculated for the a and b mixing coefficients.

Table III. Derived Expressions for the Calculation of *T* and Best-Fit Parameters

$$\text{ground state: } |\Psi_0\rangle = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$$

$$g_x = g_0 - \frac{2\lambda(a\sqrt{3}+b)^2}{\Delta E_{yz}} \quad g_y = g_0 - \frac{2\lambda(a\sqrt{3}-b)^2}{\Delta E_{xz}} \quad g_z = g_0 - \frac{8\lambda b^2}{\Delta E_{xy}}$$

$$T_x = -K + P[\alpha_x - (g_0 - g_x)]$$
$$T_y = -K + P[\alpha_y - (g_0 - g_y)]$$
$$T_z = -K + P[\alpha_z - (g_0 - g_z)]$$

where

$$\alpha_x = -\frac{2}{7}(a^2 - b^2) - \frac{4\sqrt{3}}{7}ab(1 - \frac{\lambda}{\Delta E_{xy}}) - \frac{\sqrt{3}}{14}\frac{(a + b\sqrt{3})}{(a\sqrt{3} - b)}(g_0 - g_y)$$

$$\alpha_y = -\frac{2}{7}(a^2 - b^2) + \frac{4\sqrt{3}}{7}ab(1 - \frac{\lambda}{\Delta E_{xy}}) - \frac{\sqrt{3}}{14}\frac{(a - b\sqrt{3})}{(a\sqrt{3} + b)}(g_0 - g_x)$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{\sqrt{3}}{14}\left[\frac{a + b\sqrt{3}}{a\sqrt{3} - b}(g_0 - g_y) + \frac{a - b\sqrt{3}}{a\sqrt{3} + b}(g_0 - g_x)\right]$$

$$P = g_0 g_n{}^{51}\beta\beta_n\langle r^{-3}\rangle$$

$$K = -g_0 g_n{}^{51}\beta\beta_n\frac{2}{3}\chi$$

Discussion of the EPR Results

The analysis of the principal values and directions of the hyperfine coupling interaction for $V(\eta^5\text{-}C_5H_5)_2S_5$ doped in a single crystal of $Ti(\eta^5\text{-}C_5H_5)_2S_5$ has provided a *quantitative* determination of the *relative* metal orbital character of the unpaired electron. From the unique set of coefficients for a and b, which have been evaluated for $V(\eta^5\text{-}C_5H_5)_2S_5$ from the expressions given in Table III (such that the calculated and observed principal components of **T** are in agreement), it is apparent that the unpaired electron primarily resides on the vanadium atom in an a_1-type molecular orbital composed of essentially $3d_{z^2}$ with a small amount of $3d_{x^2-y^2}$ character (i.e., with respect to a right-handed Cartesian coordinate system for which z is directed normal to the plane which bisects the VS_2 bond angle and x lies along the line of intersection of this plane with the plane containing the VS_2 fragment). Although the contributions from these two d orbitals are drastically different (as illustrated by the ratio of the per cent character of $3d_{z^2}$ to $3d_{x^2-y^2}$, $a^2/b^2 = (-0.963)^2/(0.270)^2 = 12.7$ to 1), the values for the calculated coefficients a and b are dependent on the axial labeling scheme for the reference coordinate system. To demonstrate this point the coefficients obtained for $V(\eta^5\text{-}C_5H_5)_2S_5$ were transformed to a right-handed Cartesian coordinate system which simply differs from that found for the principal directions of **T** by a permutation of axial labels (i.e., x becomes z', y becomes x', and z becomes y'). The necessary transformation for the d_{z^2} and $d_{x^2-y^2}$ AO's is $d_{z'^2} = -0.500d_{z^2} + 0.866d_{x^2-y^2}$ and $d_{x'^2-y'^2} = -0.866d_{z^2} - 0.500d_{x^2-y^2}$. The mixing coefficients, a' and b', for the (x', y', z') system are $a' = 0.715$ and $b' = 0.699$ compared to $a = -0.963$ and $b = 0.270$ for the (x, y, z) system, indicating that in the (x', y', z') system the anisotropy observed for the **T** tensor results from nearly equal contributions of the $d_{z'^2}$ and $d_{x'^2-y'^2}$ AO's. Consequently, an interpretation based entirely on the calculated mixing coefficients without reference to a particular axial system can be misleading. The directional properties of the metal components of $|\Psi_0\rangle$ and its electron density, however, are rotationally invariant properties and thus identical in either the (x, y, z) or (x', y', z') system. The metal orbital character of the unpaired electron in $V(\eta^5\text{-}C_5H_5)_2S_5$ indicates that the electron density on the metal is directed primarily normal to the plane that bisects the S–V–S bond angle. The actual spatial distribution of the unpaired electron is strongly dependent on the signs of the mixing coefficients. For $|\Psi_0\rangle = -0.963|d_{z^2}\rangle + 0.270|d_{x^2-y^2}\rangle$ the small positive contribution from the $d_{x^2-y^2}$ orbital represents an increase in the amount of electron density within the S–V–S bond angle and a corresponding decrease normal to the VS_2 plane over that for a pure d_{z^2} orbital, which indicates that the unpaired electron is localized essentially in the VS_2 plane. Although the electron density within the S–V–S bond angle (i.e., along the x direction) is by no means negligible, it is significantly smaller in magnitude than that along the z direction. The directional properties of the metal components in the MO containing the unpaired electron are completely compatible from electron repulsion arguments with the observed decrease in the L-M-L bond angle for $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes upon its occupation.[6-9]

In order to make a reasonable comparison of the metal orbital character of the unpaired electron in $V(\eta^5\text{-}C_5H_5)_2S_5$ (as calculated from the anisotropy in the hyperfine coupling interaction) with that proposed by the Ballhausen-Dahl[3] and the Alcock[4] bonding models, their *arbitrarily chosen* wave functions representing the electronic ground state must be transformed to the same coordinate system. In terms of the (x, y, z) system, the Ballhausen-Dahl wave function,[3] which contains no d-orbital character, is of the form $a|4s\rangle + b|4p_x\rangle$, while the wave function[28] given by Alcock[4] for the orbital containing the unpaired electron reduces to a pure d_{z^2} orbital. The metal composition of the MO containing the unpaired electron is in complete contradiction to that proposed by Ballhausen and Dahl.[3] Not only does the B-D wave function fail to include any d-orbital character but also it incorrectly places the unpaired electron in an orbital directed between the two L ligands. Hence, the B-D model must be rejected on the basis of these EPR results as well as the previous X-ray diffraction data as a reasonable bonding description for M(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes. Our EPR results obtained for $V(\eta^5\text{-}C_5H_5)_2S_5$ also indicate that the Alcock model[4] is not an adequate representation of the bonding in $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes in that the determined spatial distribution of the unpaired electron contains a significant contribution from the $d_{x^2-y^2}$ orbital which increases the amount of electron density within the S-V-S angle over that predicted by the Alcock model.

In addition to the "best" values for the mixing coefficients, Table II contains the corresponding values[29] for the EPR parameters K, P, $\langle r^{-3}\rangle$, and χ. The calculated value of $(-)K$, the isotropic part which is due to spin polarization, of (−)65.8 G for $V(\eta^5\text{-}C_5H_5)_2S_5$ compares favorably with the solution EPR results[11] where $A_{\text{iso}} = (-)64.8$ G. Since the solution isotropic coupling constant, A_{iso}, is related to K for a d^1 system by the expression[23] $A_{\text{iso}} = -K + (g_{\text{iso}} - 2.0023)P$, the magnitudes of A_{iso} and K are essentially identical for $g_{\text{iso}} \approx 2$. From the solution EPR data, K equals 63.7 G for $V(\eta^5\text{-}C_5H_5)_2S_5$.

The calculated value of P for $V(\eta^5\text{-}C_5H_5)_2S_5$ of 93.2 G can be compared with the P values calculated with Hartree-Fock $\langle r^{-3}\rangle$ values for various electronic configurations of vanadium. The computed P values[23] are listed as follows: V^0 ($3d^5$), 85.7 G; V^+ ($3d^4$), 107 G (extrapolated); V^{2+} ($3d^3$), 128 G; V^{3+} ($3d^2$), 150 G; V^{4+} ($3d^1$), 172 G. It is apparent that the effective nuclear charge on the vanadium is between 0 and +1.

A negative value of χ for $V(\eta^5\text{-}C_5H_5)_2S_5$ is reasonable.[23,30] The parameter χ represents the polarization of the inner s electrons through an exchange interaction with the unpaired electron. The spin polarization phenomenon is accomplished by a mixing of excited states (which result when an inner s electron has been promoted into an empty s orbital) into the ground state. Since the d_{z^2}, $d_{x^2-y^2}$, and s AO's belong to the same irreducible representation a_1 under C_{2v}-$2mm$ symmetry, the two d orbitals may directly mix with an s orbital such as the 4s, which has a positive contribution to χ.[31] For V(IV) molecules a small admixture of 4s into the electronic ground state alters the value of χ by making it less negative. The χ value of −1.97 for $V(\eta^5\text{-}C_5H_5)_2S_5$ is slightly smaller than the χ value of −2.08 reported[24] for $V(\eta^5\text{-}C_5H_5)_2Cl_2$, which leads one to conclude that the amount of 4s orbital character contained in the electronic ground state is slightly greater for $V(\eta^5\text{-}C_5H_5)_2S_5$ than for $V(\eta^5\text{-}C_5H_5)_2Cl_2$. Nevertheless, the direct 4s orbital contribution to the MO containing the unpaired electron in either molecule is of the order of 1-2%.[24]

The spin-orbit coupling parameter, λ, for $V(\eta^5\text{-}C_5H_5)_2S_5$ can be estimated only in an indirect manner. The values of λ, which for vanadium complexes are reasonably small, have been computed[32] for various electronic configurations of vanadium. They are: V^0 ($3d^5$), 19 cm^{-1} (extrapolated); V^+ ($3d^4$), 34 cm^{-1}; V^{2+} ($3d^3$), 57 cm^{-1}; V^{3+} ($3d^2$), 106 cm^{-1}; V^{4+} ($3d^1$), 255 cm^{-1}. Although the noncoincidence of **g** and **T** prevents the expressions given in Table III for the principal components of **g** from being used to determine λ directly, a value of 30 cm^{-1} has been assigned on the basis of the computed P value. This relatively small value of λ for $V(\eta^5\text{-}C_5H_5)_2S_5$ is borne out by the fact that the principal components of **g** do not differ appreciably from the free-electron value.

Acknowledgments. We are pleased to acknowledge financial support of this research by the National Science Foundation (No. GP-19175X). We are most grateful to Professors John E. Harriman (University of Wisconsin, Madison) and John A. Weil (University of Saskatchewan) for helpful discussions. J.L.P. also wishes to thank the National Science Foundation for a predoctoral National Science Foundation Traineeship.

References and Notes

(1) (a) Presented in part at the 6th International Conference on Organometallic Chemistry, University of Massachusetts, Amherst, Mass., Aug 1973; (b) based in part on a dissertation submitted by J. L. Petersen to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, May 1974.

(2) M. L. H. Green, J. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(3) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

(4) N. W. Alcock, *J. Chem. Soc. A*, 2001 (1967).

(5) Cf. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966, p 766.

(6) (a) L. F. Dahl, Plenary Lecture, 4th International Conference on Organometallic Chemistry, Bristol, 1969; (b) E. G. Muller, Ph.D. Thesis, University of Wisconsin (Madison), 1970.

(7) E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organometal. Chem.*, in press.

(8) E. G. Muller, J. L. Petersen, and L. F. Dahl, *J. Organometal. Chem.*, in press.

(9) (a) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Comm.*, 421 (1972), and references cited therein; (b) M. L. H. Green, Sectional Lecture, 5th International Conference on Organometallic Chemistry, Moscow, 1971 (cf. *Pure Appl. Chem.*, **30**, 373 (1972)); (c) K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, **30**, 2290 (1974).

(10) A preliminary outline of this paper was communicated earlier.[11]

(11) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 2248 (1974).

(12) E. F. Epstein, I. Bernal, and H. Köpf, *J. Organomet. Chem.*, **26**, 229 (1971).

(13) Although the *a*, *b*, and *c* axes in a monoclinic system do not form an orthogonal coordinate system, the angular difference of only 3° realized by a mounting of a crystal along the c rather than the *c** direction (which is perpendicular to the *ab* plane) was not considered large enough to affect appreciably the results of the EPR experiment. The experimental values determined for *g* and *T* obtained from the spectra collected about the *c* axis are not expected to vary by more than 2–3% in relative magnitude from those collected about the *c** axis, since to a first approximation Δg^2 and ΔT^2 are functions of $\sin^2 \epsilon$ where ϵ represents the angular error in the crystal orientation.

(14) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford, 1970, p 186.

(15) D. M. Close and H. N. Rexroad, *J. Chem. Phys.*, **50**, 3717 (1969).

(16) H. A. Farach and C. P. Poole, Jr., *Adv. Magn. Reson.*, **5**, 229 (1971).

(17) H. Goldstein, "Classical Mechanics", Wiley, New York, N.Y., 1965, p 107. The Eulerian angles, Φ, θ, and Ψ, represent three successive angles of rotation which specify the orientation of the principal axial system of **g** and T relative to the fixed crystallographic system of the host lattice. The transformation is performed by a rotation of the initial axial system (a, b, c^*) by Φ about the c^* axis, by θ about the resultant a axis, and by Ψ about the resultant c^* axis, in that order. A positive angle corresponds to a counterclockwise rotation.

(18) J. A. Weil, G. L. Goodman, and H. G. Hecht, "Paramagnetic Resonance", Vol. 2, W. Low, Ed., Academic Press, New York, N.Y., 1963, p 880.

(19) Private communication with Professor J. E. Harriman, University of Wisconsin (Madison).

(20) (a) P. C. Taylor and P. J. Bray, "Lineshape Program Manual", Physics Department, Brown University, 1968 (unpublished); (b) P. C. Taylor and P. J. Bray, *J. Magn. Reson.*, **2**, 305 (1970); (c) P. C. Taylor, private communication to J.L.P., 1973; P. C. Taylor, J. F. Baugher, and H. M. Kriz, *Chem. Rev.*, **75**, 203 (1975).

(22) G. Doyle and R. S. Tobias, *Inorg. Chem.*, **7**, 2479 (1968). The ^{51}V isotropic hyperfine constants for $V(\eta^5\text{-}C_5H_5)_2L_2$ (L = Cl, SCN, SeCN, N_3, OCN, CN) complexes fall within the range 60–75 G.

(23) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

(24) D. P. Bakalik and R. G. Hayes, *Inorg. Chem.*, 11, 1734 (1972). The χ value of -2.08 was calculated from the isotropic coupling constant from the solution EPR spectrum of $V(\eta^5\text{-}C_5H_5)_2Cl_2$ rather than from single-crystal EPR data.

(25) J. L. Petersen, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6433 (1975).

(26) B. R. McGarvey in "Electron Spin Resonance of Metal Complexes", Teh Fu Yen, Ed., (Plenum Press, New York, N.Y., 1969); from the Symposium of ESR on Metal Chelates at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1968.

(27) J. S. Griffith, "The Theory of Transition Metal Ions", Cambridge, England, 1964 p 427.

(28) $|\Psi_0\rangle = -0.500d_{z^2} - 0.866d_{x^2-y^2}$ with respect to a left-handed coordinate system where the *z* axis is normal to the ML_2 plane.

(29) Previously reported values[11] of *K, P,* $\langle r^{-3}\rangle$, *and* χ are too large by ca. 7% due to the earlier use of an approximate conversion factor.

(30) Reference 14, p 706.

(31) Reference 14, p 399.

(32) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

Synthesis and Structural Characterization by X-Ray Diffraction and Electron Paramagnetic Resonance Single-Crystal Techniques of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. A Study of the Spatial Distribution of the Unpaired Electron in a $V(\eta^5\text{-}C_5H_5)_2L_2$-Type Complex[1]

Jeffrey L. Petersen and Lawrence F. Dahl*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received February 24, 1975

Abstract: The preparation of $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and subsequent characterization by single-crystal X-ray diffraction and EPR methods were performed in order to delineate more clearly the bonding description of the unpaired electron in a V(IV) $V(\eta^5\text{-}C_5H_5)_2L_2$ complex upon change of the L ligands. The results of this work not only have substantiated our earlier EPR study of $V(\eta^5\text{-}C_5H_5)_2S_5$ but also have contributed to a more general understanding of the nature of bonding in $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes. An EPR measurement of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ (of crystallographic C_2-2 symmetry per se) diluted in the crystal lattice of $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ (of crystallographic C_s-*m* site symmetry) has shown that the anisotropy in the ^{51}V hyperfine coupling interaction arises primarily from the significantly different vanadium orbital character of $3d_{z^2}$ and $3d_{x^2-y^2}$ AO's comprising the a_1-type MO containing the unpaired electron. The similarity between the EPR results for $V(\eta^5\text{-}C_5H_5)_2S_5$ and $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ supports the premise that the metal orbital characters of the unpaired electron are not strongly dependent on the nature of the L ligands. The *g* and hyperfine tensors in $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ (for which $g_x = 1.9802$, $g_y = 1.9695$, $g_z = 2.0013$; $T_x = (-)80.6$ G, $T_y = (-)125.5$ G, $T_z = (-)20.6$ G) are coincident, and the orientation of their principal axial directions is identical with the orientation of the principal axial directions of the hyperfine tensor in $V(\eta^5\text{-}C_5H_5)_2S_5$. The prominent crystallographic differences between $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ are: (1) a Cl-V-Cl bond angle of 87.1 (1)° being 6° smaller than the Cl-Ti-Cl bond angle of 93.2 (1)° and (2) the one independent V-Cl bond length of 2.398 (2) Å being 0.04 Å *longer* than the average Ti-Cl bond length of 2.360 (2) Å, in contradistinction to the average V-C distance being 0.05 Å *shorter* than the average Ti-C distance. These reversed bond-length trends, which are likewise observed between the titanium and vanadium molecules with phenyl mercaptide and pentasulfide ligands, are in harmony with the unpaired electron in each V(IV) complex occupying a MO which is antibonding with respect to the V-L bonds. $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ crystallizes with four molecules in an orthorhombic unit cell of symmetry *Pnma* with $a = 11.928$ (5), $b = 15.147$ (6), and $c = 6.848$ (4) Å, while $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ crystallizes with four molecules in a monoclinic unit cell of symmetry $C2/c$ with $a = 13.614$ (2) Å, $b = 6.720$ (1) Å, $c = 13.763$ (2) Å, and $\beta = 105.99$ (1)°. Final full-matrix least-squares refinement which utilized anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 4.6\%$ and $R_2 = 6.2\%$ for $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $R_1 = 4.1\%$ and $R_2 = 4.8\%$ for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$.

Structural determinations by X-ray diffraction[2] of the paramagnetic $V(\eta^5\text{-}C_5H_5)_2L_2$-type complexes and the analogous titanium complexes provided an operational test of the Ballhausen-Dahl bonding description[3] applied to $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes. The salient structural feature resulting from these crystallographic studies was that the similar L-M-L bond angles in the d^1 V(IV) complexes were found to be ca. 6° *less* than those in the corresponding d^0 Ti(IV) complexes. This structural incompatibility of the L-M-L bond angles with the B-D model was taken as prime evidence by us[2,4] for its general invalidity for $M(\eta^5\text{-}C_5H_5)_2L_2$-type complexes. The paramagnetism of $V(\eta^5\text{-}C_5H_5)_2S_5$ along with the existence of the diamagnetic $Ti(\eta^5\text{-}C_5H_5)_2S_5$ complex provided an opportunity to employ dilute single-crystal electron paramagnetic resonance to determine quantitatively the metal orbital character as well as the directional properties of the molecular orbital containing the unpaired electron in a $V(\eta^5\text{-}C_5H_5)_2L_2$-type complex. This work[5] disclosed that the unpaired electron in $V(\eta^5\text{-}C_5H_5)_2S_5$ resides primarily on the vanadium atom in an a_1-type molecular orbital which consists mainly of $3d_{z^2}$ with a small but significant amount of $3d_{x^2-y^2}$ and negligible 4s character (i.e., with respect to a right-handed Cartesian coordinate system for which *z* is directed normal to the *xy* plane which bisects the VS_2 bond angle, and *x* lies along the line of the VS_2 bisector). This EPR study provided the first quantitative evidence for the demise of the Ballhausen-Dahl model as a valid bonding description for $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes.

Since the isotropic hyperfine coupling constants for a large number of $V(\eta^5\text{-}C_5H_5)_2L_2$ (L = Cl, SH, OCN, CN, SeCN, N_3, SCN) complexes fall within the range of 60–75