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Single-Crystal Electron Paramagnetic Resonance and Nonparameterized Fenske–Hall Molecular Orbital Calculations Substantiating the Demise of the Ballhausen–Dahl Bonding Model for d^1 and d^2 $M(IV)$ $M(h^5-C_5H_5)_2L_2$ Complexes

Sir:

The nature of bonding in $M(h^5-C_5H_5)_2L_2$ complexes has been a subject of considerable interest. In 1961 Ballhausen and Dahl¹ formulated a qualitative description to represent the bonding in $M(h^5-C_5H_5)_2H_2$ ($M = Mo, W$) in which they proposed that the lone valence electron pair is localized in a sterically active orbital situated between the two hydrogens. This bonding model has been widely accepted² and generalized to other d^1 and d^2 $M(IV)$ $M(h^5-C_5H_5)_2L_2$ -type complexes containing nonhydridic L ligands. In 1967 Alcock,³ in rationalizing the acute $H_3C-Re-CH_3$ bond angle of 75.8 (1.3)° in dimethyl(*pentahaptocyclopentadienyl*)-(methylcyclopentadiene)rhenium, modified the B–D model by placing the lone pair in an orbital primarily directed normal to the plane bisecting the $Re(CH_3)_2$ fragment.

Preparative and crystallographic investigations performed independently at Wisconsin⁴ and at Oxford⁵ provided operational tests by which the B–D model was rejected for $M(h^5-C_5H_5)_2L_2$ -type complexes. The former group based this conclusion from their comparison between the molecular parameters of $Ti(h^5-C_5H_5)_2(SC_6H_5)_2$ ^{4c} vs. $V(h^5-C_5H_5)_2(SC_6H_5)_2$ ^{4c} and $Ti(h^5-C_5H_5)_2S_5$ ^{4d,6} vs. $V(h^5-C_5H_5)_2S_5$ ^{4d} which showed the similar L–M–L bond angles in the d^1 $V(IV)$ complexes to be ca. 6° less than those in the corresponding isomorphous d^0 $Ti(IV)$ complexes; if the B–D model were correct, electron-pair repulsion arguments would necessitate that the S–V–S bond angle would be larger (rather than significantly smaller) than the S–Ti–S bond angle. From crystal structural data of at least seven new $M(h^5-C_5H_5)_2L_2$ complexes (with d^0 , d^1 , and d^2 $M(IV)$), Green, Prout, and coworkers⁵ at Oxford not only found an analogous correlation between the L–M–L bond angle and the number of nonbonding d electrons on the metal,

which they cited as strong evidence for the Alcock model for $M(h^5-C_5H_5)_2L_2$ molecules, but also suggested a MO bonding description (involving a blending of the B–D and Alcock models) for $M(h^5-C_5H_5)_2H_2$ and $(h^5-C_5H_5)_2M-(\mu_2-L)_2-M'L_n'$ systems.

This paper reports the outcome of epr measurements of the paramagnetic $V(h^5-C_5H_5)_2S_5$ complex doped in a single crystal of the diamagnetic $Ti(h^5-C_5H_5)_2S_5$ host. It provides for the first time a *quantitative* determination of the orbital character and directional properties of the previously designated nonbonding orbital (with half- or full-occupancy) in a $M(h^5-C_5H_5)_2L_2$ complex. We also present the results of nonparameterized (Fenske–Hall)-type MO calculations⁷ which give excellent agreement with the epr results.^{8,9} These studies provide concrete evidence that the B–D model applied to d^1 and d^2 $M(IV)$ $M(h^5-C_5H_5)_2L_2$ systems is incorrect.

Solution epr spectra of $V(h^5-C_5H_5)_2S_5$ and $V(h^5-C_5H_5)_2(SC_6H_5)_2$ each show eight well-resolved lines (line width, 5–8 G), due to the hyperfine interaction of the unpaired electron with the ⁵¹V nucleus ($I = 7/2$ for ⁵¹V, 99.8%). The isotropic parameters are $V(h^5-C_5H_5)_2S_5$ (in DMF), $g_{iso} = 1.9909$, $A_{iso} = (-)64.78$ G; $V(h^5-C_5H_5)_2(SC_6H_5)_2$ (in toluene), $g_{iso} = 1.9919$, $A_{iso} = (-)64.99$ G. These isotropic hyperfine constants fall within the range of 60–75 G for $V(h^5-C_5H_5)_2L_2$ complexes¹⁰ thereby indicating a similar behavior of the unpaired electron despite considerable variation in the terminal L ligands. Epr measurements were made on several crystals containing ca. 0.2% $V(h^5-C_5H_5)_2S_5$ in the diamagnetic $Ti(h^5-C_5H_5)_2S_5$ host;¹¹ experimental details are available elsewhere.¹²

The interpretation of the epr data (Table I) is based

Table I. Experimental g and T Tensors with Directions and Best Fit Parameters

$g_x = 1.9964$	$\phi = 59.05^\circ$	$T_x = (-)66.6$ G	$\phi = 32.41^\circ$
$g_y = 1.9997$	$\theta = 51.50^\circ$	$T_y = (-)111.3$ G	$\theta = 140.68^\circ$
$g_z = 1.9689$	$\psi = -59.52^\circ$	$T_z = (-)23.5$ G	$\psi = 27.97^\circ$
For $a = -0.963$ and $b = 0.270$			
$T_x = (-)66.6$ G	$P = 93.2 \times 10^{-4} \text{ cm}^{-1}$		
$T_y = (-)111.3$ G	$\langle r^{-3} \rangle = 1.99$ au		
$T_z = (-)23.5$ G	$\chi = -2.11$		
$-A_{iso} = K = 65.8 \times 10^{-4} \text{ cm}^{-1}$	$\lambda = 30 \text{ cm}^{-1}$		

upon the reasonable assumption of C_{2v} symmetry for the $V(h^5-C_5H_5)_2S_2$ fragment of the pentasulfide complex. The epr data are only compatible with an electronic ground state of a_1 representation with the unpaired electron localized mainly on the vanadium. On the basis of the computed χ value¹³ of -2.11 (almost

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

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

(4) (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; (c) E. G. Muller, S. F. Watkins, and L. F. Dahl, to be submitted for publication. (d) E. G. Muller, J. L. Petersen, and L. F. Dahl, to be submitted for publication.

(5) (a) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 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) W. E. Douglas and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1796 (1972).

(6) E. F. Epstein, I. Bernal, and H. Köpf, *J. Organometal. Chem.*, **26**, 299 (1971).

(7) Cf. M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).

(8) While this investigation was in progress, Bakalik and Hayes⁹ reported a single-crystal epr study of $V(h^5-C_5H_5)_2Cl_2$ together with MO calculations. Although they concluded that the unpaired electron is in an a_1 -type MO primarily composed of $3d_{z^2}$ and $3d_{x^2-y^2}$ $V(IV)$ character (since the crystal structure of the diamagnetic $Ti(h^5-C_5H_5)_2Cl_2$ host is unknown), they did not know the orientation of the hyperfine tensor in $V(h^5-C_5H_5)_2Cl_2$ and hence were not able to choose a unique set of coefficients specifying the metal orbital character. In addition, their MO calculations are in disagreement with their conclusions (and with our MO calculations).

(9) D. P. Bakalik and R. G. Hayes, *Inorg. Chem.*, **11**, 1734 (1972).

(10) G. Doyle and R. S. Tobias, *Inorg. Chem.*, **7**, 2479 (1968).

(11) The red, air-stable $V(h^5-C_5H_5)_2S_5$ -doped crystals of $Ti(h^5-C_5H_5)_2S_5$ are monoclinic, $P2_1/n$, $a = 9.019$, $b = 13.089$, $c = 11.294$ Å, $\beta = 93.62^\circ$, $Z = 4$.

(12) See paragraph at end of paper regarding supplementary material.

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

Table II. Per Cent Character of the HOMO^a in $M(h^5-C_5H_5)_2L_2$ (where $M = V, Cr, Mo$) and Corresponding LUMO^a in $Ti(h^5-C_5H_5)_2L_2$ (of a_1 representation)^{b,c}

Configuration	Symmetry	Molecule	% metal $3d_{z^2}$	% metal $3d_{x^2-y^2}$	Energy ^d (eV)	Ratio % $3d_{z^2}$ / % $3d_{x^2-y^2}$
d ⁰ LUMO	C_s	$Ti(h^5-C_5H_5)_2S_5$	57.9	8.2	-4.99	7.1
d ⁰ LUMO	C_2	$Ti(h^5-C_5H_5)_2(SH)_2$	65.7	7.6	-6.15	8.6
d ⁰ LUMO	C_{2v}	$Ti(h^5-C_5H_5)_2Cl_2$	69.5	4.9	-6.88	14.1
d ¹ HOMO	C_s	$V(h^5-C_5H_5)_2S_5$	50.1	6.6	-6.12	7.7
d ¹ HOMO	C_2	$V(h^5-C_5H_5)_2(SH)_2$	64.7	5.5	-7.45	11.7
d ¹ HOMO	C_{2v}	$V(h^5-C_5H_5)_2Cl_2$	67.6	3.3	-8.19	20.5
d ² HOMO	C_{2v}	$Cr(h^5-C_5H_5)_2Cl_2$	53.0	2.4	-9.03	22.4
d ² HOMO	C_{2v}	$Mo(h^5-C_5H_5)_2Cl_2$	54.0	1.3	-8.64	40.9
d ² HOMO	C_{2v}	$Mo(h^5-C_5H_5)_2H_2$	80.7	5.5	-8.32	14.6

^a LUMO = lowest unoccupied molecular orbital; HOMO = highest occupied molecular orbital. ^b In these molecules the vanadium 4s and 4p character was $\leq 0.02\%$ and 1.0% , respectively, while the titanium 4s and 4p character was ≤ 0.2 and 1.5% , respectively. ^c Per cent 3p S (or Cl) ligand character (*i.e.*, sum of contributions from both pairs of $3p_\pi$ ligand L orbitals): d⁰ LUMO, 16.9–23.2; d¹ HOMO, 22.5–34.7; d² HOMO, 37.7–40.0. Per cent e_2 (C_5H_5) ligand character (*i.e.*, represents the localized symmetry orbitals of the C_5H_5 rings with per cent character being the sum of contributions from each e_2): d⁰ LUMO, 4.6–6.1; d¹ HOMO, 3.1–4.4; d² HOMO, 2.6–5.5. ^d These energy levels are well-separated from the nearest ones (which belong to different representations), above and below. For the vanadium molecules the LUMO lies 2.7–3.1 eV above the HOMO and the highest fully occupied one 1.3–2.6 eV below the HOMO; the corresponding values are 3.3 and 1.2 eV for $Cr(h^5-C_5H_5)_2Cl_2$ and 3.7 and 1.7 eV for $Mo(h^5-C_5H_5)_2Cl_2$. For the titanium molecules the HOMO lies 2.6–4.6 eV below the LUMO.

identical with that of -2.08 reported⁹ for $V(h^5-C_5H_5)_2Cl_2$, we conclude that the direct 4s vanadium contribution to the MO containing the unpaired electron must similarly be sufficiently small⁹ to be neglected. Since d_{z^2} and $d_{x^2-y^2}$ also belong to the a_1 representation, they may be mixed by the noncubic parts of the ligand-field potential. 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. From expressions given elsewhere,¹² a unique set of these coefficients (Table I) gives rise to calculated anisotropic components of the hyperfine coupling constant which agree extremely well with the observed values. These results as well as the average principal values of the g and T tensors and their orientations in terms of Euler angles¹⁴ (with respect to the crystallographic axial system) are given in Table I. The orientation of the hyperfine tensor with respect to the $V(h^5-C_5H_5)_2S_2$ fragment in $V(h^5-C_5H_5)_2S_5$ is shown in Figure 1. Table I shows that the g tensor and the hyperfine tensor are not coincident and that the spin-orbit coupling is not appreciable. The calculated values for P , $\langle r^{-3} \rangle$, and λ (*i.e.*, the spin-orbit coupling value for vanadium) compare favorably with those between a V^0 and V^+ system.¹³

From average bond lengths and angles given elsewhere,¹² (Fenske-Hall)-type MO calculations were performed for $M(h^5-C_5H_5)_2S_5$, $M(h^5-C_5H_5)_2(SC_6H_5)_2$, $M'(h^5-C_5H_5)_2Cl_2$ ($M = Ti, V$ and $M' = Ti, V, Cr, Mo$), and $Mo(h^5-C_5H_5)_2H_2$.^{15,16} To simplify the calculation for $M(h^5-C_5H_5)_2(SC_6H_5)_2$, the two phenyl rings were replaced by hydrogen atoms at distances of 1.34 \AA from the metal-bonded sulfur atoms along the

(14) H. Goldstein, "Classical Mechanics," Wiley, New York, N. Y., 1965, p 107.

(15) The H and C functions are from Clementi,^{16a} S and Cl functions from Clementi and Raimondi,^{16b} 1s through 3d functions for Ti and V (with a +1 charge for the 3d) from Richardson, *et al.*,^{16c} and the 4s and 4p metal functions from Radtke.^{16d}

(16) (a) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964); (b) E. Clementi, and D. L. Raimondi, *ibid.*, **38**, 2686 (1963); (c) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1057 (1962); (d) D. D. Radtke, Ph.D. Thesis, University of Wisconsin (Madison), 1966.

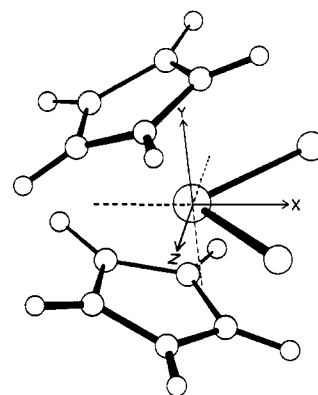


Figure 1. Orientation of principal axes of the hyperfine coupling tensor with respect to the idealized C_{2v} geometry of the $V(h^5-C_5H_5)_2S_2$ fragment of the $V(h^5-C_5H_5)_2S_5$ molecule. Within experimental error, the x axis lies along the S-V-S bisector with the y axis perpendicular to the VS_2 plane.

S-C directions. For $M(h^5-C_5H_5)_2S_5$ the atomic coordinates were idealized to C_s-m symmetry with S-S distances of 2.06 \AA , while for $M(h^5-C_5H_5)_2(SC_6H_5)_2$ the atomic coordinates were idealized to C_2-2 symmetry. For the chloride and hydride molecules the atomic coordinates were idealized to $C_{2v}-mm2$ symmetry. Although the computational method is rotationally invariant to the choice of the local coordinate system on the metal, the atomic coordinates were calculated with the master Cartesian coordinate system located on the metal being coincident with the principal directions obtained for the hyperfine tensor (Figure 1) in order to simplify the comparison between the molecular orbital calculations and the dilute single-crystal epr results. After completion of the calculation in the atomic basis set, the orbitals were transformed to the basis of the free molecular ligands (*viz.*, the cyclopentadienyl rings) in order to simplify the interpretation of the MO character. The results of prime importance to this discussion are the orbital characters in the HOMO's for the vanadium, chromium, and molybdenum complexes which for the titanium analogs correspond to those in the LUMO's. Table II clearly indicates (essentially invariant to the assumed molecular

symmetry and to the change of ligand L) that the non-bonding electron pair in each of the chromium and molybdenum complexes and the unpaired electron in each $V(h^5-C_5H_5)_2L_2$ complex reside in an a_1 orbital of high metal character, primarily $3d_{z^2}$, with only a very small amount of $3d_{x^2-y^2}$ and virtually no $4s$. Each vanadium HOMO also possesses considerable S (or Cl) p orbital character. It is highly significant that the composition of this vanadium HOMO is completely compatible from electron repulsion arguments with the observed decrease of *ca.* 6° in the L-M-L bond angle upon its occupation. Hence, it is evident that the Fenske-Hall MO treatment, even for a one-electron open-shell system, gives excellent agreement with the epr results (*i.e.*, per cent character ratio of $3d_{z^2}/3d_{x^2-y^2} = (0.963)^2/(0.270)^2 = 12.7/1$ (epr) *vs.* $0.501/0.066 = 7.7/1$ (MO)) with the contributions to the anisotropy in the hyperfine coupling tensor primarily arising from the drastically different per cent character of the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. Details of this work will be presented later together with photoelectron spectroscopic experiments, currently underway, which will provide additional insight concerning the bonding in these species.

Since the submission of this communication, an article by Stewart and Porte¹⁷ reporting the dilute glass epr spectra for several $V(h^5-C_5H_5)_2L_2$ compounds (L = Cl, SCN, OCN, and CN) has been published. Due to the nature of this type of experiment, the authors have incorrectly assigned the z component of the magnetic tensors to coincide with the C_2 -2 axes of these molecules.

The noncoincidence of the **g** and **T** tensors in $V(h^5-C_5H_5)_2S_5$ is presumed to be at least partially a consequence of the significant deviations of the molecule (of crystallographic site symmetry C_{1-1}) from C_2 -2 symmetry. The orbital character of the unpaired electron was obtained from an analysis of the principal values of the **T** tensor. Since the expressions for the anisotropic part of the hyperfine components are second order in **g** and λ , these parameters do not significantly affect either the magnitude of the anisotropic components of **T** or the subsequent values of *a* and *b*.

In order to provide an operational test of the research and resulting conclusions presented here, we have synthesized and determined the crystal structures of the nonisomorphous $V(h^5-C_5H_4CH_3)_2Cl_2$ and $Ti(h^5-C_5H_4CH_3)_2Cl_2$ (both of which possess ordered solid-state structures) and have carried out a single-crystal epr analysis of $V(h^5-C_5H_4CH_3)_2Cl_2$ (of crystallographic C_2 -2 site symmetry) diluted in the crystal lattice of $Ti(h^5-C_5H_4CH_3)_2Cl_2$ (of crystallographic C_s -*m* site symmetry). The **g** and **T** tensors are coincident for $V(h^5-C_5H_4CH_3)_2Cl_2$, and the orientation of their principal directions is identical with the orientation of the principal directions of **T** for $V(h^5-C_5H_5)_2S_5$ shown in Figure 1. The per cent character for the HOMO in $V(h^5-C_5H_5)_2Cl_2$ agrees remarkably well with that calculated for the methylcyclopentadienyl vanadium analog from its epr data (*i.e.*, per cent character ratio of $3d_{z^2}/3d_{x^2-y^2} = (0.976)^2/(0.218)^2 = 20.0$ (epr) *vs.* $(0.676)/(0.033) = 20.5/1$ (MO)). These results thereby provide

(17) C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 722 (1973).

further convincing evidence of our interpretation of the principal values and directions of the hyperfine tensor in $V(h^5-C_5H_5)_2S_5$ concerning the distribution of the unpaired electron in this d^1 V(IV) species.

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Supplementary Material Available. Experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2248.

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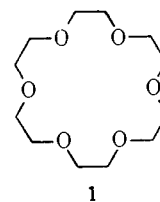
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The Chemistry of "Naked" Anions. I. Reactions of the 18-Crown-6 Complex of Potassium Fluoride with Organic Substrates in Aprotic Organic Solvents¹

Sir:

Fluoride ion, unencumbered by strong solvation forces, should prove to be both a potent nucleophile and base.² Solubility problems, however, have hampered studies of fluoride ion in weakly solvating media. The recent reports regarding the ability of crown ethers to complex metal salts and dissolve them in polar and nonpolar, aprotic solvents^{3,4} has prompted us to investigate the chemistry of metal fluoride crown complexes. We wish to report the solubilization of potassium fluoride in acetonitrile and benzene containing 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6) (1)^{5,6} and the reactions of this solubilized fluoride, which



we have termed "naked" fluoride, with a variety of organic substrates. The following reaction types are demonstrated: (1) displacement reactions at sp^3

(1) Presented in part at the First Fall Organic Conference, Cape Cod, Mass., Oct 1, 1973.

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(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970); *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **84**, 16 (1972); J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).

(4) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 4024 (1972).

(5) R. Greene, *Tetrahedron Lett.*, 1793 (1972).

(6) D. J. Cram and G. Gokel, Department of Chemistry, University of California at Los Angeles, private communication.