CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NOTRE DAME UNIVERSITY,
NOTRE DAME, INDIANA 46556

Electron Paramagnetic Resonance Studies of the Electronic Structure of Bis(cyclopentadienyl)vanadium Dichloride and a Comparison with Simple Molecular Orbital Calculations

BY DENNIS P. BAKALIK AND ROBERT G. HAYES*

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Dilute single-crystal electron paramagnetic resonance experiments have been performed on bis(cyclopentadienyl)vanadium dichloride dissolved in bis(cyclopentadienyl)titanium dichloride. Principal values of the spectroscopic splitting constant are $g_1 = 1.946$, $g_2 = 1.967$, and $g_3 = 1.965$. The vanadium hyperfine values are $A_1 = (-)118.9$, $A_2 = (-)28.9$, and $A_3 = (-)74.9$ ($\times 10^{-4}$ cm^{-1}). The unpaired electron is in an a_1-type molecular orbital which is primarily composed of d_{z^2} and $d_{x^2-y^2}$ and has a small amount of 4s character. Self-consistent charge-configuration calculations of the modified Wolfsberg-Helmholz type and the type proposed by Fenske have been performed and the results are related to the optical and epr spectra.

Introduction

The dihalide derivatives of the transition metal bis(cyclopentadienyl) compounds have received considerable attention. Dipole moment[1] and electron diffraction[2] work directed at the geometry of bis(cyclopentadienyl)titanium dichloride, $(C_5H_5)_2TiCl_2$, indicated this complex to be a "wedge-shaped sandwich" compound of distorted tetrahedral structure. More recent X-ray results indicate the complexes bis(cyclopentadienyl)zirconium difluoride and bis(cyclopentadienyl)zirconium diiodide to be of this geometry.[3]

The electronic structure and the bonding in this class of compounds have been the subject of some investigation. Druce, *et al.*,[4] have interpreted the infrared spectrum of $(C_5H_5)TiCl_2$ and suggested considerable ionic character of the metal-ring bonding. Beachell[5] has offered pπ-dπ metal-halogen bonding as an explanation of the decrease in chemical shift of ring protons in the Cl, Br, and I series of bis(cyclopentadienyl)titanium complexes. Chien[6] has reported the electronic spectra of the series $(C_5H_5)_2MX_2$ where X = Cl, Br, or I when M = Ti and X = Cl in the case M = V.

The optical spectra provide an experimental criterion for the acceptability of a molecular orbital interpretation of the electronic structure of these compounds but definitive conclusions concerning the ordering of molecular orbitals cannot be drawn easily from the optical data. The complex bis(cyclopentadienyl)vanadium dichloride, $(C_5H_5)_2VCl_2$, lends itself to an analysis of the electronic structure using electron paramagnetic resonance. Though the solution epr spectrum has been reported,[7] dilute single-crystal work has not been done. The work we report herein was performed to obtain information from magnetic resonance concerning the electronic structure of the compound and to test the compatibility of these results with molecular orbital calculations of the modified Wolfsberg-Helmholz[8,9] type and of the type proposed by Fenske[10] and Hillier and Canadine.[11,12]

Experimental Section

Bis(cyclopentadienyl)vanadium dichloride and bis(cyclopentadienyl)titanium dichloride were purchased from Alfa Inorganics. Single crystals of about 1% $(C_5H_5)_2VCl_2$ in the $(C_5H_5)_2TiCl_2$ diamagnetic diluent were grown by solvent evaporation from a chloroform solution. The chloroform was dried over lithium aluminum hydride, outgassed several times, and distilled into a vessel containing $(C_5H_5)_2VCl_2$-$(C_5H_5)_2TiCl_2$ powder. Outgassing and distillation were done on a vacuum rack operating at approximately 10^{-4} Torr. Solvent evaporation was carried out by passing purified nitrogen through inlet and outlet ports of the vessel. Nitrogen was deoxygenated using a column filled with BTS catalyst (BASF AG, Ludwigshaferr) maintained at a temperature of 150°. The crystals were elongated plates, 0.1 mm or so thick, 0.5 mm wide, and a few millimeters long.

Crystals were mounted on small quartz cubes (2.5 mm on an edge) and coated with General Electric vacuum sealant GEVAC in order to preserve the sample while measurements were made. No discernible changes in the appearance of the spectrum were noted during the course of the measurements.

Epr spectra were taken using a Varian V-4502-15 spectrometer equipped with a Fieldial and a 100-kc modulation unit. Magnetic field calibrations were done using a proton probe and klystron frequencies were measured with an adjustable cavity wavemeter.

A crystal-fixed coordinate system with axes along the long, intermediate, and short axes at the crystals established three orthogonal directions for rotation. In a given plane the direction of the magnetic field with respect to the crystal-fixed axis system was changed in 15° increments.

Computational Details

Self-consistent charge-configuration calculations were done according to the modified Wolfsberg-Helmholz[8,9] formulation and that proposed by Fenske[10] and Hillier and Canadine.[11,12]

The geometry for $(C_5H_5)_2VCl_2$ was assumed to be the same as that determined for $(C_5H_5)_2TiCl_2$.[2] Figure 1 represents the geometry, atomic numbering system, and coordinate choices employed.

Vanadium 3d, 4s, and 4p, chlorine 3s and 3p, and the pπ orbitals of the cyclopentadienyl ring system were chosen to represent the valence-electron basis set. All functions were Roothaan-Hartree-Fock functions of

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(1) S. A. Giddings and R. J. Best, *J. Amer. Chem. Soc.*, **83**, 2393 (1961).

(2) N. V. Alekseev and I. A. Ronova, *Zh. Strukt. Khim.*, **7**, 103 (1966).

(3) M. Bush, private communication, Agricultural Research Council Unit of Structural Chemistry, London, England.

(4) P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc.*, 2106 (1969).

(5) H. L. Beachell and S. A. Butter, *Inorg. Chem.*, **4**, 1133 (1965).

(6) J. C. W. Chien, *J. Phys. Chem.*, **67**, 2477 (1963).

(7) J. C. W. Chien and C. R. Boss, *J. Amer. Chem. Soc.*, **83**, 3767 (1961).

(8) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(9) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

(10) R. F. Fenske, K. G. Caulton, D. D. Radke, and C. C. Sweeney, *ibid.*, **5**, 951 (1966).

(11) R. M. Canadine and I. H. Hillier, *J. Chem. Phys.*, **50**, 2984 (1969).

(12) I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, **47**, 27 (1969).

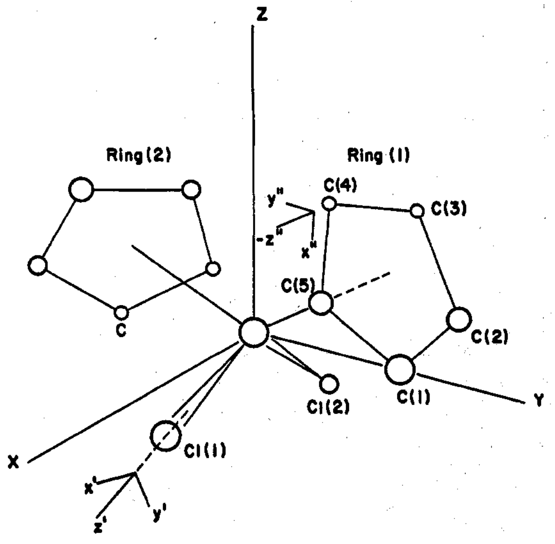

Figure 1.—The geometry of the compounds $M(C_5H_5)_2Cl_2$ (M = Ti, V) and the coordinate systems used in discussing bonding in these compounds.

Clementi[13] with the exception of the vanadium 4p virtual orbital which was that of Richardson.[14] Hückel molecular orbitals (Table I) were constructed from the pπ basis set. Molecular symmetry orbitals, represented in Table II, were formed in accordance with the representations of the group C_{2v}.

Overlap and kinetic energy integrals were calculated using FORTRAN routine ONE4 available from the Quantum Chemistry Program Exchange.[15] Two-center nuclear attraction integrals were evaluated using a routine we prepared. Ligand–ligand integrals were ignored in both calculations. Valence-state ionization potentials for vanadium and chlorine were taken from Ballhausen and Gray[16] while cyclopentadienyl radical VSIP's were obtained using values of 8.69 and −3 eV for the first ionization potential and resonance integral,[17] respectively. Consistency of input and output configuration and charge was obtained *via* a pattern search minimization routine[18] which minimized the difference between input and output parameters. For the modified Wolfsberg–Helmholz calculation only matrix elements involving the metal atom were explicitly charge and configuration dependent, thereby producing a three-parameter minimization problem of the function given by (1). Subscripts i and o indicate input and out-

$$\text{Dif} = |Q_i - Q_o| + |S_i - S_o| + |P_i - P_o| \quad (1)$$

put values of the metal charge (Q) and the metal configurational amplitudes (S and P). The Fenske-type calculation involves a six-parameter minimization problem. The metal charge, two metal populations, and three carbon-ring charges completely characterize the valence-electron distribution.

Results

The angular variation of the epr spectrum yielded the spin-Hamiltonian parameters listed in Table III. The principal values were obtained from maximum, minimum, and intermediate turning points of the angular variation of the spectra with respect to the aforementioned coordinate system. A first-order treatment of the data, employing a least-squares analysis for each plane, gives principal values which are in essential agreement with those of Table III. This indicates that the

TABLE I

HÜCKEL MOLECULAR ORBITALS FOR THE CYCLOPENTADIENYL RADICAL[a]

A_1	$(1/\sqrt{5})(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5)$
E_1	$(\sqrt{2/5})(\phi_1 + \phi_2 \cos \omega + \phi_3 \cos 2\omega + \phi_4 \cos 2\omega + \phi_5 \cos \omega)$
E_1'	$(\sqrt{2/5})(\phi_2 \sin \omega + \phi_3 \sin 2\omega - \phi_4 \sin 2\omega - \phi_5 \sin \omega)$
E_2	$(\sqrt{2/5})(\phi_1 + \phi_2 \cos 2\omega + \phi_3 \cos \omega + \phi_4 \cos \omega + \phi_5 \cos 2\omega)$
E_2'	$(\sqrt{2/5})(\phi_2 \sin 2\omega - \phi_3 \sin \omega + \phi_4 \sin \omega - \phi_5 \sin 2\omega)$

[a] $\omega = 2\pi/5$; $\phi_1 = p\pi_1$.

TABLE II

$(C_5H_5)_2VCl_2$ SYMMETRY-ADAPTED BASIS SET[a]

A_1	A_2	B_1	B_2
V	V	V	V
(1) = $3d_{z^2}$	(11) = $3d_{xy}$	(15) = $3d_{xz}$	(22) = $3d_{yz}$
(2) = $3d_{x^2-y^2}$		(21) = $4p_x$	(26) = $4p_y$
(8) = 4s	Cl		
(9) = $4p_z$	(14) = $3p_y(1) + 3p_y(2)$	Cl	Cl
		(18) = $3s_1(1) - 3s_2(2)$	(25) = $3p_x(1) - 3p_x(2)$
Cl	Cp	(19) = $3p_z(1) - 3p_z(2)$	
(6) = $3s(1) + 3s(2)$	(12) = $E_1'(1) + E_1'(2)$	(20) = $3p_y(1) - 3p_y(2)$	Cp
(7) = $3p_z(1) + 3p_z(2)$	(13) = $E_2'(1) + E_2'(2)$		(23) = $A_1(1) - A_1(2)$
(10) = $3p_x(1) + 3p_x(2)$		Cp	(24) = $E_1(1) - E_1(2)$
		(16) = $E_1'(1) - E_1'(2)$	(27) = $E_2(1) - E_2(2)$
Cp		(17) = $E_2'(1) - E_2'(2)$	
(3) = $A_1(1) + A_1(2)$			
(4) = $E_2(1) + E_2(2)$			
(5) = $E_1(1) + E_1(2)$			

[a] $1/\sqrt{2}$ normalization factor understood for orbitals which are linear combinations; $A_1(1)$ represents the Hückel A_1 orbital (Table I) for ring 1 (Figure 1).

TABLE III

$(C_5H_5)_2VCl_2$ PRINCIPAL g VALUES AND VANADIUM COUPLING CONSTANTS

$g_1 = 1.946$	$g_2 = 1.967$	$g_3 = 1.965$
$A_1 = -118.9$[a]	$A_2 = -26.7$	$A_3 = -74.9$
	$\bar{A} = -73.5$	

[a] Coupling constants in 10^{-4} cm^{-1}.

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[13] E. Clementi, "Tables of Atomic Functions," International Business Machine Corp., 1966.

[14] J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 796 (1963).

[15] ONE4 Program No. 134, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

[16] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965, p 120.

[17] R. D. Fischer, *Theor. Chim. Acta*, **1**, 418 (1963).

[18] C. J. Hebert, Thesis, University of Notre Dame, Notre Dame, Ind.

chosen coordinate system represents the principal axis system, within our experimental accuracy. Detailed examination of the spectra indicate, however, that this relationship is only approximate. Spectra taken at angles close to principal directions appear to arise from one species. At intermediate angles slightly split spectra are observed, however, indicating two inequivalent species tipped by a few degrees from the apparent principal axis system. Our inability to follow a single species through a complete rotation prohibited refinement of the apparent principal axis system.

Tables IV and V contain the self-consistent charges and configurations along with the important eigenvalues and orbital symmetries from the two different types of calculations. The value of the function Dif appearing in eq 1 is also given.

TABLE IV

RESULTS OF WOLFSBERG–HELMHOLZ CALCULATIONS[a]

Eigenvalue, kK	Symmetry	Charge, V	Confign
−71.17	B_2	+0.232	4s = 0.665
−70.09	B_2		4p = 0.239
−69.93	E_1[b]		3d = 3.86
−68.00	A_1		
−65.34	A_1		

[a] 1 kK = 10^3 cm^{-1}; Dif = 0.45. [b] Highest occupied MO.

TABLE V

RESULTS OF FENSKE–HILLIER CALCULATIONS[a]

Eigenvalue, kK	Symmetry	Charge, V	Confign
−136.5	B_2	+1.29	4s = 0.441
−134.4	A_1		4p = 0.188
−106.9	A_2[b]		3d = 3.08
−100.0	A_1		
−95.6	B_1		

[a] Dif = 0.28. [b] Highest occupied MO.

Discussion

One conclusion is obvious immediately from our data. The electronic ground state of $(C_5H_5)_2VCl_2$ has the unpaired electron localized heavily on the metal. This follows from the magnitude of the ^{51}V hyperfine constants.

The primary object of our study is a description of the electronic ground state of $(C_5H_5)_2VCl_2$, so we must first decide upon the symmetry of the ground state. This is made difficult by the fact that the crystal structure of the host molecule, $(C_5H_5)_2TiCl_2$, is not known. We must, thus, deduce the symmetry of the ground electronic state of $(C_5H_5)_2VCl_2$ from the various magnetic parameters without knowing how the magnetic tensors are oriented in the molecule.

The marked departure of the vanadium coupling constant from axial symmetry is sufficient evidence to rule out the possibility of an A_2 ground state. The A_2 representation contains only d_{xy} of the vanadium basis set so the hyperfine tensor must have axial symmetry.

A B_1 or a B_2 ground state can be compatible with the observed **A** tensor anisotropy if substantial 3d–4p mixing occurs. The ground-state function (2) produces the expressions given by eq 3 for the principal components of the anisotropic part of **A**. We have assumed that the function given in eq 2 represents the ground state accurately and have ignored admixture of higher states. The ratio P_d/P_p may be estimated from the corresponding spin–orbit coupling constants since both contain a $\langle r^{-3}\rangle$ dependence.[19] From the spectroscopic term splitting for V(V)[20] we obtain the values $\zeta_{3d} = 250$ cm^{-1} and $\zeta_{4p} = 846$ cm^{-1} which give $P_d/P_p \approx {}^1/_3$. This leads to values of $\alpha = \pm 0.91$ and $\beta = \pm 0.41$ for the amplitudes in eq 2, in order to fit the data. The argument above is valid for either B-type ground state. The ground state of A_1 symmetry is also compatible with the anisotropy of the coupling constants as we shall discuss later.

$$|\psi_g\rangle = \alpha|d_{xz}\rangle + \beta|4p_x\rangle \qquad (2)$$

$$\begin{aligned} T_x &= \frac{2\alpha^2P_d}{7} - \frac{4\beta^2P_p}{5} \\ T_y &= \frac{4\alpha^2P_d}{7} - \frac{2\beta^2P_p}{5} \\ T_z &= \frac{2\alpha^2P_d}{7} - \frac{2\beta^2P_p}{5} \\ P_{d,p} &= g_e\beta_e\beta_Ng_N\langle r^{-3}\rangle_{d,p} \end{aligned} \qquad (3)$$

We turn to the isotropic component of the coupling constant and an empirical argument to obtain the correct ground state. McGarvey[21] has compiled and analyzed isotropic coupling constants for a large number of transition metal compounds. From the isotropic coupling constant[7] we obtain the value of −2.08 for the quantity χ defined by eq 4. κ is the isotropic contact term and the other constants have their usual meaning. This value is significantly larger than values McGarvey listed for other vanadium(IV) compounds and indicates a ground state which contains direct 4s mixing. We therefore exclude both B-type ground states as it would be difficult to reconcile the large value for κ with a ground state in which direct s admixture is forbidden by symmetry.

$$\chi = -{}^3/_2\left(\frac{hca_0^3}{g_eg_N\beta_e\beta_N}\right)\kappa \qquad (4)$$

Robertson[22] gave a value of 4600 Mc for the coupling of a 4s electron in V^{2+} from which we obtain a value of 49.2 for χ. Comparing the experimental value of −2.08 with the value obtained for vanadium tetraphenylporphyrin (−2.78) gives a difference of 0.7. This amount may be attributed to direct 4s mixing since the ground state of vanadium tetraphenylporphyrin is well known.[23] We calculate 1.42% 4s mixing in the A_1 ground state of $(C_5H_5)_2VCl_2$.

The following treatment of the A_1 ground state from the hyperfine data and the analyses of the excited orbitals from the **g** tensor anisotropy will be solely in terms of a crystal field model for the electronic structure of the complex. This is justified by our previous observation of the strong localization of the unpaired electron on the vanadium.

Given an A_1 ground state, the anisotropic components

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(19) L. Pauling and S. Goudschmidt, "The Structure of Line Spectra," McGraw-Hill, New York, N. Y., 1930, p 206 ff.

(20) R. F. Bacher and S. Goudschmidt, "Atomic Energy States," McGraw-Hill, New York, N. Y., 1932, p 499.

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

(22) R. E. Robertson and H. M. McConnell, *ibid.*, **64**, 70 (1960).

(23) D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).

of the hyperfine coupling constant lead to the evaluation of the mixing coefficients of eq 5. Using (5) we obtain

$$|\psi_g\rangle = a|\mathrm{d}_{z^2}\rangle + b|\mathrm{d}_{x^2-y^2}\rangle \qquad (5)$$

for the principal anisotropic coupling constants of vanadium

$$\begin{aligned} T_x &= \left[-\frac{2}{7}(a^2 - b^2) + \frac{4\sqrt{3}}{7}\,ab\right]P_\mathrm{d} \\ T_y &= \left[-\frac{2}{7}(a^2 - b^2) - \frac{4\sqrt{3}}{7}\,ab\right]P_\mathrm{d} \qquad (6) \\ T_z &= \frac{4}{7}(a^2 - b^2)P_\mathrm{d} \end{aligned}$$

This leads to values of a and b of ± 0.70, ± 0.72, or ± 0.27, ± 0.96, or ± 0.96, ± 0.27 for anisotropies in accord with our data. Unfortunately, since the host crystal structure has not been determined, we are unable to choose the unique set of coefficients for (5).

We should point out that the inclusion of spin-orbit mixing and orbital hyperfine effects in the derivation of (6) leads to values of the mixing coefficients that are within 10% of those reported above. Equation 6 leads to a value of 9.44×10^{-3} cm^{-1} for P. From Freeman and Watson's Hartree-Fock functions[24] we get 8.57, 10.7, 12.8, and 17.2 ($P \times 10^3$ cm^{-1}) for V^0, V^+, V^{2+}, and V^{4+}, respectively. If we use the change obtained from the Fenske-Hillier calculations, which seem reasonable on the whole, we obtain a metal amplitude of 0.82 for the unpaired electron.

The function given by (5) yields eq 7 for the principal

$$\begin{aligned} g_x &= 2.0023 - \frac{2\zeta(\sqrt{3}a + b)^2}{\Delta E_{yz}} \\ g_y &= 2.0023 - \frac{2\zeta(\sqrt{3}a - b)^2}{\Delta E_{xz}} \qquad (7) \\ g_z &= 2.0023 - \frac{8\zeta b^2}{\Delta E_{xy}} \end{aligned}$$

values of the spectroscopic splitting tensor where ζ is the spin-orbit coupling constant and ΔE gives the energy difference between the orbital represented by (4) and the excited d orbitals. In writing eq 7 we have assumed that the various excited states, as well as the ground state, are composed entirely of d orbitals and that no other states having large d-orbital amplitudes are nearby. We use $\zeta = 170$ cm^{-1} which corresponds to the spin-orbit coupling constant for V^{2+}. This value has been used in the g value analysis of other V^{4+} systems.[21] Taking $a = 0.70$ and $b = 0.72$ we obtain for the crystal field excited states $\Delta E_{xz} = 2266$ cm^{-1}, $\Delta E_{xy} = 19{,}500$ cm^{-1}, and $\Delta E_{yz} = 23{,}868$ cm^{-1}. The other values for a and b yield excited-state energies of the same separation but not necessarily of the same ordering.

The optical spectrum of $(C_5H_5)_2VCl_2$ gives no indication of the proximity of these excited states since the assignment of the spectrum contains no transition which involves the a_1 level. We can, however, obtain an estimate of the first excited orbital from the spectrum of $(C_5H_5)_2TiCl_2$, which places d_{xz} in our scheme at 6000 cm^{-1}. We cannot rationalize this discrepancy within the framework of the crystal field model used above.

Unfortunately, we observe ligand hyperfine coupling neither at room temperature nor at 77°K so a detailed description of the spin-Hamiltonian parameters from a molecular orbital point of view is impossible. We can say little about ligand contribution to the ground state MO other than placing a maximum on chlorine 3s mixing. From the observed line widths we get a maximum isotropic chlorine coupling constant of 6.6 G for two equivalent chlorine nuclei. Using a value of 1666 G for the coupling of a chlorine 3s electron[25] puts the maximum 3s chlorine participation at 0.4%.

The modified Wolfsberg-Helmholz method has been used with some success to explain the optical spectra and spin densities of transition metal complexes.[26] The widespread use of this method, despite its many approximations, stems from the computational ease with which a calculation may be performed. Recently criticism of the method has been put forth by several authors, who offer alternative schemes within the SCCC framework.[10,11,27] Major criticism centers around the claim that metal-ligand covalency is an artifact of the approximations used in the calculation. We performed the Wolfsberg-Helmholz (type I) and the Fenske (type II) calculations in order to evaluate their validity when applied to an organometallic system for which both optical and epr data are available.

Table II indicates the eigenvalues obtained for the type I calculation. The energy levels are extremely close together near the MO in which the unpaired electron resides. This calculation gives us neither a correct ground-state symmetry nor qualitative agreement with the optical spectrum.

There are several features that should be mentioned in conjunction with the type II results. We see that the metal charge increases substantially ($0.23 \rightarrow 1.29$) when some electrostatic terms are included explicitly in the Hamiltonian. The predicted ground state which results from the type II calculation is of symmetry A_2 and is not compatible with our epr results. The a_1 MO located approximately 7 kK above the highest occupied orbital would produce a ground state of correct symmetry if the a_2 (-106.9) and a_1 (-100.0) were reversed, however. The major composition of a_1 (-100.0) is $-0.69(d_{z^2}) + 0.50(d_{x^2-y^2}) + 0.11(A_1(1) + A_1(2)) - 0.38(E_2(1) + E_2(2)) - 0.138(3s(1) + 3s(2)) + 0.31(3p_z(1) + 3p_z(2)) - 0.26(3p_x(1)) + 3p_x(2))$. The notation used for the ligand orbitals is defined in Table II. The d_{z^2} and $d_{x^2-y^2}$ coefficients of this orbital are reasonably close to experimentally consistent values. The set ± 0.70 and ± 0.72 for a and b, when multiplied by the overall occupation of metal orbitals, gotten from P (0.82) yields 0.565 and 0.59. We note, however, that the orbital deduced to be low lying from the **g** value analysis using $a = -0.7$ and $b = +0.72$ is of b_2 and not a_2 symmetry. This may be due to an approach to the calculation of **g** which is too simple, but there are too many uncertainties in the ordering of levels to permit a better calculation.

The type II calculation gives a value of 34.4 kK for the transition $\psi_g \rightarrow (\mathrm{core})(b_2)^2(a_1)^1(a_2)^1(a_1)^1$ compared

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(24) A. J. Freeman and R. E. Watson "Magnetism," Vol. II-A, G. T. Rado and H. Shul, Ed., Academic Press, New York, N. Y., 1965, p 167.

(25) M. C. R. Symons, *J. Chem. Soc.*, 570 (1963).

(26) See, for example, ref 16, p 128.

(27) R. F. Fenske, *Inorg. Chem.*, **4**, 33 (1965).

to the 26-kK value observed by Chien. The second transition $\psi_g \rightarrow (\text{core})(b_2)^1(a_1)^2(a_2)^1(a_1)^1$ gives 36.5 compared to the 37 kK measured. We know however that the a_1 and a_2 levels should be reversed, which involves the 7 kK which separates them.

We conclude that the "crystal field terms" play a significant role in a valid discussion of the electronic structure of $(C_5H_5)_2VCl_2$. Though the type II calculation predicts a ground state of incorrect symmetry, our previous discussion indicates that an energy shift of about 7 kK produces a MO picture which is in reasonable agreement with both the optical and epr data.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BRISTOL, BRISTOL, UNITED KINGDOM

Electronic Spectra of the Negative Ions of Some Metal Phthalocyanines

BY D. W. CLACK* AND J. R. YANDLE

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Reduction of metal phthalocyanines with sodium in tetrahydrofuran (or electrochemically at a mercury pool or platinum cathode) produces a series of negative ions, corresponding to the stepwise addition of electrons. The complexes with Zn(II), Ni(II), Fe(II), Mn(II), Mg(II), and $Al^{III}Cl$ form four distinct reduction stages, but for $Co^{II}Pc$ five reduction steps are found. The electronic absorption spectra are reported and used to discuss the electronic structures of the metal phthalocyanine negative ions. The spectroscopic observations indicate that all complexes, with the exception of $Co^{II}Pc$ and $Fe^{II}Pc$ give reduced species in which the additional electrons are confined essentially to the ring e_g orbital. Reduction of $Co^{II}Pc$ and $Fe^{II}Pc$ and possibly also $Mn^{II}Pc$ appears to involve electron addition to both ligand (e_g) and metal orbitals.

Introduction

Metal phthalocyanines and the closely related metal porphyrins may be reduced chemically[1,2] or electrochemically[3,4] to give a series of negative ions. This reduction corresponds to the successive addition of electrons to vacant or partially occupied orbitals of the metal complex. Which orbitals are used depends on the proximity of the vacant metal orbitals and the lowest unoccupied orbital e_g of the phthalocyanine ligand system. For complexes with closed-shell central ions (Mg^{2+}, Zn^{2+}) electron addition is confined to the π orbitals of the ligand system. It has been shown by both chemical[5] and polarographic[3,4,6] techniques that up to four electrons can be donated to these systems, and it is generally accepted that these negative ions result from the addition of electrons to the lowest vacant e_g orbital of the ring. On the other hand, when the central ion is transitional, the metal d orbitals lie close to the highest filled a_{1u} ring orbital and it is therefore possible that in some cases reduction of the central metal will take place.

Shablya and Terenin[7] first reported an anion of a metal phthalocyanine together with its electronic absorption spectrum by reducing magnesium phthalocyanine in tetrahydrofuran with sodium. A two-electron reduction of $Cu^{II}Pc$ (the abbreviation Pc for phthalocyanine will be used throughout this paper) using potassium in liquid ammonia has been observed and assigned to the species Cu^0Pc.[8] Taube has isolated higher reduction products of metal phthalocyanines as crystalline solids from solution by electron transfer from alkali metals and radical ions.[5] More recently the electronic absorption and electron spin resonance spectra of the mono- and dinegative ions of some metal phthalocyanine tetrasulfonates in dimethyl sulfoxide[9] and the electron spin resonance spectra of some transition metal phthalocyanines in tetrahydrofuran and hexamethylphosphoramide[10] have been reported. Polarographic measurements in dimethylformamide on the analogous metal porphyrins[3] have indicated that four reduction steps are possible which were assigned to the formation of mono-, di-, tri-, and tetranegative porphyrin ions, the latter having the e_g orbital filled to its complement of four electrons.

Polarographic measurements on the metal phthalocyanines have yielded similar results,[6] and in general four reduction waves are observed with the exception of $Co^{II}Pc$, which exhibits five steps.

Experimental Section

Electrochemical reduction in dimethylformamide–tetra-*n*-propylammonium perchlorate was effected in a three-electrode cell under an atmosphere of dry nitrogen using a controlled cathode potential. The absorption spectra were measured using a Beckman DK2 ratio recording spectrophotometer. Only the mono- and dinegative ions were sufficiently stable under these conditions to permit spectral measurements, the higher ions being oxidized by traces of atmospheric oxygen which unavoidably leaked into the cathode compartment.

The chemical reduction was carried out under high vacuum by slowly washing a solution of the metal phthalocyanine (10^{-3} *M*) in tetrahydrofuran over a sodium film, prepared by thermal decomposition of sodium azide. The reduction was monitored by following the changes in the absorption spectra of the metal phthalocyanine after each washing. In this way it was possible by washing only small amounts at any one time to characterize

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* Address correspondence to this author at the Department of Chemistry, University College, Cardiff, CF1 1XL, United Kingdom.

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