Paramagnetic Resonance of Some Carborane Analogs of Ferricenium Cation

August H. Maki and Thomas E. Berry[1]

Contribution from the Department of Chemistry, University of California, Riverside, California 92507. Received June 22, 1965

Paramagnetic resonance measurements have been made on a series of carborane analogs of π-$(C_5H_5)_2Fe^+$. The sandwich mode of bonding of the carborane cage through a five-atom face has been verified crystallographically only for the "mixed" sandwich π-(C_5H_5)-$Fe(B_9C_2H_{11})$ by Templeton and co-workers. The similarity in the g-values for this compound and the other members of the series of carborane–iron(III) complexes is taken as evidence that the carborane–metal bonding is alike. These complexes have been investigated theoretically using existing molecular orbital treatments of ferrocene in D_{5d} or D_{5h} symmetry as a starting point. It is assumed that the configuration of the six most highly energetic electrons of ferrocene is $(a_{1g}')^2(e_{2g}^{\pm})^4$, which is that given by many theories. Good agreement of the magnetic resonance data with theory is found for the zero-order configuration $(e_{2g}^{\pm})$ for the hole. Spin-orbit coupling is taken into account, and the departure of the carborane analogs from D_5 symmetry is treated as an effective crystal field perturbation. The configuration (a_{1g}') cannot account for the magnetic resonance data, on the other hand. The $e_{2g}^{\pm}$ orbitals are found to be principally localized on the iron atom.

Introduction

The molecular orbital theory of the metal sandwich compounds of cyclopentadienyl anion has been the subject of extensive investigation and debate for over 10 years.[2–12] The high symmetry of the bis-π-cyclopentadienyl metal complexes (either D_{5d} or D_{5h}) simplifies the calculations to a large extent, but there are generally large areas of disagreement among the various investigators concerning the ordering of the molecular orbitals by their one-electron energies. Wilkinson and Cotton[13] discuss and compare the results of the several theories published through 1958. The interpretation of the optical spectrum of ferrocene is also not firmly established because of the uncertainty

in the ground- and excited-state molecular orbital configurations. Most of the molecular orbital theories assign the six highest energy electrons of ferrocene to the configuration $(a_{1g}')^2(e_{2g}^{\pm})^4$, or $(e_{2g}^{\pm})^4(a_{1g}')^2$ in D_{5d} symmetry, although there is much variance in the atomic orbital description of these molecular orbitals. There is, on the other hand, a paucity of experimental data on the paramagnetic resonance of π-cyclopentadienyl metal compounds. Experiments of this nature are expected to yield a great deal of information about the ground-state molecular orbital descriptions of the paramagnetic sandwich compounds, which would be of use in checking various bonding theories as well as an aid in the assignments of optical transitions. A discussion of the magnetic resonance properties of some sandwich compounds has been given by Robertson and McConnell,[11] although the theory could not be carried very far because of the lack of experimental data. The data at that time were limited to magnetic resonance measurements on vanadocene,[14] $S = 3/2$, and $Cr(C_6H_6)_2^+$,[15] $S = 1/2$. The experimentally observed diamagnetism of titanocene[16] is consistent with a one-electron-energy ordering $a_{1g}' < e_{2g}^{\pm}$ in the π-cyclopentadienyls, whereas the observation of $g \sim 2.00$ for $Cr(C_6H_6)_2^+$,[15] which is low spin, argues for the ordering $e_{2g}^{\pm} < a_{1g}'$ in the π-benzene sandwich compounds. The work of Robertson and McConnell,[11] however, emphasizes the closeness of the one-electron energies of the a_{1g}' and $e_{2g}^{\pm}$ orbitals as an essential feature in the explanation of the magnetic susceptibilities of the π-cyclopentadienyl compounds $Ti(C_5H_5)_2^{+2}$ through $Fe(C_5H_5)_2$.

In this paper, we report on the paramagnetic resonance of some newly discovered[17,18] carborane analogs of ferricenium cation. These are sandwich compounds in which one (or two) carborane anion(s) of the general formula $B_9C_2H_{11-x}R_x^{-2}$ ($x = 2$, R = CH_3; $x = 1$, R = C_6H_5; $x = 0$) replaces one (or two) $C_5H_5^-$ ion(s) in sandwich bonding to the iron atom. A word of description of this unique carborane anion[17] is perhaps appropriate. $B_9C_2H_{11}^{-2}$ is formally related to the highly symmetric icosahedral $B_{12}H_{12}^{-2}$ ion. Formally, the removal of a BH^{+2} fragment yields the (hypothetical) ion $B_{11}H_{11}^{-4}$ which has a planar five-boron face with six electrons in delocalized orbitals directed roughly towards the vacant icosahedral position. Substitution of two isoelectronic CH^+ fragments for adjacent BH fragments on the five-boron face leads to the stable icosahedral fragment. This

(1) National Institutes of Health Predoctoral Fellow.

(2) (a) H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953); (b) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953); *J. Chem. Phys.*, **23**, 954 (1955).

(3) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

(4) M. Yamasaki, *J. Chem. Phys.*, **24**, 1260 (1956).

(5) E. Rush, *Rec. trav. chim.*, **75**, 638 (1956).

(6) A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957).

(7) F. A. Matsen, *J. Am. Chem. Soc.*, **81**, 2023 (1959).

(8) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959); **131**, 113 (1960); **133**, 141 (1960); *Zh. strukt. Khim.*, **3**, 345 (1962).

(9) J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **33**, 5 (1961).

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

(11) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.*, **64**, 70 (1960).

(12) L. L. Lohr, Jr., *J. Chem. Phys.*, to be published.

(13) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

(14) H. M. McConnell, W. W. Porterfield, and R. E. Robertson, *J. Chem. Phys.*, **30**, 442 (1959).

(15) R. D. Feltham, P. Sogo, and M. Calvin, *ibid.*, **26**, 1354 (1957).

(16) A. K. Fischer and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 149 (1956).

(17) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(18) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965).

ion has only C_{2s} symmetry in contrast with the parent ion $B_{11}H_{11}^{-4}$, which would have C_{5v} symmetry. The R group when present is bonded to a carbon atom. This description of the ion emphasizes the similarity between the electronic structure of the B_3C_2 face and the delocalized π electrons of $C_5H_5^-$.

The sandwich mode of bonding, predicted by Hawthorne,[17] which is utilized by the ion $B_9C_2H_{11}^{-2}$ has recently been established by an X-ray structure determination of the "mixed" sandwich compound π-$(C_5H_5)Fe(B_9C_2H_{11})$ by Templeton and co-workers.[19] In spite of the relatively low symmetry of $B_9C_2H_{11}^{-2}$, the Fe nearest neighbor atom bond distances in the compound π-$(C_5H_5)Fe(B_9C_2H_{11})$ are remarkably uniform. These are given[19] as Fe–B(4, 5, 6) = 2.09 Å.; Fe–C(2, 3) = 2.04 Å.; Fe–C(cyclopentadienyl) = 2.07 Å., with no significant differences within the groups listed. Within the uncertainty of the relatively large thermal parameters, the five-carbon face of the cyclopentadienyl, and the two-carbon, three-boron face of the carborane are very nearly parallel. The icosahedral fragment is also found to be nearly regular. The eclipsed conformation appears to be favored in the crystal, although a great deal of thermal motion is found, as in ferrocene.[20]

The compelling similarity of the molecular structure of the carborane ferricenium analog to ferrocene has prompted us to use a ferrocene molecular orbital description as a first approximation of the electronic structure of these compounds. Thus, beginning with a ground-state configuration based on D_5 symmetry, deviations of the carborane local symmetry from C_{5v} are treated as ligand-field perturbations of lower than fivefold symmetry. These perturbations, along with the spin–orbit coupling Hamiltonian, are used to find the ground-state Kramers' doublet wave functions by means of perturbation theory. Expressions for $g_{||}$ and $g_\perp$ are obtained from the perturbed wave functions and are compared with experiment. All compounds investigated in this work are low spin, $S = {}^1/_2$, as evidenced by their magnetic susceptibilities.[21]

Experimental Section

All paramagnetic resonance measurements were made using a Varian Associates V-4500 e.p.r. spectrometer, employing 100-kc./sec. field modulation. The klystron frequency was measured by means of a transfer oscillator and electronic counter (Hewlett-Packard, 540 B, and 5245 L, respectively). Magnetic field measurements were made with a proton resonance gaussmeter using the same electronic counter.

Measurements were made at $\sim85°K$. Samples were frozen in liquid nitrogen and maintained at 85°K. during the measurement by means of a cooled-nitrogen flow system. Concentrated 1:1 v./v. $CHCl_3$–DMF glasses of the $(CH_3)_4N^+$ salts of $Fe(B_9C_2H_{11})_2^-$, $Fe[B_9H_9C_2-(CH_3)_2]_2^-$, and $Fe[B_9H_9C_2H(C_6H_5)]_2^-$ were run, as well as a similar glass of neutral π-$(C_5H_5)Fe(B_9C_2H_{11})$. Solid, polycrystalline $(CH_3)_4NFe[B_9H_9C_2H(C_6H_5)]_2$ was

(19) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, 87, 3988 (1965).
(20) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 9, 373 (1956).
(21) D. C. Young, private communication, has measured the magnetic susceptibilities of analyzed samples of the carbornane–iron(III) complexes investigated in this work.

also measured at 85°K. Analytical samples of these compounds were generously provided by Professor M. F. Hawthorne.

In each case, the observed polycrystalline line shape could be fitted with an axial g-tensor. No hyperfine structure was observed, and the lines were very broad, averaging about 500 gauss. The lines in the polycrystalline salts were too broad to be observed at room temperature.

The observed values of $g_{||}$ and $g_\perp$ are given in Table I.

Theory

We begin with the assumption that the molecular orbital configuration of the six highest energy electrons of ferrocene is $(a_{1g}')^2(e_{2g}^\pm)^4$ in D_{5d} symmetry, and that the configuration of ferricenium cation is either $(a_{1g}')^2$-$(e_{2g}^\pm)^3$ or $(e_{2g}^\pm)^4(a_{1g}')^1$ if the symmetry remains D_{5d}. This assumption is consistent with most of the molecular orbital calculations presently available for ferrocene. We will confine the theory further by neglecting admixtures of states outside the two lowest energy configurations. Several molecular orbital calculations yield the result that these configurations should be well separated in energy from the next excited configuration. Lohr's calculation,[12] for instance, gives the relative one-electron energies of the three lowest energy configurations of ferricenium ion as $\ldots(e_{2g}^\pm)^4(a_{1g}')^1 = 0.000, \ldots(e_{2g}^\pm)^3(a_{1g}')^2 = 0.818$, $\ldots(e_{2g}^\pm)^4(e_{1g}^\pm*)^1 = 2.975$, where the energies are expressed in electron volts. An earlier SCF LCAO–MO calculation by Shustorovich and Dyatkina[8] gives the relative one-electron energies of the three lowest configurations as $\ldots(e_{1g}^\pm)^4(a_{1g}')^2(e_{2g}^\pm)^3 = 0.00, \ldots(e_{1g}^\pm)^4$-$(a_{1g}')^1(e_{2g}^\pm)^4 = 2.05$, and $\ldots(e_{1g}^\pm)^3(a_{1g}')^2(e_{2g}^\pm)^4 = 4.63$ e.v.

Thus, confining ourselves to a manifold of the two lowest energy configurations, the five-electron problem may be replaced with one of a single hole, which will have the configuration $(e_{2g}^\pm)$ or (a_{1g}'). We will calculate the expected paramagnetic resonance properties of $Fe(C_5H_5)_2^+$ in D_5 symmetry for each of these configurations, taking into account spin–orbit coupling and the effects of crystal fields of lower symmetry. Electron–electron Coulomb interactions need not be considered as long as we restrict ourselves to this manifold of two configurations.

1. The Configuration $(e_{2g}^\pm)$ Lies Lowest in Energy. It we assume that the site symmetry of the iron atom remains rigorously D_5, we need consider only the spin–orbit coupling, represented by the Hamiltonian $\mathcal{H}_{so} = \xi(r)\mathbf{l}\cdot\mathbf{s}$. $\mathcal{H}_{so}$ contains no matrix elements connecting the manifold of states $\{e_{2g}^+\alpha, e_{2g}^-\alpha, e_{2g}^+\beta, e_{2g}^-\beta,\}$ with the excited manifold $\{a_{1g}'\alpha, a_{1g}'\beta\}$. The states $e_{2g}^+\alpha$, $e_{2g}^-\beta$ remain degenerate and span the irreducible representation E'' of the double group D_5' (see Appendix). The states $e_{2g}^+\beta$, $e_{2g}^-\alpha$, on the other hand, form a basis for the representation A', A'', and must also remain degenerate according to Kramers' theorem. The states $a_{1g}'\alpha$, $a_{1g}'\beta$ form a basis for the E' representation of D_5'.

With $\xi = \langle e_{2g}^+|\xi(r)|e_{2g}^+\rangle$, we find the energies of the three lowest doublets at $W(E'') = +\xi$, $W(A',A'') = -\xi$, and $W(E') = \Delta$, where Δ is the excitation energy to the hole configuration (a_{1g}'). Since ξ is negative for a hole, $\Psi_\pm(E'')$ is the ground doublet

Compound[a]	$g_{||}$	$|g_\perp|$	$|\zeta|$	k'	$|\delta|$, cm.$^{-1}$
$Fe(B_9C_2H_{11})_2^-$	3.944 ± 0.032^b	1.532 ± 0.011	0.466	0.76	364
$Fe[B_9H_9C_2(CH_3)_2]_2^-$	3.786 ± 0.029	1.711 ± 0.003	0.562	0.86	572
$\pi\text{-}(C_5H_5)Fe(B_9C_2H_{11})^{0c}$	3.579 ± 0.010	1.778 ± 0.003	0.610	0.86	679
$Fe[B_9H_9C_2H(C_6H_5)]_2^-$	3.572 ± 0.029	1.799 ± 0.005	0.626	0.90	750
$Fe[B_9H_9C_2H(C_6H_5)]_2^{-d}$	3.700 ± 0.026	1.725 ± 0.006	0.573	0.84	580

^{a} Run as glasses of the $(CH_3)_4N^+$ salt in 1:1 v./v. $CHCl_3$–DMF at $\sim 85°K.$, unless noted. ^{b} Uncertainties are average deviations in several measurements. ^{c} Neutral molecule. ^{d} Polycrystalline solid.

state. The g-values are given by the following equations.

$$g_{||} = 2\langle \Psi_+(E'')|l_z + 2s_z|\Psi_+(E'')\rangle = 6$$

$$g_\perp = 2\langle \Psi_+(E'')|l_x + 2s_x|\Psi_-(E'')\rangle = 0 \quad (1)$$

If the wave functions $e_{2g}^\pm$ are covalent and represented by the molecular orbitals

$$e_{2g}^\pm = k(d_{\pm 2}) + \sqrt{1 - k^2}(cpe_{2g}^\pm) \quad (2)$$

where $cpe_{2g}^\pm$ are linear combinations of atomic orbitals of the cyclopentadienyl rings transforming in the same manner as the metal $d_{\pm 2}$ orbitals, then we would expect that $\xi \sim -k^2\xi_o$, where ξ_o is the one-electron spin-orbit coupling constant of a free iron atom. We might also expect a reduction of the orbital contribution to $g_{||}$ calculated above to the extent that the orbital angular momentum of the $cpe_{2g}^\pm$ wave function is quenched by low-symmetry external fields and unsymmetrical skeletal vibrations of the ring atoms. If k' is the orbital reduction factor, we find

$$g_{||} = 2(2k' + 1), \quad g_\perp = 0 \quad (3)$$

Generally, $k^2 \leq k' \leq 1$, is expected to hold.

With $\xi_o \sim 400$ cm.$^{-1}$, relatively small external electric fields may cause considerable admixture of $(\Psi A', A'')$ with $\Psi(E'')$. This admixture will have a profound effect upon the paramagnetic resonance properties of the compound. We proceed next to consider the effects of low-symmetry crystal fields, which may have their source either external to the ion, or internally, if, as an example, a carborane face with three boron atoms and two carbon atoms is substituted for the C_5H_5 ring. If $\mathcal{K}_0$ is the effective one-electron molecular Hamiltonian which results in the previously described molecular orbital configuration in D_5 symmetry, we will let $\mathcal{K}'$ represent a crystal-field Hamiltonian which describes either externally generated electric fields, or a reduction in symmetry due to the substitution of boron atoms for carbon atoms in the molecule. The complete one-electron Hamiltonian for the system is thus

$$\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_{so} + \mathcal{K}' \quad (4)$$

Initially, we will assume that $\mathcal{K}'$ is relatively small, and that Δ is comparatively large, i.e., $\Delta \gg \mathcal{K}' \simeq \mathcal{K}_{so}$. Therefore, we need consider only matrix elements of $\mathcal{K}'$ and $\mathcal{K}_{so}$ within the lowest-energy manifold of $\mathcal{K}_0$, $\{\Psi(A',A''), \Psi(E'')\}$. Furthermore, $\mathcal{K}'$ may be expanded in a series of spherical harmonics in the coordinates of the hole

$$\mathcal{K}' = \sum_{l, m} r^l[A_l^m Y_l^m(\theta, \phi) + A_l^{m*} Y_l^{-m}(\theta, \phi)] \quad (5)$$

where r, θ, and ϕ are the polar coordinates of the hole in a coordinate system centered on the iron atom, the Y_l^m are normalized spherical harmonic functions, and the A_l^m are coefficients. We will ignore all terms of $\mathcal{K}'$ with $m = 0$, since these contribute equally to the energies of all levels within the ground manifold. Within this manifold, the only nonzero matrix elements occur for $l = 4$ and $|m| = 4$, and thus eq. 5 is considerably simplified to the following effective perturbation Hamiltonian

$$\mathcal{K}'_{eff} = (2\pi)^{-1/2}r^4P_4^4(\cos\theta)[A_4^4e^{4i\phi} + A_4^{4*}e^{-4i\phi}] \quad (6)$$

$P_l^{|m|}(\cos\theta)$ is a normalized Legendre polynomial. Using $\mathcal{K}'' = \mathcal{K}_{so} + \mathcal{K}'_{eff}$ as a new perturbation Hamiltonian within the manifold $\{\Psi(A'A''), \Psi(E'')\}$, we obtain the following pair of Kramers' doublet states by solving the appropriate 2 by 2 secular determinants.

$$\Psi_\pm^{(a)} = \begin{cases} N(e_{2g}^+ + \zeta e_{2g}^-)\alpha \\ N(e_{2g}^- + \zeta e_{2g}^+)\beta \end{cases} \quad W^{(a)} = -(\xi^2 + \delta^2)^{1/2} \quad (7)$$

$$\Psi_\pm^{(b)} = \begin{cases} N(e_{2g}^- - \zeta e_{2g}^+)\alpha \\ N(e_{2g}^+ - \zeta e_{2g}^-)\beta \end{cases} \quad W^{(b)} = +(\xi^2 + \delta^2)^{1/2} \quad (8)$$

In these equations, $\delta = \langle e_{2g}^+|\mathcal{K}'_{eff}|e_{2g}^-\rangle$, $N = (1 + \zeta^2)^{-1/2}$, and $\zeta = x/[1 + (1 + x^2)^{1/2}]$, where $x = \delta/\xi$. The g-values of the ground state are readily calculated. We find

$$g_{||}^{(0)} = 2\langle \Psi_+^{(a)}|l_z + 2s_z|\Psi_+^{(a)}\rangle = 2 + 4k'(1 - \zeta^2)/(1 + \zeta^2) \quad (9)$$

$$g_\perp^{(0)} = 2\langle \Psi_+^{(a)}|l_x + 2s_x|\Psi_-^{(a)}\rangle = 4\zeta/(1 + \zeta^2) \quad (10)$$

The limiting values of ζ are 0, corresponding to $x = 0$, and ± 1, corresponding to $x = \pm\infty$. The sign of $g_\perp^{(0)}$ is the same as that of x, and thus depends upon the sign of the effective crystal field matrix element δ. Since $\mathcal{K}'$ varies as r^l, we would expect effective quenching of the orbital angular momentum of the electron when it appears in the ring orbitals. The orbital reduction factor k' then becomes a measure of the covalency of the $e_{2g}^\pm$ functions, with $k' \sim k^2$.

A plot of $g_{||}^{(0)}$ and $g_\perp^{(0)}$ vs. ζ is given in Figure 1. The $g_{||}$ curves are symmetric to reflection about $\zeta = 0$, whereas the $g_\perp$ curve is antisymmetric. The experimentally measured values of $g_{||}$ and $g_\perp$ are given in Table I, along with values of $|\zeta|$ and k' calculated from eq. 9 and 10. The value of $|\delta|$ is also included. We have used $\xi = -k'\xi_0$ to obtain $|\delta|$, with $\xi_0 = 405$ cm.$^{-1}$.[22]

The g-values will also be affected, but to a lesser

(22) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961). We have used a value of ξ_0 corresponding to iron in the oxidation state Fe(II). This choice is made because population analysis of the electron distribution in the ferrocene ground-state configuration gives a charge close to +1 in several calculations. The highest-filled orbital in these calculations is localized principally on the metal.
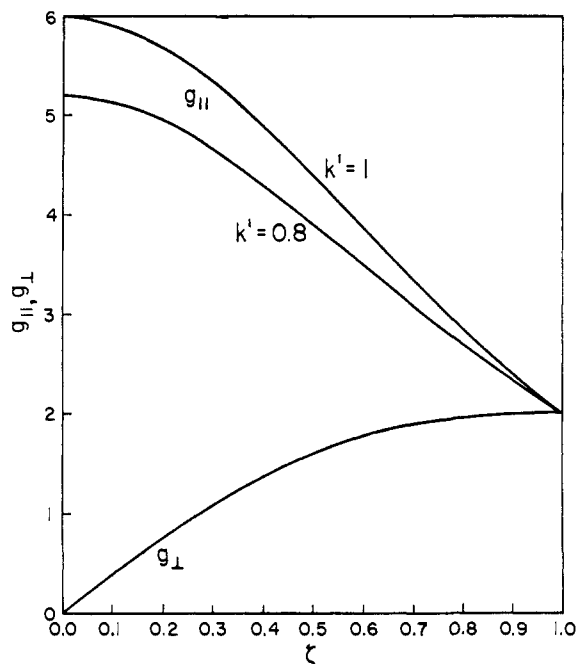
Figure 1. Plot of $g_{||}^{(0)}$ and $g_{\perp}^{(0)}$ vs. the parameter ζ for two values of the orbital reduction factor k'. The g-values are computed from eq. 9 and 10.

extent by components of $\mathfrak{IC}'$ with $|m| = 2, l = 2, 4$. These will result in the mixing of the states $\Psi_{\pm}(E')$ with the ground state $\Psi_{\pm}^{(a)}$. If Δ is sufficiently large, this mixing will not be important. Treating the $|m| = 2$ components of $\mathfrak{IC}'$ by perturbation theory through second order, we find that

$$g_{||} \simeq g_{||}^{(0)} - \frac{8\epsilon^2 k' \zeta (1 - \zeta^2)^2}{|\xi|\Delta(1 + \zeta^2)^3} + \text{terms in } \epsilon^2/\Delta^2$$

$$g_{\perp} \simeq g_{\perp}^{(0)} + \text{terms in } \epsilon^2/\Delta^2$$

where $\epsilon = \langle e_{2g}^{\pm}|\mathfrak{IC}'|a_{1g}'\rangle$. If $|\epsilon| \sim |\delta|$, Δ would have to be less than about 0.5 e.v. to make the correction terms at all significant.

2. The Configuration (a_{1g}') Lies Lowest in Energy. In the absence of a low-symmetry crystal field perturbation $\mathfrak{IC}'$, the g-value is expected to be very nearly isotropic and equal to 2. This is because the state $\Psi_{\pm}(E')$ carries no orbital momentum, and the excited manifold $\{\Psi(A',A''), \Psi(E'')\}$ is not admixed by $\mathfrak{IC}_{so}$. Components of $\mathfrak{IC}'$ with $|m| = 2, l = 2, 4$, however, will cause the admixture of the excited manifold with $\Psi_{\pm}(E')$. Defining Δ as the average excitation energy to the $\{\Psi(A',A''), \Psi(E'')\}$ manifold, and assuming that $\mathfrak{IC}' < \Delta$, we find

$$g_{||} \simeq 2 - 8k'\zeta\epsilon^2/\Delta^2(1 + \zeta^2) + \text{terms in } \epsilon^2|\xi|/\Delta^3$$

$$g_{\perp} \simeq 2$$

Thus, unless Δ is very small, the g-tensor will be nearly isotropic with a value close to that of a free spin. The (a_{1g}') configuration is thus seen to be in very poor agreement with the g-tensors observed in the carborane ferricenium analogs. It may be concluded that the ground-state configuration of the carborane ferricenium analogs investigated in this work is most likely $(e_{2g}^{\pm})$, which leads to magnetic properties in good agreement with the experiments.

Discussion

We find that the paramagnetic resonance of a series of carborane ferricenium analogs can be explained by a theory based upon a set of ferrocene-like molecular orbitals in which an electron has been removed from the highest-filled $e_{2g}^{\pm}$ molecular orbital. The reduction of symmetry of the ligands from ferrocene has been treated by an effective crystal-field Hamiltonian of lower than fivefold symmetry. The qualitative similarity of the paramagnetic resonance spectra within this series of compounds is good evidence for sandwich bonding in all of them, even though this structure has been established crystallographically only for the member, $(C_5H_5)Fe(B_9C_2H_{11})$.[19]

Ferricenium cation itself, if it should have rigorously D_5 symmetry, is predicted to have $g_{||} \sim 6$, $g_{\perp} = 0$, and consequently the paramagnetic resonance would be extremely difficult to observe in a polycrystalline or glassy sample. On the other hand, $Fe(C_5H_5)_2^+$, D_5, should be extremely sensitive to external fields arising from the environment, and thus a distribution of g-values may occur in glassy samples.

All samples are predicted to have short spin–lattice relaxation times at room temperature, because of the proximity of the excited state $\Psi_{\pm}^{(a)}$ to the ground state. This energy splitting in our theory is $2(\xi^2 + \delta^2)^{1/2}$, which is predicted to be 950 cm.$^{-1}$ in $Fe(B_9C_2H_{11})_2^-$, and about 1300 to 1500 cm.$^{-1}$ in the others. The splitting is largest in a glass of $Fe[B_9H_9C_2H(C_6H_5)]_2^-$ which also gives the narrowest resonance lines at $85°K$. The solid salt $(CH_3)_4NFe[B_9H_9C_2H(C_6H_5)]_2$ was the only crystalline material in which $g_{||}$ and $g_{\perp}$ could be resolved at $85°K$. There is apparently a large medium effect on $g_{||}$ and $g_{\perp}$ which results mainly from a reduction in $|\delta|$ for the solid salt compared with the glass. In this case we find evidence that a significant part of $\mathfrak{IC}'$ originates from the external environment of the ion. Although all the solid tetramethylammonium salts showed intense paramagnetic resonance absorption at $85°K.$, these signals were virtually undetectable at room temperature. It appears that T_1 may be as short as 10^{-9}–10^{-10} sec. at room temperature.

The values of k' are a measure of the covalency of the $e_{2g}^{\pm}$ orbitals. For these compounds, $k' \sim k^2$ should hold, where k is the coefficient of the $d_{\pm 2}$ orbitals in the $e_{2g}^{\pm}$ orbitals. Several molecular orbital calculations on ferrocene predict that this orbital should be principally localized on the metal. Shustorovich and Dyatkina[8] give $k^2 = 0.72$, while Lohr[12] gives $k^2 = 0.82$. Our values of k' are thus in substantial accord with the theoretical picture of these orbitals. We find that the most covalent orbital occurs in the unsubstituted $Fe(B_9C_2H_{11})_2^-$ ion.

Several attempts to measure paramagnetic resonance in $Fe(C_5H_5)_2^+$ samples at $85°K.$ failed to give any signals which could be attributed to this ion. The systems investigated were $Fe(C_5H_5)_2I_{20}$(solid), $Fe(C_5H_5)_2I_6$(solid), $Fe(C_5H_5)_2[B(C_6H_5)_4]$(solid), and $Fe(C_5H_5)_2NO_3$ as a glass in $CHCl_3$–DMF, as well as in methanol. It is probable that T_1 is extremely short, and that measurements must be made at lower temperature. It is unlikely that the configuration of $Fe(C_5H_5)_2^+$, if D_5, is (a_{1g}'), because of the difficulty in observing paramagnetic resonance in these systems.

Table II. Characters of the Double-Valued Representations of D_5'

D_5'	E	R	$2C_5$	$2RC_5$	$2C_5^2$	$2RC_5^2$	$5C_2'$	$5RC_2'$
A'	1	-1	-1	1	1	-1	i	$-i$
A''	1	-1	-1	1	1	-1	$-i$	i
E'	2	-2	$2\cos(x/2)$	$-2\cos(x/2)$	$2\cos x$	$-2\cos x$	0	0
E''	2	-2	$-2\cos x$	$2\cos x$	$-2\cos(x/2)$	$2\cos(x/2)$	0	0

$$(x = 2\pi/5)$$

Science Foundation for the support of this research through the Grant GP-3398. We wish to thank Professor M. F. Hawthorne for samples of the carborane ferricenium analogs, as well as for many stimulating discussions about the properties of these interesting molecules. We are grateful to Professor D. H. Templeton and Dr. L. L. Lohr for copies of their manuscripts prior to publication.

Appendix

The character table for the double group D_5' does not appear to be readily available in the literature. We have worked out this table, and present the characters of the double-valued representations in this Appendix. The point group D_5 consists of four ir-

reducible representations, generally labeled[23] A_1, A_2, E_1, and E_2. In the double group D_5', the number of classes is doubled by multiplication by the operation R, a rotation of 2π about the C_5 axis.[24,25] We label the added double-valued representations A', A'', E', and E''. The characters of these new representations are given in Table II.

(23) See, for instance, M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p. 327.

(24) H. A. Bethe, *Ann. Physik*, 3, 133 (1929).

(25) W. Opechowski, *Physica*, 7, 552 (1940), has shown that C_2 and RC_2 belong to the same class if, and only if, the group contains another twofold axis perpendicular to the first. This second twofold axis does not occur in the groups D_n' where n is odd. Consequently, the elements C_2' and RC_2' belong to different classes of D_5'.

The Photochromism of Metal Dithizonates

L. S. Meriwether, E. C. Breitner, and C. L. Sloan

Contribution from the Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut. Received April 1, 1965

Twenty-four metal complexes of dithizone have been prepared, characterized, and examined for their photochemical and photochromic behavior in solution. The following nine complexes are photochromic under steady illumination with visible light: $Pd(HDz)_2$, $Pt(HDz)_2$, $AgHDz$, $Zn(HDz)_2$, $Cd(HDz)_2$, $Hg(HDz)_2$, $Pb(HDz)_2$, $Bi(HDz)_3$, and $Bi(HDz)_2Cl \cdot 2HCl$. Various color changes are observed, ranging from orange → blue to green → yellow. Return reactions are very fast. The photochemical stability of the complexes in benzene solution to ultraviolet light decreases in the order $Ni(HDz)_2 > Zn(HDz)_2 > Hg(HDz)_2 > Pd(HDz)_2 > Pt(HDz)_2 \sim AgHDz > Pb(HDz)_2 > H_2Dz > Cd(HDz)_2$. Several generalizations are made regarding the colors and photochromism of dithizone complexes.

Introduction

Dithizone (diphenylthiocarbazone, H_2Dz) has long been used as a reagent for the colorimetric analysis of trace metals.[1,2] However, it is only recently that evidence has begun to accumulate on the properties and structures of the complexes thus formed.[3–5]

Even less is known of the photochemical behavior of the free ligand and its complexes. Although several workers[1–3,6] have noted light sensitivity in this class of compounds and have carried out their experiments in the dark or diffuse light, the possible adverse effects on the analytical applications of these complexes have not been generally recognized, and no detailed investigations of photochemical effects have been made. Around 1950 Irving, et al.,[7] and Webb, et al.,[8] reported independently that the mercury(II) complex is photochromic. When benzene or chloroform solutions of $Hg(HDz)_2$ were irradiated or placed in bright sunlight, they changed from their normal orange-yellow color to "an intense royal-blue." They found that the orange-yellow color returned slowly in the dark and that these color changes could be repeated many times. Apparently, these unusual observations were never followed up. We now wish to report on a more detailed study of this system, which has led to the discovery of a large number of photochromic metal dithizonates and a better understanding of the photochemical behavior of these complexes.

(1) G. Iwantscheff, "Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse," Verlag Chemie, G.m.b.H., Weinheim/Bergstr., Germany, 1958.

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1959.

(3) H. Irving and R. S. Ramakrishna, *J. Chem. Soc.*, 2118 (1961), and earlier papers in this series.

(4) M. M. Harding, *ibid.*, 4136 (1958).

(5) R. F. Bryan and P. M. Knopf, *Proc. Chem. Soc.*, 203 (1961).

(6) G. Venturello and A. M. Ghe, *Ann. chim.*, 45, 1054 (1955).

(7) H. Irving, G. Andrew, and E. J. Risdon, *J. Chem. Soc.*, 541 (1949).

(8) J. L. A. Webb, I. S. Bhatia, A. H. Corwin, and A. G. Sharp, *J. Am. Chem. Soc.*, 72, 91 (1950).