I

ISOTROPIC NUCLEAR RESONANCE SHIFTS

II

THE MAGNETIC RESONANCE PROPERTIES OF SOME SANDWICH MOLECULES

Thesis by

Richard Earl Robertson

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1960

"Heaven keep me from ever completing anything. This whole book is but a draught -- nay, but a draught of a draught."

Herman Melville
Moby Dick

ACKNOWLEDGMENT

For his able leadership, unceasing concern, and contagious enthusiasm, I wish to pay gratitude to my research advisor, Dr. Harden M. McConnell. It has been a privilege to have worked with a man of such quick scientific insights. My work owes, as well, to fellow students who furnished necessary experimental data.

My sincere thanks go to the following groups without whose aid graduate study would have been beyond my financial reach: California Institute of Technology, duPont Chemical Company, Dow Chemical Company, U. S. Rubber Company, General Electric Educational and Charitable Fund, National Science Foundation.

Finally, I wish to acknowledge the irreplaceable stimulus of the "Caltech environment." For the rich exchange of ideas, the memorable warmth of fellowship, the inspiration of fine minds, I will always be in debt.

ABSTRACT

Isotropic Nuclear Resonance Shifts

It is shown that isotropic or average nuclear resonance shifts for a nucleus in a paramagnetic molecule in solution, and in a polycrystalline solid, can be used to distinguish between Fermi contact and "pseudo contact" contributions to isotropic nuclear hyperfine interactions. The pseudo contact interaction is that isotropic hyperfine coupling which arises from the combined effects of (electron-spin)-(nuclear-spin) coupling, (electron-orbit)-(nuclear-spin) coupling, and electron spin-orbit interaction. When the magnetic hyperfine interaction between the electronic moment and nuclear spin is approximated by a point dipolar interaction, and the isotropic hyperfine interaction is exclusively pseudo contact, then the isotropic nuclear shift in a polycrystalline solid exceeds the solution shift by the factor $3(g_{\parallel} + g_{\perp})/(g_{\parallel} + 2g_{\perp})$ where $g_{\parallel}$ and $g_{\perp}$ are the spectroscopic splitting factors parallel and perpendicular to the molecular symmetry axis. Isotropic shifts due to the Fermi contact interaction are the same for both solid state and solution cases.

The Magnetic Resonance Properties of Some Sandwich Molecules

Estimates are given for the magnetic resonance properties of the dicyclopentadienyl and dibenzene sandwich compounds containing the transition metals titanium to nickel. This work follows that of Abragam and Pryce.

To obtain a first orientation to the orbital arrangements and splittings two models are considered, the ionic and covalent models. The ionic model is represented by the ligand field approximation and with the exception of $Mn(C_5H_5)_2$ strong ligand field theory has general applicability although not to the exclusion of weak ligand field theory in several molecules. It has been assumed that the ionic model applies only to the dicyclopentadienyl metal molecules and ions. The covalent model is considered for both the dicyclopentadienyl and dibenzene molecules and ions. The covalent model leads to the same general results as the ionic model. One important result with the covalent model is that orbital angular momentum about the symmetry axis is not necessarily quenched - the ionic model shows it to be conserved in first-order. Both models show that with the exception of $Mn(C_5H_5)_2$ three one-electron orbitals lie considerably lower than the other 3d orbitals and electrons are added to these orbitals according to Hund's rule. The ground state of $Mn(cp)_2$ is apparently the ^6S atomic term of Mn^{+2}.

Using the results of the two models as a first orientation the results of the magnetic susceptibility experiments (i.e., the observed deviation from spin only values) are used to choose appropriate arrangements for the three low-lying one-electrons in calculating the fine structure. The fine structure is considered for both when the Jahn-Teller effect splits a degenerate orbital ground state and when spin-orbit interaction splits the orbital ground state without the Jahn-Teller distortion. However, it is found that the Jahn-Teller effect operates when appropriate in all the molecules and ions with the possible exception of $Fe(C_5H_5)_2^+$. Expressions are given for the g-factors and zero-field splittings, although the lack of knowledge as to the values of many of the parameters precluded numerical estimates in most cases.

Hyperfine structure is considered although not in much detail. Cognizance is taken of the fact that "exchange polarization", which results from paramagnetism of the ion causing the α and β spins in the $1s^2$, $2s^2$, and $3s^2$ configurations to be in slightly different orbitals, leads to negative hyperfine coupling coefficients while unpaired electrons being in orbitals having s-character leads to a positive coupling coefficient.

TABLE OF CONTENTS

Section Page

II. (cont'd.)

I

ISOTROPIC NUCLEAR RESONANCE SHIFTS

Introduction

Important information on the molecular electronic structure of paramagnetic molecules can sometimes be deduced from experimentally measured terms in a molecular (electron-spin)-(nuclear-spin) spin Hamiltonian:

$$A \underset{\sim}{S} \cdot \underset{\sim}{I} + \underset{\sim}{S} \cdot \underset{\sim}{\mathcal{D}} \cdot \underset{\sim}{I} + \underset{\sim}{S} \cdot \underset{\sim}{\mathcal{E}} \cdot \underset{\sim}{I} \qquad (1)$$

In equation 1 $\underset{\sim}{\mathcal{D}}$ is a symmetric dyadic with zero trace, and $\underset{\sim}{\mathcal{E}}$ is an antisymmetric dyadic. Of particular interest is the isotropic hyperfine coupling term A. Especially interesting features of molecular electronic structure can sometimes be obtained from experimental values for A when this isotropic interaction is dominated by the Fermi contact coupling. From this point of view it is unfortunate that the combined effects of (electron-spin)-(nuclear-spin) coupling, (electron-orbit)-(nuclear-spin) coupling, and electron spin-orbit interaction can also lead to an isotropic component of the hyperfine interaction. Thus, in general, $A = A_c + A_p$, where A_c is the contact contribution to A, and A_p is the pseudo contact contribution. This pseudo contact coupling is well known in the theory of hyperfine interaction of ions in crystals (1), and it has also been considered in connection with proton hyperfine splittings in the paramagnetic resonance spectra of polyatomic radicals in solution (2).

The present paper is concerned with the problem of relating isotropic (or average) nuclear resonance shifts to the contact and pseudo contact interactions, $\mathbf{A}_c$ and $\mathbf{A}_p$. As will be shown in the present work, the isotropic shift of a nucleus in a rapidly tumbling paramagnetic molecule in solution is determined by the isotropic contact and pseudo contact hyperfine terms, $\mathbf{A} = \mathbf{A}_c + \mathbf{A}_p$. The isotropic shift of an ensemble of non-tumbling molecules in a polycrystalline solid involves not only the isotropic but also the anisotropic hyperfine terms in equation 1. This means that the isotropic resonance shifts will be different in the two cases if the pseudo contact coupling makes a significant contribution to the isotropic hyperfine interaction. This is because a pseudo contact contribution to $\mathbf{A}$ implies the simultaneous presence of anisotropic terms in equation 1, whereas a pure isotropic contact contribution to equation 1 requires no anisotropic terms.

This fact suggests a particularly convenient method for distinguishing between contact and pseudo contact contributions to hyperfine interactions when isotropic nuclear shifts can be measured both in the solid state and in solution.

Isotropic shifts in solutions due to a pseudo contact interaction were first discussed by Bloembergen and Dickinson (3, 4) in connection with resonance shifts of nuclei in ions in solutions. Our theoretical expression for the isotropic shift in solution is, however, not

precisely the same as that obtained by Bloembergen and Dickinson (3, 4). Isotropic shifts in solution are known that are due exclusively to the contact interaction (5). The present work was stimulated by our earlier studies of proton resonance shifts in the bicyclopentadienyl complexes of paramagnetic metal ions, and by the question as to whether these shifts were due to contact or pseudo contact interactions (6, 7).

In section A we will derive the isotropic nuclear resonance shifts from the (electron-spin)-(nuclear-spin) spin Hamiltonian such as equation 1 for the cases where the paramagnetic molecule is a) in a polycrystalline solid, b) in solution where the rate of electron-spin relaxation is very much greater than the rate of tumbling, $\tau_c \gg T_{1e}$, and c) in solution where $\tau_c \ll T_{1e}$. In section B we will consider the results obtained in section A when the spin Hamiltonian arises from the Fermi contact and from the pseudo contact interactions.

A. Derivation of the Isotropic Nuclear Resonance Shifts from the Spin Hamiltonian

General Considerations. For our problem of the isotropic resonance shifts of a nucleus contained in a paramagnetic molecule, the spin Hamiltonian has the form

$$\mathcal{H} = |\beta| \underset{\sim}{S} \cdot \underset{\sim}{g} \cdot \underset{\sim}{k} H_o - \gamma\hbar \underset{\sim}{I} \cdot \underset{\sim}{k} H_o + |\beta| \gamma\hbar \underset{\sim}{S} \cdot \underset{\sim}{a} \cdot \underset{\sim}{I} \qquad (2)$$

It should be noted that the last term of equation 2 corresponds to equation 1, but for present purposes it is more convenient to express the (electron-spin)-(nuclear-spin) interaction through the dyadic $\underset{\sim}{a}$. Equation 2 can also be written as

$$\mathcal{H} = |\beta| \underset{\sim}{S} \cdot \underset{\sim}{g} \cdot \underset{\sim}{k} H_o - \gamma\hbar (\underset{\sim}{k} H_o - \underset{\sim}{H}_N) \cdot \underset{\sim}{I}, \qquad (3)$$

where

$$\underset{\sim}{H}_N = |\beta| \underset{\sim}{S} \cdot \underset{\sim}{a} \qquad (4)$$

Henceforth we shall only be concerned with $\underset{\sim}{H}_N$. Providing, however, that $|\underset{\sim}{H}_N| \ll H_o$, we need only consider $\underset{\sim}{H}_N \cdot \underset{\sim}{k} = H_{Nz}$. This is because the components of $\underset{\sim}{H}_N$ perpendicular to $\underset{\sim}{k}$ produce only a second-order contribution to the field at the nucleus relative to the components of $\underset{\sim}{H}_N$ parallel to $\underset{\sim}{k}$.

To calculate the isotropic shift we proceed as follows. We set up a rectangular coordinate system in the molecule, and express $\underset{\sim}{S}$ and $\underset{\sim}{a}$ in terms of this coordinate system. As the electron spin relaxes at such a rate that the Larmor period of the nucleus is long compared to the lifetime of the spin orientation, T_{1e}, the nucleus senses only the averaged orientation of the electron spin. Then the paramagnetic moment induced in the molecule by the magnetic field is obtained from the Boltzmann distribution of the electron spin states. The Boltzmann average will depend on whether the molecule is fixed in a rigid lattice or is free to undergo rapid random tumbling, and also on the rate of relaxation of the electron. Then, in order to obtain the isotropic component of the shift, we average $\underset{\sim}{H}_N \cdot \underset{\sim}{k}$ over all orientations of $\underset{\sim}{k}$ relative to the molecular coordinate system.

We let $\underset{\sim}{\kappa}$, $\underset{\sim}{\lambda}$, and $\underset{\sim}{\nu}$ denote the unit vectors which determine the molecular coordinate system. For convenience we consider a molecule with axial symmetry and let $\underset{\sim}{\kappa}$ point along this symmetry axis. Then the g-factor can be written

$$\underset{\sim}{g} = g_{\parallel} \underset{\sim}{\kappa}\underset{\sim}{\kappa} + g_{\perp} (\underset{\sim}{\lambda}\underset{\sim}{\lambda} + \underset{\sim}{\nu}\underset{\sim}{\nu}) \qquad (5)$$

where $g_{\parallel}$ and $g_{\perp}$ are the g-dyads parallel and perpendicular to the symmetry axis, respectively. We denote the orientation of the

molecular coordinate system relative to $\underset{\sim}{k}$ by ϑ and Ω :

$\underset{\sim}{k}^{\circ} \underset{\sim}{\nu} = \cos\vartheta$, $\underset{\sim}{k}^{\circ} \underset{\sim}{\lambda} = \sin\vartheta \cos\Omega$, $\underset{\sim}{k}^{\circ} \underset{\sim}{\nu'} = \sin\vartheta \sin\Omega$.

For the present we require no more prescription than this of the molecular coordinate system. We will let $\underset{\sim}{q}$ be the direction of quantization of the electron spin. ($\underset{\sim}{q}$ may not be in the direction $\underset{\sim}{k}$.)

The Boltzmann averaged component of spin along the direction $\underset{\sim}{q}$ will be denoted by $\overline{S}_q$ and is given by

$$\overline{S}_q = \left[\sum_{S_q=-S}^{S} S_q \exp(-E_{S_q}/kT) \right] / \left[\sum_{S_q=-S}^{S} \exp(-E_{S_q}/kT) \right]. \quad (6)$$

Here E_{S_q} is the energy eigenvalue corresponding to the eigenvalue of spin S_q. The energy E_{S_q} is proportional to S_q:

$$E_{S_q} = |\beta| H_o S_q \, f(g, \vartheta, \Omega). \quad (7)$$

In equation 7, $f(g, \vartheta, \Omega)$ is some function of the g-factors and the orientation of $\underset{\sim}{k}$ that will vary from one problem to another. For the usual Curie-formula-type approximation, $|E_{S_q}| \ll kT$, equations 6 and 7 lead to the result

$$\overline{S}_q = - \xi \, f(g, \vartheta, \Omega) \quad (8)$$

where

$$\xi = |\beta| H_o S(S+1)/3kT. \quad (9)$$

Then, symbolically, the isotropic nuclear shift, ΔH is

$$\Delta H = \overline{\langle \underset{\sim}{H}_N \cdot \underset{\sim}{k} \rangle_{\vartheta,\Omega}} = -\xi|\beta| \left\langle f(g, \vartheta, \Omega) \underset{\sim}{q} \cdot \underset{\sim}{\mathcal{A}} \cdot \underset{\sim}{k} \right\rangle_{\vartheta,\Omega} . \qquad (10)$$

It must be noted that we have chosen the signs such that at a fixed frequency, when ΔH is positive the shift is up-field, while when ΔH is negative the shift is down-field.

Isotropic Shifts in a Solid. Consider a paramagnetic molecule to be contained in a single crystal with fixed orientation relative to the external field. We may look upon the first term in the spin Hamiltonian, equation 2, as representing the coupling of a free electron spin with g-factor $g_o = 2.0023$ to an effective field $\underset{\sim}{H}_e$:

$$\underset{\sim}{H}_e = \underset{\sim\sim}{g} \cdot \underset{\sim}{k} \; H_o / g_o \qquad (11)$$

The free spin energy eigenstates are then characterized by the spin components in the direction of $\underset{\sim}{H}_e$; i.e., $\underset{\sim}{H}_e$ defines a cannonical axis of quantization $\underset{\sim}{q}$:

$$\underset{\sim}{q} = \underset{\sim}{H}_e / \left| \underset{\sim}{H}_e \right| \qquad (12)$$

$$= \underset{\sim}{g} \cdot \underset{\sim}{k} \; / \left| \underset{\sim}{g} \cdot \underset{\sim}{k} \right| \qquad (13)$$

The energy eigenvalues E_{S_q} in equation 7 are simply the free spin eigenvalues of the first term of $\mathcal{H}$ in equation 2; i.e.,

$$E_{S_q} = |\beta| S_q \underset{\sim}{q} \cdot \underset{\sim}{g} \cdot \underset{\sim}{k} H_o \tag{14}$$

Thus, by comparison with equation 7 we see that for the present problem,

$$f(g, \vartheta, \Omega) = \underset{\sim}{q} \cdot \underset{\sim}{g} \cdot \underset{\sim}{k}. \tag{15}$$

The isotropic shift is then given by the general equation,

$$\Delta H = - \xi |\beta| \left\langle (\underset{\sim}{q} \cdot \underset{\sim}{g} \cdot \underset{\sim}{k}) (\underset{\sim}{q} \cdot \underset{\sim}{a} \cdot \underset{\sim}{k}) \right\rangle_{\vartheta, \Omega} \tag{16}$$

Performing the average indicated in equation 16, the isotropic shift in a solid is

$$\Delta H = - \xi \frac{|\beta|}{3} [g_{\parallel} a_{\kappa\kappa} + g_{\perp} (a_{\lambda\lambda} + a_{\nu\nu})]. \tag{17}$$

$a_{\kappa\kappa}$, $a_{\lambda\lambda}$, and $a_{\nu\nu}$ are the principal dyads along the $\underset{\sim}{\kappa}$, $\underset{\sim}{\lambda}$, and $\underset{\sim}{\nu}$ directions. Equation 17 can be written in terms of the coefficient A and the dyads of $\underset{\sim}{\mathcal{g}}$ used in equation 1 instead of the dyads of $\underset{\sim}{a}$:

$$\Delta H = - \xi \frac{|\beta|}{3} [A(g_{\parallel} + 2g_{\perp}) + \mathcal{g}_{\kappa\kappa}(g_{\parallel} - g_{\perp})]. \tag{18}$$

In equation 18 we have used the relations

$$A = \frac{1}{3} (a_{\kappa\kappa} + a_{\lambda\lambda} + a_{\nu\nu}) \tag{19}$$

and

$$\mathcal{S}_{\kappa\kappa} = \frac{1}{3} (2 a_{\kappa\kappa} - a_{\lambda\lambda} - a_{\nu\nu}). \tag{20}$$

Isotropic Shifts in Solution. We now consider the case in which the paramagnetic molecule undergoes rapid random tumbling motions in the liquid state. That is, ϑ and Ω are functions of time. We can write the first term of the Hamiltonian equation 2 as (8):

$$\mathcal{H} = [g_{\parallel} \cos^2\vartheta(t) + g_{\perp} \sin^2\vartheta(t)] |\beta| H_o S_k$$

$$+ \frac{1}{2} |\beta| H_o (g_{\parallel} - g_{\perp}) \sin\vartheta(t) \cos\vartheta(t) \left\{ S_+ e^{-i\Omega(t)} + S_- e^{i\Omega(t)} \right\}. \tag{21}$$

In equation 21 S_+ and S_- are the electron spin raising and lowering operators. For the moment, let us consider the second part of equation 21:

$$\mathcal{H}' = \frac{1}{2} (g_{\parallel} - g_{\perp}) \sin\vartheta(t) \cos\vartheta(t) |\beta| H_o \left\{ S_+ e^{-i\Omega(t)} + S_- e^{i\Omega(t)} \right\}. \tag{22}$$

Let $\mathcal{H}'$ act on the spin system for a time τ_c. The time τ_c is essentially the time required for the molecule to turn through a radian, or to move through a distance comparable with its dimensions. Then if

$$1/\tau_c \gg |g_{\parallel} - g_{\perp}| \quad |\beta| H_o, \tag{23}$$

to a good approximation, $\mathcal{H}'$ has no effect on the spin system (9). Thus $\underset{\sim}{q} = \underset{\sim}{k}$ and we can write the remaining part of equation 21, $(\mathcal{H}-\mathcal{H}')$, as

$$\mathcal{H}_o = [(g_{\parallel} + 2g_{\perp})/3]|\beta|H_o S_k + (g_{\parallel} - g_{\perp})|\beta|H_o [\cos^2\vartheta(t) - 1/3] S_k. \tag{24}$$

Assuming that equation 23 is satisfied, we consider the two cases where a) the rate of electron spin relaxation is much smaller than the tumbling rate, which is the most likely case to be met with experimentally, $\tau_c \ll T_{1e}$, and where b) the rate of relaxation is much greater than the tumbling rate, $\tau_c \gg T_{1e}$. In case a), $T_{1e} \gg \tau_c$, the spin system "sees" only the average Hamiltonian. That is, whereas it takes a time T_{1e} for the electron spin system to adjust to any change in the interaction, τ_c being much shorter than T_{1e}, the interaction changes many times before the spin system can adjust to a previous change, and hence, the spin system senses only the average interaction. Thus the energy E_{S_q} is simply

$$E_{S_q} = |\beta| H_o S_k (g_{||} + 2g_{\perp})/3. \tag{25}$$

Comparison with equation 7 shows that

$$f(g, \vartheta, \Omega) = f(g) = (g_{||} + 2g_{\perp})/3. \tag{26}$$

Thus, the isotropic shift from equation 10 is

$$\Delta H = \overline{\left\langle \underset{\sim}{H}_N \cdot \underset{\sim}{k} \right\rangle_{\vartheta,\Omega}} = -\xi|\beta| [(g_{||} + 2g_{\perp})/3] \left\langle \underset{\sim}{k} \cdot \underset{\sim}{a} \cdot \underset{\sim}{k} \right\rangle_{\vartheta,\Omega} \tag{27}$$

$$= -(1/9)(a_{xx} + a_{yy} + a_{zz}) \xi |\beta| (g_{||} + 2g_{\perp}). \tag{28}$$

Referring to equation 19, equation 28 can be written

$$\Delta H = -(1/3) \xi |\beta| A (g_{||} + 2g_{\perp}). \tag{29}$$

In case b), $\tau_c \gg T_{1e}$, the spin system can rapidly adjust to the instantaneous change caused by molecular tumbling. Under this circumstance we should consider that thermal equilibrium among the energy eigenstates

$$E_{S_q} = |\beta| H_o S_k (g_{||} \cos^2 \vartheta + g_{\perp} \sin^2 \vartheta) \tag{30}$$

was established for every value of ϑ. Then

$$f(g, \vartheta, \Omega) = f(g, \vartheta) = (g_{\parallel}\cos^2\vartheta + g_{\perp}\sin^2\vartheta), \qquad (31)$$

and the isotropic shift is therefore

$$\Delta H = -\xi|\beta|\left\langle (g_{\parallel}\cos^2\vartheta + g_{\perp}\sin^2\vartheta)\,(\underset{\sim}{k}\cdot\underset{\sim}{a}\cdot\underset{\sim}{k})\right\rangle_{\vartheta,\Omega} \qquad (32)$$

$$\Delta H = -(\xi|\beta|/15)\left\{ a_{\kappa\kappa}(3g_{\parallel} + 2g_{\perp}) + (a_{\lambda\lambda} + a_{\nu\nu})(g_{\parallel} + 4g_{\perp})\right\}. \qquad (33)$$

Then referring to equations 19 and 20, equation 33 becomes

$$\Delta H = -(\xi|\beta|/15)\,[5A(g_{\parallel} + 2g_{\perp}) + 2\,\delta_{\kappa\kappa}(g_{\parallel} - g_{\perp})]. \qquad (34)$$

B. Considerations When the Spin Hamiltonian Arises from the Fermi Contact and Pseudo Contact Interactions

General Considerations. Quite often the principal (electron-spin)-(nuclear-spin) interaction giving rise to an isotropic shift is the Fermi contact interaction. The form of this interaction is

$$\mathcal{H} = (16\pi/3)\,|\beta|\,\gamma\hbar\,\underset{\sim}{S}\cdot\underset{\sim}{I}\,|\psi(0)|^2, \qquad (35)$$

where $|\psi(0)|^2$ is the electron density at the nuclear site. However, the contribution to the isotropic shift of the pseudo contact interaction may be as large as or larger than the contribution from the Fermi contact interaction. The pseudo contact interaction is that isotropic hyperfine coupling which arises from the combined effects of (electron-spin)-(nuclear-spin) coupling, (electron-orbit)-(nuclear-spin) coupling, and electron spin-orbit interaction. We will approximate pseudo contact interaction between the electronic moment and nuclear spin by a point dipolar interaction. We express the paramagnetic moment in terms of a g-factor, thereby taking into consideration the combined effects of spin and orbit.

This dipole field at the nucleus does not average to zero over molecular orientations, because the induced paramagnetic moment itself depends upon the molecular orientation relative to the external

field. In certain solids — especially ionic crystals — one may have to include in the calculation several nearby molecular paramagnetic moments, in addition to the far away dipole whose effects may be calculated using bulk magnetization formulae. The extension of our calculations to this more general situation is trivial when the coupling of the paramagnetic moments with one another is small compared to kT.

We will now complete the prescription of the molecular coordinate system. We take the origin of the coordinate system to be situated at the electronic point dipole and let $\underset{\sim}{r}$ denote the position of the nucleus of interest. We take $\underset{\sim}{\nu}$ to be perpendicular to $\underset{\sim}{r}$ so that $\underset{\sim}{r}$ lies in the plane formed by $\underset{\sim}{\kappa}$ and $\underset{\sim}{\lambda}$ and describe the angle between $\underset{\sim}{\kappa}$ and $\underset{\sim}{r}$ by χ : $\underset{\sim}{r}\cdot\underset{\sim}{\kappa} = \cos\chi$, $\underset{\sim}{r}\cdot\underset{\sim}{\lambda} = \sin\chi$.

The pseudo contact interaction between the electronic magnetic moment $\underset{\sim}{\mu}$ and the nuclear magnetic moment $\gamma\hbar\underset{\sim}{I}$ is

$$\mathcal{H} = -\gamma\hbar\,\underset{\sim}{\mu}\cdot\underset{\sim}{T}\cdot\underset{\sim}{I} \tag{36}$$

where

$$\underset{\sim}{T} = \frac{1}{r^3}\left(3\underset{\sim}{r}\underset{\sim}{r}/r^2 - \underset{\sim}{\mathcal{I}}\right) \tag{37}$$

and $\underset{\sim}{\mathcal{I}}$ is the unit dyadic. The spin Hamiltonian for the hyperfine coupling is therefore

$$\mathcal{H} = \gamma \hbar \, |\beta| \underset{\sim}{S} \cdot \underset{\sim}{g} \cdot \underset{\sim}{T} \cdot \underset{\sim}{I} \tag{38}$$

Then, referring to equations 3 and 4,

$$\underset{\sim}{a} = \underset{\sim}{g} \cdot T \tag{39}$$

which on expansion gives

$$\underset{\sim}{a} = \begin{pmatrix} a_{\kappa\kappa} & a_{\kappa\lambda} & a_{\kappa\nu} \\ a_{\lambda\kappa} & a_{\lambda\lambda} & a_{\lambda\nu} \\ a_{\nu\kappa} & a_{\nu\lambda} & a_{\nu\nu} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{r^3} g_{\parallel} (\cos^2 \chi - 1) & \frac{3}{r^3} g_{\parallel} \cos \chi \sin \chi & 0 \\ \frac{3}{r^3} g_{\perp} \cos \chi \sin \chi & \frac{1}{r^3} g_{\perp} (3 \sin^2 \chi - 1) & 0 \\ 0 & 0 & -g_{\perp}/r^3 \end{pmatrix} \tag{40}$$

In terms of the symbols in equation 1,

$$A = \frac{1}{3r^3} (g_{\parallel} - g_{\perp}) (3 \cos^2 \chi - 1), \tag{41}$$

$$\underset{\sim}{\mathcal{S}} = \begin{pmatrix} \mathcal{S}_{\kappa\kappa} & \mathcal{S}_{\kappa\lambda} & \mathcal{S}_{\kappa\nu} \\ \mathcal{S}_{\kappa\lambda} & \mathcal{S}_{\lambda\lambda} & \mathcal{S}_{\lambda\nu} \\ \mathcal{S}_{\kappa\nu} & \mathcal{S}_{\lambda\nu} & \mathcal{S}_{\nu\nu} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{3r^3} (\cos^2 \chi - 1) (2g_{\parallel} + g_{\perp}) & \frac{3}{r^3} \frac{(g_{\parallel} + g_{\perp})}{2} \cos \chi \sin \chi & 0 \\ \frac{3}{r^3} \frac{(g_{\parallel} + g_{\perp})}{2} \cos \chi \sin \chi & \frac{1}{r^3} \left[g_{\perp} - \frac{(g_{\parallel} + 2g_{\perp})}{3} (3 \cos^2 \chi - 1) \right] & 0 \\ 0 & 0 & \frac{-1}{r^3} \left[g_{\perp} + \frac{(g_{\parallel} - g_{\perp})}{3} (3 \cos^2 \chi - 1) \right] \end{pmatrix} \tag{42}$$

and,

$$\underset{\sim}{\varepsilon} = \begin{pmatrix} 0 & \varepsilon_{\kappa\lambda} & \varepsilon_{\kappa\nu} \\ -\varepsilon_{\kappa\lambda} & 0 & \varepsilon_{\lambda\nu} \\ -\varepsilon_{\kappa\nu} & -\varepsilon_{\lambda\nu} & 0 \end{pmatrix} = \begin{pmatrix} 0 & \frac{3}{r^3}\cdot\frac{(g_{\parallel}-g_{\perp})}{2}\cdot\sin\chi\cos\chi & 0 \\ \frac{3}{r^3}\cdot\frac{(g_{\perp}-g_{\parallel})}{2}\cdot\sin\chi\cos\chi & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (43)$$

On the other hand, for the Fermi contact interaction

$$a_{\kappa\kappa} = a_{\lambda\lambda} = a_{\nu\nu} = A = \frac{16\pi}{3}\,|\psi(0)|^2 \quad (44)$$

with all off-diagonal components zero.

Isotropic Shifts for Molecules in Solids and in Solution. Having the values of the components of $\underset{\sim}{a}$ for the Fermi contact and the pseudo contact interaction, we can now obtain formulae for the isotropic shifts from the results of section A. These formulae are summarized below.

Pseudo Contact Interaction

The general formula for the resonance shift (isotropic and anisotropic components included) obtained from equation 16 before averaging over ϑ and Ω is

$$\Delta H(\vartheta, \Omega) = -(1/r^3)\,|\beta|\,\xi \left\{ g_{\parallel}^2 \cos^2\vartheta\,(3\cos^2\chi - 1) \right.$$

$$+ g_{\perp}^2 \sin^2\vartheta\,(3\sin^2\chi\cos^2\Omega - 1)$$

$$\left. + \frac{3}{4}\,(g_{\parallel}^2 + g_{\perp}^2)\sin 2\vartheta \sin 2\chi \cos\Omega \right\}. \quad (45)$$

The isotropic shift for a paramagnetic molecule in a crystal from equation 17 or 18 is

$$\Delta H = -(1/r^3)\,|\beta|\,\xi\,(3\cos^2\chi - 1)\,(g_{\parallel} + g_{\perp})(g_{\parallel} - g_{\perp})/3. \quad (46)$$

The isotropic shift for a paramagnetic molecule in solution for $T_{1e} \gg \tau_c$ is, from equation 28 or 29,

$$\Delta H = -(1/r^3)\,\xi\,|\beta|\,(3\cos^2\chi - 1)\,[(g_{\parallel} + 2g_{\perp})/3][(g_{\parallel} - g_{\perp})/3]. \quad (47)$$

From equation 33 or 34 the isotropic shift in solution with $T_{1e} \ll \tau_c$ is

$$\Delta H = -(1/15\,r^3)\,\xi\,|\beta|\,(3\cos^2\chi - 1)(3g_{\parallel}^2 + g_{\parallel} g_{\perp} - 4g_{\perp}^2). \quad (48)$$

Fermi Contact Interaction

The isotropic shift, regardless of whether the molecule is in a crystal or in solution is

$$\Delta H = -\xi\,\frac{|\beta|}{3}\,(g_{\parallel} + 2g_{\perp})\,\frac{16\pi}{3}\,|\psi(0)|^2. \quad (49)$$

C. Discussion and Conclusions

Separation of the Contact and Pseudo Contact Interactions.

According to the foregoing results one can distinguish between the contact and pseudo contact contributions to isotropic nuclear resonance shifts. Thus, if all of the hyperfine interactions were purely dipolar in origin, then the isotropic shift for a crystalline solid is calculated to be greater than the isotropic shift in solution for the most likely case, $\tau_c \ll T_{1e}$, by the factor

$$3(g_{\parallel} + g_{\perp})/(g_{\parallel} + 2g_{\perp}). \qquad (50)$$

This result is in marked contrast to isotropic shifts for a nucleus due to the pure contact isotropic hyperfine interaction, which are the same for both the solid and solution cases. As pointed out in the introduction, the basic reason that one can distinguish between contact and pseudo contact contributions to isotropic shifts involves two factors: (a) The anisotropic hyperfine terms in equation 1 contribute to the isotropic shifts in the solid, but not in solution. (b) The presence of a pseudo contact term in equation 1 implies the presence of anisotropic terms.

These considerations may be illustrated by reference to the work of McConnell and Holm (6, 7) on proton resonance shifts in

nickelocene, $Ni(C_5H_5)_2$. These shifts were interpreted in terms of proton contact hyperfine interaction, and were used to draw conclusions regarding the unpaired spin density on the cyclopentadienyl rings in this substance. The observation that the average proton shifts in this substance in solid and in solution were nearly the same (1.20 and 1.10 $\pm$ 0.02 gauss, respectively) supports the previous interpretation of these shifts in terms of contact interaction.

Limitations. It must be remarked, however, that there are several possibly serious limitations in the present method for distinguishing the two possible contributions to the isotropic coupling. In some cases there possibly might be important but quantitatively uncertain bulk demagnetization corrections in the event that the isotropic shifts are of comparable magnitude.

There are errors implicit in the paramagnetic point dipole approximation. In many practical problems the molecular paramagnetic moment will be distributed, rather than concentrated at a point. We may expect that the ratio of equation 50 will overestimate the shift ratio. Zero-field splittings comparable to $|\beta|H_o$ would require modifications of the basic Hamiltonian, equation 2, and the spin polarization equations 6 and 7.

Finally, our formulae for the solid case have little quantitative validity if in the single crystal the intermolecular exchange

interaction J (radians/sec) is large relative to $|g_{\parallel} - g_{\perp}| H_o |\beta| / \hbar$ and to the electron spin lattice relaxation time T_{1e}. In this case an averaged set of g-factors over certain molecules in the unit cell would be necessary for calculating the approximate f(g). Of course, the entire treatment breaks down in the limit $\hbar|J| > kT$. On the other hand, we expect our calculations for the solid to be valid in cases where $1/T_{1e} \gg |J|$; i.e., when the electron spin relaxes fast enough to preclude any phase coherence between electron spins in neighboring molecules. In favorable circumstances paramagnetic resonance spectra can show whether or not any of the above complications need be considered in any particular case.

References

(1) A. Abragam and M.H.L. Pryce, Proc. Roy. Soc. (London) A205, 135-153 (1951).

(2) H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107-117 (1958).

(3) N. Bloembergen and W. C. Dickinson, Phys. Rev. 79, 179-180 (1950).

(4) W. C. Dickinson, Phys. Rev. 81, 717-731 (1951).

(5) H. M. McConnell and C. H. Holm, J. Chem. Phys. 26, 1517-1522 (1957).

(6) H. M. McConnell and C. H. Holm, J. Chem. Phys. 27, 314-315 (1957).

(7) H. M. McConnell and C. H. Holm, J. Chem. Phys. 28, 749-750 (1958).

(8) H. M. McConnell, J. Chem. Phys. 25, 709-711 (1956).

(9) L. I. Schiff, Quantum Mechanics, McGraw-Hill Book Co., New York (1955), pp. 217-218.

II

THE MAGNETIC RESONANCE PROPERTIES OF SOME SANDWICH MOLECULES

Introduction

Of unceasing appeal is the aesthetically pleasing structure of the "sandwich" molecule: the bis-cyclopentadienyl metal and dibenzene metal molecules and ions. The analysis of paramagnetic spectra is simplest when the molecules have a high degree of symmetry - most previous work has been done on molecules with cubic symmetry. So it is interesting now to explore not cubic, but five-fold and six-fold axial symmetry coupled with a center of inversion. As will be shown first-order spin-orbit interaction may occur in one of the sandwich ions. Moreover, while there is a fairly complete understanding of the electronic structure of octahedral complexes, the same is not true of the sandwich molecules. It is hoped that the paramagnetic resonance study will shed some light on this problem as well.

Much of the early theoretical work was non-specific, as insufficient experimental data had been gathered for guidance. However, after an X-ray crystallographic determination of the structure of ferrocene Dunitz and Orgel (1) proposed a theoretical model, which, except for a slight modification given by Moffitt (2), has had a fair degree of success. The model finally obtained by Moffitt (2) gave ferrocene two covalent bonds between the metal atom and the

two cyclopentadienyl rings. The orbitals used in bonding were 3d orbitals --- Moffitt assumed that the 4p orbitals were too high energetically to contribute appreciably to the bonding. This left three 3d orbitals which were assumed to be comparatively non-bonding or magnetic orbitals. Then with ferrocene the six electrons beyond the argon configuration of Fe^{+2} can be put into the three non-bonding orbitals forming a diamagnetic compound, as is found experimentally. Moffitt (2), following Dunitz and Orgel (1), considered the $3d_{\pm 1}$ orbitals to be the bond-forming orbitals of the metals atom, the $3d_{\pm 2}$ and $3d_0$ orbitals being comparatively non-bonding. (The subscript denotes the value of the angular momentum about the symmetry axis in units of $\hbar$.) On the other hand, Moffitt assumed that the $3d_0$ and 4s orbitals mix giving a low lying, non-degenerate, comparatively non-bonding orbital ($3d_0'$). Liehr and Ballhausen (3) have more recently attempted to correlate with Moffitt's model (2) the measured magnetic susceptibilities (i.e., the number of unpaired electrons) of a variety of metal atoms in various oxidation states. Liehr and Ballhausen calculated the separation between the $3d_0'$ and $3d_{\pm 2}$ orbitals using an electrostatic or ligand field approximation, replacing each of the carbon atoms by point charges.

Dunitz and Orgel (4), admitting Moffitt's modification while at the same time making their previous work more quantitative, ap-

proximated the splitting of the 3d orbitals by assigning an energy value to the degree of overlap between the 3d orbitals and the π-orbitals of the cyclopentadiene groups rather than using the electrostatic model of Liehr and Ballhausen (3). This showed quite clearly that the $3d_0$ and 4s and $3d_{\pm 2}$ orbitals could participate in bonding to a limited extent by sharing of the electrons in these orbitals with the aromatic rings. Dunitz and Orgel (4) also attempted to calculate the heat of formation of ferrocene and nickelocene, and their calculations agreed fairly well with experiment. But still the role played by the 4p orbitals remained undetermined and its study somewhat neglected.

More recently the 4p orbitals have received a fair amount of attention experimentally (5, 6, 7). The K X-ray absorption edge data is assumed to arise from the electronic transition from the metal 1s(K) level to the nearest unfilled np-orbital. Thus, if the 4p orbital is involved in bonding, the nearest np-orbital is a 4p-antibonding-orbital. This transition should be greater in energy than the corresponding 1s-4p transition in a free ion. However, owing to the difficulty in estimating the energy of the 1s-4p transition in an isolated atom, the quantitative significance of this work is still uncertain (8). Brown has considered just the rudiments of the theory of the 4p orbital role in the sandwich compound (8). For the most part the paramagnetic resonance experiments will not shed much light on the importance of the 4p orbitals.

Consideration is given in the present investigation to sandwich compounds containing the metals titanium to nickel in various states of oxidation. Estimates of the magnetic resonance properties are given for each of the transition metal sandwich molecules for various possible electronic structures. As no one electronic structure is assumed superior to any other, the results are somewhat indeterminate. However, as the paramagnetic resonance experiments are somewhat difficult to perform, it is hoped that this work may be a guide for experimentation. Also, it is hoped that this investigation will provide a basis for later interpretation of spectra. Hence, upon completion of more experimental work, those electronic structures which conform to the experimental results can be selected, this work then assuming the character of a theoretical calculation based on experiment.

In this thesis, we will consider ligand field theory; i.e., an electrostatic field representation of the aromatic groups, for the biscyclopentadienene metal ions and molecules. Then by considering the covalent model we will see what changes are necessary in the results of the ligand field theory. For the dibenzene metal molecules and ions we will consider only the covalent model. But, except as a first-order orientation, neither the ionic nor the covalent models yield detailed enough results to calculate the necessary magnetic resonance

properties. Therefore, we will base estimates of the g-factors and zero-field splittings on reasonable orbital arrangements which are consistent with the observed magnetic moments from susceptibility measurements.

We will consider the hyperfine structure expected, but enough is still unknown about the magnitude in general to render our results useful only as a rough guide.

General Theory (9)

The paramagnetic properties of the sandwich compounds are determined by the interplay between various electromagnetic interactions with different relative strengths. The Hamiltonian for the molecules is given by the sum of the kinetic energy of the electrons and the terms representing the various electrostatic and magnetic interactions. By far the dominant terms in the Hamiltonian are the spin-independent terms representing the kinetic and electrostatic potential energies. We will write these terms as $2W_L + W_F + V$. W_L and W_F are the kinetic and electrostatic potential energies of an aromatic group and the free metal ion, respectively, and V represents the interaction between the metal ion and the rings. We could add a term representing the interaction between the electronic and nuclear vibrational motions. This interaction becomes important if the ground state of the molecule under $2W_L + W_F + V$ is orbitally degenerate; and it results in the distortion of the molecule to lower symmetry. Hence, we will let

$$V = K + T \qquad (1)$$

where K represents the metal ion-rings interaction when normal symmetry exists and T represents the interaction under lower symmetry.

Next in importance to the electrostatic terms is the spin-orbit interaction,

$$W_{s-o} = \sum_i \zeta_i \underset{\sim}{\ell}_i \cdot \underset{\sim}{s}_i \qquad (2)$$

where the summation is taken over the unpaired electrons on the metal ion, $\underset{\sim}{\ell}_i$ and $\underset{\sim}{s}_i$ are the one-electron operators of orbital and spin angular momenta. ζ_i is the one-electron spin-orbit coupling coefficient, its value is determined by the hydrogen-like quantum numbers n, ℓ. That is, if all of the unpaired electrons are in 3d orbitals, then ζ_i is the same for each electron and can be taken out of the summation. Moreover, if it is sufficiently accurate to discuss the ion as an atomic term of a configuration $3d^{\mu}$, we can write

$$W_{s-o} = \lambda \underset{\sim}{L} \cdot \underset{\sim}{S}, \qquad (3)$$

where $\underset{\sim}{L} = \sum_i \underset{\sim}{\ell}_i$ and $\underset{\sim}{S} = \sum_i \underset{\sim}{s}_i$ are the total orbital and spin angular momenta, and λ is related to ζ by a simple factor (see Condon and Shortley (10)). Using the atomic term corresponds to the weak ligand field theory. Another interaction, independent of the nuclear spin and external fields, is the spin-spin interaction

$$W_{s-s} = \beta^2 \sum_{i<j} \left\{ \frac{\underset{\sim}{s}_i \cdot \underset{\sim}{s}_j}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|^3} - 3 \frac{[\underset{\sim}{s}_i \cdot (\underset{\sim}{r}_i - \underset{\sim}{r}_j)][\underset{\sim}{s}_j \cdot (\underset{\sim}{r}_i - \underset{\sim}{r}_j)]}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|^5} \right\} . \qquad (4)$$

The summation in equation 4 is again over unpaired electrons and β is the Bohr magneton. W_{s-s} is difficult to treat and its effects are usually small so we will not consider it in much detail.

The interaction with the nuclear spin arises from two causes; the magnetic interaction with the nuclear magnetic moment (linear in the nuclear spin vector $\underset{\sim}{I}$), and the electrostatic interaction with the electric quadrupole moment of the nucleus (quadratic in $\underset{\sim}{I}$). Explicitly, the nuclear interaction is

$$W_N = 2|\beta|\gamma\hbar \sum_i \left\{ \frac{(\underset{\sim}{\ell}_i - \underset{\sim}{s}_i)\cdot\underset{\sim}{I}}{r_i^3} + 3\,\frac{(\underset{\sim}{r}_i\cdot\underset{\sim}{s}_i)(\underset{\sim}{r}_i\cdot\underset{\sim}{I})}{r_i^5} + \frac{8\pi}{3}\,\delta(\underset{\sim}{r}_i)(\underset{\sim}{s}_i\cdot\underset{\sim}{I})\right\} + \frac{3eQ}{4I(2I-1)}\left(\frac{\partial^2\Phi}{\partial z^2}\right)_{z=0}\left\{I_z^2 - \frac{1}{3}I(I+1)\right\} \tag{5}$$

The magnetic interaction includes the dipolar interaction with orbital and spin angular momenta (the orbital magnetic moment is centered on the nucleus) and the Fermi contact interaction. γ is the gyromagnetic ratio of the nucleus in units of $\hbar$. Q is the quadrupole moment in units of $10^{-24}\,cm^2$ (a property of the nucleus), and Φ is the time-averaged electrostatic potential (11). In writing the quadrupole interaction in the diagonal form given in equation 5 we have assumed the molecules of interest to have axial or near-axial symmetry, which is, in general, true. We will not consider the quadrupole interaction further as it is usually small and is here mentioned only for completeness.

Finally, there is the interaction with the external magnetic field $\underset{\sim}{H}$,

$$|\beta| (\underset{\sim}{L} + 2\underset{\sim}{S}) \cdot \underset{\sim}{H} - \gamma \hbar \underset{\sim}{I} \cdot \underset{\sim}{H} \ . \qquad (6)$$

The total Hamiltonian is then

$$\mathcal{H} = 2W_L + W_F + V + W_{s-o} + W_{s-s}$$

$$+ |\beta| (\underset{\sim}{L} + 2\underset{\sim}{S}) \cdot \underset{\sim}{H} + W_N - \gamma \hbar \underset{\sim}{I} \cdot \underset{\sim}{H} , \qquad (7)$$

where the terms have been arranged in what is normally a decreasing order of strength. The level separations of $2W_L + W_F$ are of the order of $10^5 cm^{-1}$, V causes splittings of the order of $10^4 cm^{-1}$, W_{s-o}, $10^2 cm^{-1}$, W_{s-s}, $1 cm^{-1}$, $|\beta|(\underset{\sim}{L} + 2\underset{\sim}{S}) \cdot \underset{\sim}{H}$, $1 cm^{-1}$, W_N, $10^{-2} cm^{-1}$, and the last term $10^{-3} cm^{-1}$.

Equation 7 is then the basis on which we will estimate the paramagnetic parameters, and we will see how each of the terms affects the sandwich molecules, starting with the potential V in the next section.

Electronic Structure in the Absence of Magnetic Interactions

Ionic Model for Bis-Cyclopentadiene Metal Molecules and Ions.

Ideally $2W_L + W_F + V$ should represent the spin-independent Hamiltonian for the entire bis-cyclopentadienyl metal molecule. Even if $2W_L + W_F + V$ represents only the interaction between electrons in 3d, 4s, and 4p orbitals of the metal, the π-orbitals of cyclopentadienyl rings, and the shielded carbon and metal nuclei, a far simpler problem than the first, we could not solve the wave equation without a great deal of labor. However, we can obtain a first orientation for the problem by considering a ligand field approximation. Assuming the paramagnetism of the molecule is to be located principally on the metal atom, we will let V represent an electrostatic field arising from the cyclopentadienide (cp) rings acting on the metal atom. Later we will restrict V even more by letting the ligand field arise from a geometrically simple distribution of charge.

As is customary in these problems we consider a central-field approximation for the metal atom and let the effect of the electrons in the argon configuration be a shielding of the nucleus. Then for electrons formally in 3d orbitals we consider the perturbation

$$\sum_{i}\sum_{j}\frac{e^2}{r_{ij}} + V. \qquad (8)$$

The summation over i and j is the electrostatic repulsion between electrons above the argon configuration, and V is the ligand field. If V is considerably smaller than the electrostatic repulsion between 3d electrons, we let V act on the atomic states of W_F, the states being characterized by a total L and S. This is called the weak ligand field approximation. On the other hand, if V is considerably larger than the electrostatic potential energy, we let V act on the 3d, 4s, and 4p orbitals in a one-electron orbital approximation and consider $\sum_{i<j} \frac{e^2}{r_{ij}}$ to be a perturbation which determines the total spin S. This is called the strong ligand field approximation.

The ligand field approximation boils down to the evaluation of matrix elements of the form

$$\int \psi_a^*(\underset{\sim}{r}')\, V(\underset{\sim}{r}')\, \psi_b(\underset{\sim}{r}')\, d\underset{\sim}{r}' \qquad (9)$$

whether the wave functions ψ be atomic states or one-electron orbital states. We will let $\underset{\sim}{r}$ be the vector from the origin at the metal nucleus to an element of change giving rise to the ligand field, and let $\underset{\sim}{r}'$ be an arbitrary field point. For the sandwich compounds $V(\underset{\sim}{r}')$ can be taken to be the potential energy arising from a simple distribution of charges. Thus,

$$V(\underset{\sim}{r}') = -e \int \frac{(\text{ligand field})}{|\underset{\sim}{r} - \underset{\sim}{r}'|}\, d\underset{\sim}{r} \qquad (10)$$

We can expand $(1/|\underset{\sim}{r}-\underset{\sim}{r}'|)$ in terms of a series of spherical harmonics (12):

$$\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \frac{4}{2k+1} \sum_{m=-k}^{k} Y^*_{km}(\vartheta, \varphi) Y_{km}(\vartheta', \varphi') \quad (11)$$

where $r_<$ and $r_>$ are the lesser and greater, respectively, of r and r' and $Y_{km}(\vartheta, \varphi)$ is the normalized spherical harmonic which we know to be the angular solutions of the hydrogen-atom problem.

Since the spherical harmonics form a complete set, we can expand the ligand field in terms of them:

$$(\text{ligand field}) = \sum_{\bar{\ell}\bar{m}} R_{\bar{\ell}}(r) Y_{\bar{\ell},\bar{m}}(\vartheta, \varphi) \quad (12)$$

where $R_{\bar{\ell}}(r)$ is some function of r. Considering one-electron orbital states and writing them as

$$\psi_a(\underset{\sim}{r}') = R_{n'\ell'}(r') Y_{\ell'm'}(\vartheta', \varphi') \quad (13)$$

and

$$\psi_b(\underset{\sim}{r}') = R_{n''\ell''}(r') Y_{\ell''m''}(\vartheta', \varphi') \quad (14)$$

we obtain

$$\int \psi^{*}_{a}(\underset{\sim}{r'})V(\underset{\sim}{r'})\,\psi_{b}(\underset{\sim}{r'})d\underset{\sim}{r'} = -e\sum_{k=0}^{\infty}\sum_{m=-k}^{k}\frac{4\pi}{2k+1}\,x$$

$$x\sum_{\bar{\ell},\bar{m}}\left\{\int_{o}^{\infty}\int_{o}^{\infty}\frac{r_{<}^{k}}{r_{>}^{k+1}}\,[R_{\bar{\ell}}(r)]\,R_{n'\ell'}(r')R_{n''\ell''}(r')r^{2}r'^{2}drdr'\right\}x$$

$$x\left\{\int_{o}^{\pi}\int_{o}^{2\pi}Y^{*}_{km}(\vartheta,\varphi)\,Y_{\bar{\ell}\bar{m}}(\vartheta,\varphi)\sin\vartheta\;d\varphi\;d\vartheta\right\}x$$

$$x\left\{\int_{o}^{\pi}\int_{o}^{2\pi}Y_{km}(\vartheta',\varphi')Y_{\ell',m'}(\vartheta',\varphi')Y_{\ell''m''}(\vartheta',\varphi')\sin\vartheta'd\varphi'd\vartheta'\right\} \quad (15)$$

Integrating over ϑ and φ gives ($\delta_{k\bar{\ell}}\;\delta_{m\bar{m}}$). We can simplify the resulting expression by looking at the integration over ϑ' and φ'. The product $Y^{*}_{\ell'm'}\,Y_{\ell''m''}$ can be expanded in terms of spherical harmonics of order $(\ell' + \ell'')$ and lower. At most $(\ell' + \ell'')$ equals 4, because we are only considering 3d, 4s, and 4p orbitals. Then for the one-electron orbital case,

$$\int \psi^{*}_{a}(\underset{\sim}{r'})\,V(\underset{\sim}{r'})\,\psi_{b}(\underset{\sim}{r'})d\underset{\sim}{r'} = -e\sum_{k=0}^{4}\sum_{m=-k}^{k}\frac{4\pi}{2k+1}\,x$$

$$x\left\{\int_{o}^{\infty}\int_{o}^{\infty}\frac{r_{<}^{k}}{r_{>}^{k+1}}\,[R_{k}(r)]\,R_{n'\ell'}(r')\,R_{n''\ell''}(r')\,r^{2}r'^{2}drdr'\right\}\,x$$

$$x\left\{\int_{o}^{\pi}\int_{o}^{2\pi}Y_{km}(\vartheta',\varphi')\,Y^{*}_{\ell'm'}\,(\vartheta',\varphi')\,Y_{\ell''m''}(\vartheta',\varphi')\sin\vartheta'\,d\varphi'\,d\vartheta'\right\} \quad (16)$$

It is also worth noting at this point that s, d, g, ...-functions are even, while p, f, ...-functions are odd. That is, under inversion the

p, f, . . . -functions change sign while the s, d, g, . . . -functions do not. Thus, for example, in the expansion of $Y^*_{\ell'm'}\ Y_{\ell''m''}$ where $\ell' = \ell'' = 2$ we obtain spherical harmonics of order 0, 2, and 4 only.

If we are dealing with atomic terms with total L and S, we write V as

$$V = \sum_i \left\{ \sum_{k=0}^{4} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \int_0^\infty \frac{r_<^k}{r_>^{k+1}} [R_k(r)] r^2 dr\ Y_{km}(\vartheta', \varphi') \right\}_i \quad (17)$$

where we sum over the electrons in the term configuration beyond argon. If the electrons in the configuration have the same n and ℓ, the radial integral can be factored out of the sum over i, and the sum $\sum_i Y_{km}(\vartheta', \varphi')$ can be handled most conveniently by expressing it in terms of operators acting on the 2L + 1 states of the total orbital angular momentum L (13). That is, if

$$\psi_a = \left| L, m_\ell ; S, m_s \right\rangle \quad (18)$$

and

$$\psi_b = \left| L, m'_\ell ; S, m'_s \right\rangle \quad (19)$$

then

$$\int \psi_a^* V \psi_b d\tau = -e \sum_{k=0}^{4} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \times$$

$$\times \left\{ \int_o^\infty \int_o^\infty \frac{r_<^k}{r_>^{k+1}} [R_k(r)] (R_{n'\ell'}(r'))^2 r^2 r'^2 dr dr' \right\} \times \qquad (20)$$

$$\times \xi_k \left\langle L, m_\ell \middle| f_k(L_x, L_y, L_z) \middle| L, m'_\ell \right\rangle \delta_{m_s, m'_s} ,$$

where $R_{n'\ell'}$ is the radial factor of ψ_a and ψ_b, $f_k(L_x, L_y, L_z)$ is a function of L_x, L_y, L_z, and ξ_k is a constant from the transformation to operators. If, for instance, we consider the configuration $3d^3$ of V^{+2}, the ground state is ^4F. Then $R_{n'\ell'} = R_{3,2}$ and $L = 3$. The convenience in using the operator method is that $f(L_x, L_y, L_z)$ is determined only by the ligand field and ξ_k depends on the term considered and is independent of m_ℓ and m'_ℓ.

A more complete treatment will be found in Stevens' paper (13) where tables are given for the various matrix elements $\left\langle L, m_\ell \middle| f_k(Lx, Ly, Lz) \middle| L, m'_\ell \right\rangle$. Also values for ξ_k are given for various ground terms by Bleaney and Stevens (14), although their values of ξ_k are good only for terms obeying Hund's rule of maximum multiplicity. However, this operator method is not particularly convenient for determining the matrix elements between different terms. (For the treatment of these matrix elements see Abragam and Pryce (15).)

Although the above equations for the matrix elements of the ligand field are written in terms of complex spherical harmonics, henceforth we will only be interested in real functions. Thus, we will redefine the Y's so that the φ -dependence is in terms of sines and cosines. We will let

$$Y_{\ell,|m|}(\vartheta,\varphi) = \sqrt{\frac{2\ell+1}{2\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, P_\ell^{|m|}(\cos\vartheta)\sin m\varphi \tag{21}$$

$$Y_{\ell,-|m|}(\vartheta,\varphi) = \sqrt{\frac{2\ell+1}{2\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, P_\ell^{|m|}(\cos\vartheta)\cos m\varphi$$

With this definition the factor $\frac{4\pi}{2k+1}$ in equations 16 and 20 should be replaced by $\frac{2\pi}{2k+1}$.

We will now consider an explicit form for the ligand field. As

$$(\text{ligand field}) = \sum_{km}{}' R_k(r)\, Y_{km}(\vartheta,\varphi), \tag{22}$$

we can use the fact that the spherical harmonics form an orthogonal set of functions and can write

$$R_k(r) = \int_0^{\pi}\int_0^{2\pi} Y_{km}(\vartheta,\varphi)[\text{ligand field}]\sin\vartheta\, d\varphi\, d\vartheta. \tag{23}$$

By considering the symmetry properties of the molecule we can determine for which k and m this integral vanishes because the spherical

harmonics occurring in equation 22 must have the same symmetry as the ligand field. First, if the origin is a center of symmetry for the molecule, then only even spherical harmonics yield a non-vanishing integral. Thus only spherical harmonics with k = 0, 2, and 4 will give a non-vanishing result. Secondly, if the xy-plane is a plane of symmetry, then spherical harmonics with sin m φ dependence vanishes, because under $\varphi \rightarrow -\varphi$, sin m$\varphi \rightarrow$ - sin mφ . Thirdly, the molecule may have an n-fold axis of symmetry through the origin. Then a rotation of the molecule or ligand field by $\frac{2\pi}{n}$ radians about the axis of symmetry (the z-axis) leaves the molecule unchanged. Thus equation 26 vanishes for all m except where m is a multiple of n: Under $\varphi \rightarrow \varphi + \frac{2\pi}{n}$, cos mφ (or sin mφ) $\longrightarrow$ cos $(m\varphi + \frac{m}{n} 2\pi)$(or sin $(m\varphi + \frac{m}{n} 2\pi)$). But cos $(m\varphi + \frac{m}{n} 2\pi)$ = cos mφ , or sin $(m\varphi + \frac{m}{n} 2\pi)$ = sin mφ , only if m is a multiple of n.

To evaluate the non-vanishing integrals it is convenient to introduce a model for the ligand field, the model being a distribution of point or line charges. First we will consider the model for the normal sandwich configuration, where the cp rings are parallel and the molecule has a five-fold axis of symmetry. One ligand field model replaces each of the ten carbon atoms by point charges. From the above consideration of axial symmetry we see that the lowest order

spherical harmonic with $m \neq 0$, which will describe the ligand field, is of order five. But since we need consider only spherical harmonics of order four and less, the ligand field will be adequately represented by $Y_{0,0}$, $Y_{2,0}$, and $Y_{4,0}$ --- we drop $Y_{1,0}$ and $Y_{3,0}$ because they are odd with respect to both inversion through the origin and reflection in the xy-plane. Therefore, we obtain the same energy level splitting if we consider a circular line charge threading through the five carbon atoms of each ring. This is a general physical result. Even if cp rings are not parallel or are translated with respect to each other, the 3d, 4s, and 4p orbitals still "see" only circular line charges and not the five-fold charge periodicity.

The radial part of the ligand field will be represented by Dirac delta functions, delta functions of r, ϑ, and φ for point charges and functions of r and ϑ for the line charge discussed above. When the Dirac delta function is used in coordinate systems other than Cartesian, we have to be careful about integrating factors. In fact, the integrating factor has to be eliminated. Therefore, for a point charge of strength -q at r_o, ϑ_o, φ_o in spherical coordinates, we write the ligand field as

$$-q\,\delta(r_o - r)\cdot\frac{\delta(\vartheta_o - \vartheta)}{r}\cdot\frac{\delta(\varphi_o - \varphi)}{r\sin\vartheta} \qquad (24)$$

because a volume element in spherical coordinates is $dr(r\,d\vartheta)(r\sin\vartheta\,d\varphi)$. If we have a line charge independent of φ, we write

the radial function as

$$-q\,\delta(r_o - r)\cdot \frac{\delta(\vartheta_o - \vartheta)}{r} \qquad (25)$$

where -q is the charge per unit line distance.

Working with two circular line charges instead of the ten point charges,

$$\text{(ligand field)} = \sum_{k=0}^{4} \sum_{m=-k}^{k} R_k(r)\, Y_{km}(\vartheta, \varphi)$$

$$= -2(q\, 2\pi\, r_o \sin\vartheta_o)\, \frac{\delta(r - r_o)}{r_o^2} \qquad \times \qquad (26)$$

$$\times \left\{ \frac{1}{2\sqrt{\pi}}\, Y_{0,0} + \frac{1}{2}\sqrt{\frac{5}{\pi}}\left(1 - \frac{3}{2}\gamma^2\right) Y_{2,0} + \frac{3}{16\sqrt{\pi}}\left(8 - 40\gamma^2 + 35\gamma^4\right) Y_{4,0} \right\},$$

where $(-q\, 2\pi\, r_o \sin\vartheta_o)$ is the total charge of each circular line charge and

$$\gamma = 0.851\, \frac{b}{r_o} \qquad (27)$$

where b is the carbon-carbon distance in the cyclopentadienyl groups and r_0 is the distance from the origin to the circular line charge. We will call the potential arising from this normal molecular configuration K. Acting on one-electron orbitals, equation 10 can be written as

$$K(\underset{\sim}{r}') = 2e(q\,2\pi r_o \sin\vartheta_o)\left\{ 2\sqrt{\pi}\,\frac{1}{r_>}\,Y_{0,0}(\vartheta',\varphi') \right.$$

$$+\sqrt{\frac{\pi}{5}}\,\frac{r_<^2}{r_>^3}\left(1-\frac{3}{2}\Upsilon^2\right)Y_{2,0}(\vartheta',\varphi') + \frac{\sqrt{\pi}}{12}\left(8-40\Upsilon^2+35\Upsilon^4\right)\times$$

$$\left.\times\,\frac{r_<^4}{r_>^5}\,Y_{4,0}(\vartheta',\varphi')\right\} \qquad (28)$$

Because of the explicit dependence of equation 28 on Υ, the splitting of the 3d-orbitals has been calculated for various values of this parameter. To make the calculation systematic, we have chosen to keep the radius of the charged loop constant ($b = 1.41$ Å) and vary r_o by moving the loops closer to the metal ion. These results are shown in figure 1, Appendix, p. 106 . We have calculated these results using the 3d radial function for Mn^{+2} given by Hartree (16). The energy units of figure 1 are based on letting $|q| = |e|$, the electronic charge. The orbitals are denoted by the subscript which is the orbital angular momentum about the symmetry axis in terms of $\hbar$. The carbon-metal distances for $V(cp)_2$, $Cr(cp)_2$, $Fe(cp)_2$, $Co(cp)_2$, and $Ni(cp)_2$ given in table 1 are also shown in figure 1. However, because the π-electrons of the aromatic rings are distributed in regions closer than the carbon-metal distance to the metal ion, it may be better to evaluate the 3d-orbital splitting of these molecules with r_o between 1.5 and 1.7 Å. This corresponds to taking the charged loops about 0.8 Å, or a little less than half the

Table 1

Carbon-Metal Distances

M	M-C distance (Å)	ref.
V	2.3_0*	(17)
Cr	2.2_2*	(17)
Fe	2.05	(18)
Co	2.1_3*	(17)
Ni	2.20	(19)

*These values of the carbon-metal distance were estimated by comparing these unit cell dimensions with $Fe(C_5H_5)_2$, where the carbon-metal distances are known from X-ray work.

van der Waals radius of aromatics, closer than the aromatic groups to the metal ion. Although we have calculated only the splitting of the 3d orbitals, it should be pointed out that K mixes the 4s- and $3d_o$-orbitals. These are the only orbitals that mix under K. This will lower the energy of the $(3d_o\text{-}4s)$ mixed orbital.

From these considerations, we will assume that the $3d_o$- and $3d_{\pm 2}$- orbitals lie close together while the $3d_{\pm 1}$- orbitals are considerably higher in energy. We will later show that this assumption is borne out by the observed magnetic susceptibilities.

Figure 1, Appendix, p. 106 shows that $3d_{+m}$ and $3d_{-m}$ are degenerate. This indicates that ℓ_z, the orbital angular momentum about the symmetry axis, is a good quantum number. This is a result of being able to replace point charges by a circular line charge.

We now turn to consider the ligand field splitting of atomic states characterized by a total L and S under the potential K. The potential can be written

$$K = \sum_i 2e(q2\pi r_o \sin \vartheta_o) \left\{ 2\sqrt{\pi} \left(\frac{1}{r_>}\right)_i Y_{0,0}(\vartheta_i, \varphi_i) \right.$$

$$+\sqrt{\frac{\pi}{5}}\left(1-\frac{3}{2}\gamma^2\right)\left(\frac{r_<^2}{r_>^3}\right)_i Y_{2,0}(\vartheta_i, \varphi_i) + \frac{\sqrt{\pi}}{12}\left(8-40\gamma^2+35\gamma^4\right)\left(\frac{r_<^4}{r_>^5}\right)_i Y_{4,0}(\vartheta_i, \varphi_i) \tag{29}$$

$$= 2e(q2\pi r_o \sin \vartheta_o)\left\{\left(\frac{1}{r_>}\right)_{3d} + \frac{\alpha}{4}\left(1-\frac{3}{2}\gamma^2\right)\left(\frac{r_<^2}{r_>^3}\right)_{3d}\left[L_z^2 - L(L+1)\right]\right.$$

$$\left. + \frac{\beta}{64}\left(8-40\gamma^2+35\gamma^4\right)\left(\frac{r_<^4}{r_>^5}\right)_{3d}\left[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2\right]\right\} \tag{30}$$

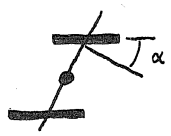
where in equation 30 we have substituted the operator equivalents to the spherical harmonics as given by Stevens (13). Only for the metal ions in $V(C_5H_5)_2$, $Cr(C_5H_5)_2^+$, $Mn(C_5H_5)_2$, and $Ni(C_5H_5)_2$ is this approximation possible because only for these compounds does the magnetic susceptibility correspond to the multiplicity of the ground state terms of the respective metal ions. The ground state terms of these ions are V^{+2}: $3d^3\ {}^4F$; Cr^{+3}: $3d^3\ {}^4F$; Mn^{+2}: $3d^5\ {}^6S$; and Ni^{+2}: $3d^8\ {}^3F$. The ${}^6S$ state of Mn^{+2} is orbitally non-degenerate so it is not split by the ligand field. For $3d^3\ {}^4F$ and $3d^8\ {}^3F$, Bleaney and Stevens (19) give

$$\alpha = \frac{2}{105}$$

$$\beta = \frac{2}{315} \qquad (31)$$

Using these values for α and β, and again using Hartree's radial functions for the 3d orbitals of Mn^{+2}(16) as representative, we plot in figure 2, Appendix, p. 107, the splitting of the F-state versus the distance between the metal atom and the charged loops with fixed radius (1.22 Å). The energy scale is based on taking the charge on each loop to be equal to the electronic charge. Figure 3 shows that for $V(C_5H_5)_2$, $Cr(C_5H_5)_2^+$, and $Ni(C_5H_5)_2$ an orbital singlet lies lowest.

If under K the ground state is orbitally degenerate or nearly degenerate we must consider the Jahn-Teller effect. The Jahn-Teller effect results from the interaction between molecular vibration and the orbitally degenerate ground electronic state (see Moffitt and Liehr (20), for example). But for our purposes the Jahn-Teller effect just produces a distortion of the normal molecular configuration. We will consider the distortion where the cp groups remain parallel and as regular pentagons, but are translated with respect to each other (I), measuring the distortion by the angle α. We will not



(I)

consider distortions of the cp rings because it does not produce splittings different from (I).

Then under the distortion (I), with a slight translation in the y-direction,

$$\frac{1}{2}\left(1-\frac{3}{2}\gamma^2\right)Y_{2,0} \rightarrow \frac{1}{2}\left[1-\frac{3}{2}\gamma^2\left(1-\frac{\alpha^2}{2}\right)\right]Y_{2,0} + \frac{\sqrt{3}}{4}\gamma^2\alpha Y_{2,1} + \frac{\sqrt{3}}{8}\gamma^2\alpha^2 Y_{2,-2} \quad (32)$$

and

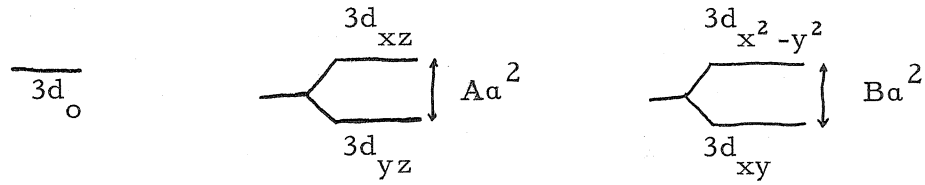
$$\frac{1}{16}\left(8-40\gamma^2+35\gamma^4\right)Y_{4,0} \rightarrow \frac{1}{16}\left[8-\gamma^2(40-36\alpha^2)+\gamma^4(35-51\alpha^2)\right]Y_{4,0}$$

$$+\frac{3\sqrt{10}}{16}\gamma^2(1-5\gamma^2)\alpha Y_{4,+1} + \frac{3\sqrt{5}}{16}\gamma^2(2-3\gamma^2)\alpha^2 Y_{4,-2}$$

$$-\frac{3\sqrt{5}}{64}\gamma^2\alpha^3 Y_{4,+3} + \frac{3\sqrt{35}}{128}\gamma^2\alpha^2 Y_{4,-4}\ , \quad (33)$$

where we have used the convention for denoting spherical harmonics as given in equation 21. From these transformations we see that we can divide the potential V roughly into K and T, $V \rightarrow K$ as $\alpha \rightarrow 0$.

Qualitatively, this distortion removes the orbital degeneracy as shown for the one-electron orbitals:



It is to be noted that the splitting varies as α^2, for small distortions, as it should since a distortion of $-\alpha$ obviously cannot reverse the splitting. Also, under the distortion the one-electron wave functions mix. For the slight translation in (I) along the y-axis,

$$
\begin{aligned}
3d_o &\longrightarrow 3d_o + a\ 3d_{yz} + b\ 3d_{x^2-y^2} \\
3d_{yz} &\longrightarrow 3d_{yz} - a\ 3d_o + e\ 3d_{x^2-y^2} \\
3d_{xz} &\longrightarrow 3d_{xz} + e\ 3d_{xy} \\
3d_{xy} &\longrightarrow 3d_{xy} - e\ 3d_{xz} \\
3d_{x^2-y^2} &\longrightarrow 3d_{x^2-y^2} - b\ 3d_o - c\ 3d_{yz}
\end{aligned}
\qquad (34)
$$

where the coefficients a, b, c, and e depend on the strength of the distortion and on the energy separation between the orbitals under K.

Within the strong ligand field approximation we have tentatively assumed that the d_o and $d_{\pm 2}$ orbitals lie considerably below the $d_{\pm 1}$

orbitals energetically. But we have not been able to determine convincingly whether the d_o-orbital lies lowest or the $d_{\pm 2}$ orbitals. Nor do we know the extent of the Jahn-Teller distortion. However, we are able to learn some of the answers empirically by comparing the observed values of the magnetic susceptibility.

The experimental values of the magnetic susceptibility can be expressed in terms of effective magnetic moments by the relation

$$\mu = \sqrt{\frac{3kT\chi}{N}} \quad \beta \qquad (35)$$

after correcting the magnetic susceptibility χ for the diamagnetism of the ligands. In equation 35, k is the Boltsmann's constant, T is the absolute temperature, N is Avogadro's number, and β is the Bohr magneton. The effective magnetic moments for the sandwich compounds are tabulated in table 2. The metal appears to be doubly-charged in the bis-cyclopentadienyl metal molecules and correspondingly more charged in the sandwich ions, but it appears to be uncharged in the dibenzene metal molecules. We will come back to the dibenzene compounds in the next section where we consider the covalent model.

For the cp sandwich molecules and ions we can discern a general orbital arrangement from table 2: three d-orbitals lie considerably below the other two d-orbitals (we are neglecting the 4s- and 4p-orbitals for the moment, although the 4p-orbitals are presumably considerably higher than the d-orbitals) and electrons are added to the

Table 2

Experimentally Measured Magnetic Moments of the Sandwich Compounds

Compound*	Number of d-electrons	μ Expt.(β)	μ Spin only(β)	Number of unpaired electrons	Ref.
$Ti(cp)_2^{++}$	0	0	0	0	(21)
$Ti(cp)_2^{+}$	1	2.29±.05	1.73	1	(22)
$V(cp)_2^{++}$	1	1.90±.05	1.73	1	(22)
$Ti(cp)_2$	2	0	0	0	(23)
$V(cp)_2^{+}$	2	2.86±.06	2.83	2	(22)
$V(cp)_2$	3	3.84±.04	3.87	3	(24)
$Cr(cp)_2^{+}$	3	3.73±.08	3.87	3	(25)
$Cr(cp)_2$	4	3.20±.16	2.83	2	(26)
$V(bz)_2$	5	1.68±.08	1.73	1	(27)
Cr(bz)(cp)	5	1.70	1.73	1	(28)
$Cr(bz)_2^{+}$	5	1.71	1.73	1	(29)
$Mn(cp)_2$	5	5.71±.29**	5.91	5	(30)
$Fe(cp)_2^{+}$	5	2.34±.12	1.73	1	(26)
$Cr(bz)_2$	6	0	0	0	(25)
$Fe(cp)_2$	6	0	0	0	(26)
$Co(cp)_2^{+}$	6	0	0	0	(26)
$Co(cp)_2$	7	1.76±.07	1.73	1	(26)
$Ni(cp)_2^{+}$	7	1.82±.09	1.73	1	(26)
$Ni(cp)_2$	8	2.86±.11	2.83	2	(26)

*cp = cyclopentadiene negative ion, bz = benzene.

**Diluted with $Mg(cp)_2$.

three low-lying d-orbitals according to Hund's rule of maximum multiplicity. There are two exceptions to this general pattern, however. Ti^{+2} has only two d-electrons, but it is diamagnetic. This might arise from the interaction with neighboring molecules in the crystal which quenches the spin; although, it may arise from the d_o-orbital being considerably below the $d_{\pm 2}$-orbital. $Mn(cp)_2$ has five unpaired electrons instead of only one. This must arise from the especially great stability of the ^6S state of free Mn^{+2}.

Except for $Ti(cp)_2$, the sandwich ion with two d-electrons has two unpaired electrons, while the compounds with three d-electrons have three unpaired electrons. Except for $Mn(cp)_2$, the cp sandwich molecules with ν d-electrons (ν = 4, 5, 6) have $(6 - \nu)$ unpaired electrons. These latter are $Cr(cp)_2$, $Fe(cp)_2^+$, $Fe(cp)_2$, and $Co(cp)_2^+$. Then the molecules $Co(cp)_2$ and $Ni(cp)_2^+$ with seven d-electrons have only one unpaired electron.

The three low-lying orbitals are not pure 3d-orbitals. One of them is some combination of $3d_o$ and 4s orbitals. The other orbital formed from the $3d_o$ and 4s orbitals must be considerably above the three low-lying orbitals.

Deviations of the observed magnetic moment from the spin only value are a measure of the amount of orbital angular momentum in the ground and low-lying ($\sim 10^3 cm^{-1}$) excited states. We will con-

sider the results of the magnetic susceptibility measurements in detail later when we discuss the fine structure for each of the sandwich molecules in table 2.

Covalent Model. In considering quantum mechanically the change in energy in the formation of a sandwich molecule from two cyclopentadienide ions and a free metal ion, we calculate an exchange integral and a coulomb integral. Except for using the point or line charge model, the ligand field approach represents the coulomb integral. That is, the exchange integral is assumed to be zero. That this is not a good approximation in the sandwich compounds is demonstrated by Dunitz and Orgel's calculation of the overlap between the 3d orbitals of iron in ferrocene and the cyclopentadienyl rings. Using molecular orbitals of the appropriate symmetry for the rings Dunitz and Orgel obtained (4)

$$\begin{aligned} S(a_{1g}, 3d_o) &= 0.01 \\ S(e_g^{\pm 1}, 3d_{\pm 1}) &= 0.37 \\ S(e_g^{\pm 2}, 3d_{\pm 2}) &= 0.29 \\ S(a_{1g}, 4s) &= 0.50 \end{aligned} \qquad (36)$$

These values, however, may be considered to be extreme, because the carbon-metal distance in ferrocene is shorter than any others that have been obtained (Table 1). Therefore, in this section, instead of assuming that each of the magnetic electrons moves in an orbital

associated completely with the metal ion, we will assume that the π -electrons of the aromatic system and the electrons beyond argon of the metal move in molecular orbitals, orbitals which are constructed from orbitals associated with both the metal atom and the aromatic rings. We will start by forming π, symmetry orbitals for the aromatic rings.

For cyclopentadienyl using the five $2p_z$ orbitals we can obtain the symmetry orbitals

$$a_1 = \mathcal{N}'_o \left\{ p_{z1} + p_{z2} + p_{z3} + p_{z4} + p_{z5} \right\} \tag{37}$$

$$e^m = \mathcal{N}'_m \left\{ p_{z1} + \omega^m p_{z2} + \omega^{2m} p_{z3} + \omega^{3m} p_{z4} + \omega^{4m} p_{z5} \right\} \tag{38}$$

$$m = \pm 1, \pm 2 \tag{39}$$

where $\omega = e^{i2\pi/5}$, the $\mathcal{N}$'s are normalizing factors, and the subscripts of p_z number the carbon atoms around the ring. We have generated these functions by using the five-fold rotation operator C_5. Similarly, for benzene we obtain the molecular orbitals

$$a_1 = \mathcal{N}''_o \left\{ p_{z1} + p_{z2} + p_{z3} + p_{z4} + p_{z5} + p_{z6} \right\} \tag{40}$$

$$e^m = \mathcal{N}''_m \left\{ p_{z1} + \omega^m p_{z2} + \omega^{2m} p_{z3} + \omega^{3m} p_{z4} + \omega^{4m} p_{z5} + \omega^{5m} p_{z6} \right\} \tag{41}$$

$$m = \pm 1, \pm 2 \tag{42}$$

$$b_1 = \nu'' 3 \left\{ p_{z1} - p_{z2} + p_{z3} - p_{z4} + p_{z5} - p_{z6} \right\} \qquad (43)$$

where for benzene $\omega = e^{i2\pi/6}$. The calculated energy for these molecular orbitals is shown in table 3. Q is a constant and β, which is negative, is the usual resonance integral.

Table 3

Aromatic Molecular Orbital Energies

Cyclopentadienyl		Benzene	
Molecular Orbital	Energy	Molecular Orbital	Energy
a_1	$Q+2\beta$	a_1	$Q+2\beta$
e^{+1}, e^{-1}	$Q+2\beta\cos(\frac{2\pi}{5})$	e^{+1}, e^{-1}	$Q+\beta$
e^{+2}, e^{-2}	$Q-2\beta\cos(\frac{2\pi}{5})$	e^{+2}, e^{-2}	$Q-\beta$
		b_1	$Q-2\beta$

Moreover, with the two aromatic groups of the sandwich molecule in a staggered conformation, the molecule has inversion symmetry. Then we can combine the molecular orbitals for the two aromatic groups into symmetrical and unsymmetrical (gerade and ungerade) molecular orbitals under inversion. To a first

approximation, the g and u aromatic orbitals of the same rotational symmetry remain degenerate.

We now have to see what metal ion orbitals mix with what aromatic molecular orbitals. First we see that since s- and d-orbitals are even functions they will mix with g aromatic molecular orbitals, while the p-funttions are odd so they will mix with u-orbitals. Also, the e^m-molecular orbitals have been formed so that they have the same rotational symmetry as metal orbitals with the component of orbital angular momentum about the symmetry axis m. We thus obtain the molecular orbitals for the sandwich molecule

$$d'_o = \nu_o(d_o + \gamma s + \delta a_{1g}) \tag{44}$$

$$d'_{\pm 1} = \nu_1(d_{\pm 1} + \epsilon\, e_g^{\pm 1}) \tag{45}$$

$$d'_{\pm 2} = \nu_2(d_{\pm 2} + K e_g^{\pm 2}) \tag{46}$$

$$s' = \nu_3(s + \zeta d_o + \eta a_{1g}) \tag{47}$$

$$a'_u = \nu_4(a_{1u} + \iota p_o) \tag{48}$$

$$e_u^{\pm 1} = \nu_5(e_u^{\pm 1} + \lambda\, p_{\pm 1}) \tag{49}$$

$$a'_{1g} = \nu_6(a_{1g} + \mu d_o + \xi s) \tag{50}$$

where the γ's are normalizing factors. Except for d'_o and s' we have here defined only the bonding orbitals; there is an analogous set of antibonding orbitals.

From table 3, for the dicyclopentadienyl system the ground state configuration is $(a_{1g})^2(a_{1u})^2(e_g^{+1}e_g^{-1}e_u^{+1}e_u^{-1})^6$ and for dibenzene $(a_{1g})^2(a_{1u})^2(e_{g\pm1})^4(e_{u\pm1})^4$. Let us now consider the bonding between a metal ion with two electrons beyond argon (e.g., Ti^{+2}) and the dicyclopentadienyl system. Which of the metal orbitals to be used in bonding will depend on a) the overlap with the aromatic rings and b) promotional energy involved in rearranging the electrons in the metal ion and the dicyclopentadienyl system. From these considerations it would seem that the configuration $(a'_{1g})^2(a'_u)^2(e_{u\pm1})^4(d'_{+1})^4$ would be more important than the configuration $(a'_{1g})^2(a'_u)^2(e_{u\pm1})^4(d'_{\pm2})^4$: first, because $S(e_{g\pm1}, d_{\pm1}) > S(e_{g\pm2}, d_{\pm2})$ and secondly, because the $d'_{\pm2}$-orbitals are presumably higher energetically than $d'_{\pm1}$. Moffitt (2) has estimated that the $e_{g\pm1}$-orbitals of the dicyclopentadienyl system have about the same energy as the $3d_{\pm1}$-orbitals of iron which gives considerable credence to the second mentioned reason. However, a mixture of these two configurations is closer to the reality than either alone. This explains how an ionic model gave useful results: the $d'_{\pm2}$ and d'_o orbitals lie considerably lower than what is now the $d'^*_{\pm1}$-antibonding orbitals.

In the dibenzene metal compounds there may be only one low-

lying magnetic orbital, the d'_o orbital, because from table 2 the observed value of the magnetic moment is the same as the spin only value. The use of the $d'_{\pm 2}$-orbitals is of great importance to the stability of the dibenzene molecules as follows from the electroneutrality principle (31). Charge transferred to the metal atom through the a'_g-, a'_u-, e''_u-, and $d'_{\pm 1}$-orbitals is balanced by the charge transferred to the aromatic groups through the $d'_{\pm 2}$-orbitals.

Before the configurations for the ground states of the sandwich molecules having unpaired electrons can be written down, we have to investigate an apparent difficulty: If an electron in a $d'_{\pm 1}$-orbital, say, is out on the rings at a certain instant, does it "lose its sense of direction" and come back to the metal atom in the d_{-1}-orbital? If this were so it would admit sub-configurations of the form $\{d'_{+1} + d'_{-1}\}$. This problem has considerable relevance because in a later section we will be interested in the effects of spin-orbit interaction on the mixing of spin and orbital angular moments. However, we can dispose of this problem by expanding the molecular orbitals e^{+2}, e^{+1}, e^{-1}, and e^{-2} of cyclopentadienyl and benzene in terms of spherical harmonics taking the origin at the center of the aromatic ring: we will find that the sets of spherical harmonics associated with these four molecular orbitals are mutually exclusive.

If we let

$$P = \int_0^{2\pi} p_{zl} \exp(im'\varphi)\, d\varphi \tag{51}$$

then

$$\int_0^{2\pi} (e^m)^* \exp(im'\phi)\, d\varphi = \nu_m P \sum_{n=0}^{5,6} \omega^{n(m'-m)} \tag{52}$$

For cyclopentadienyl the right side of equation 52 can be written as

$$\nu_m P \left\{ 1 + 4(-1)^{m'-m} \cos(m'-m)\frac{\pi}{5} \cos(m'-m)\frac{2\pi}{5} \right\} \tag{53}$$

First, if we replace m' by m'+ 5 or m'- 5, the expression in equation 53 remains unchanged. Therefore, what we obtain for m' is true for m'+ 5 and m' - 5, as well as m' + 10, m' - 10, etc. Proceeding further we find

$$e^m = \sum_{\nu=-\infty}^{\infty} \sum_{l \geq |m+5\nu|} R_l Y_{l,(m+5\nu)} \qquad \text{(cyclopentadienyl)} \tag{54}$$

Similarly,

$$e^m = \sum_{\nu=-\infty}^{\infty} \sum_{l \geq |m+6\nu|} R_l Y_{l,(m+6\nu)} \qquad \text{(benzene)} \tag{55}$$

From equation 54 or 55 we see that if $Y_{l,m''}$ occurs in the expansion of e^{+1}, say, it will not occur in the expansion of e^{+2}, e^{-1}, or e^{-2}.

Therefore, if an electron is in the d_{+1}-orbital it will not be found at a later time in the d_{-1}-orbital. Formally, m_ℓ, the orbital angular momentum about the symmetry axis is still approximately a good quantum number even with bonding, and configurations may be written accordingly.

With regard to the orbital angular momentum operator, $\underset{\sim}{\ell}$, in general,

$$(e^m | \ell_z | e^m) \neq 0 \tag{56}$$

although the expectation value of ℓ_z for these molecular orbitals is probably small. Also, these molecular orbitals will obey the same rules for the raising and lowering operators as do the corresponding d-orbitals, except that for cyclopentadienyl

$$(e^{+2} | \ell_- | e^{-2}) \neq 0 \tag{57}$$

and for benzene

$$(e^{+2} | \ell_- | b_1) = (b_1 | \ell_- | e^{-2}) \neq 0 \tag{58}$$

We will not be too much concerned about the magnitude of the matrix elements of $\underset{\sim}{\ell}$ with respect to the molecular orbitals associated with the aromatic system because our later results are dependent on spin-orbit interaction and the spin-orbit coupling coefficient for the aromatic groups is quite small.

The orbital splittings with the covalent model are essentially in accord with those of the ionic model. The main difference is that the orbital angular momentum is reduced. Thus, for instance,

$$(d'_{+2}|\ell_z|d'_{+2}) = 2\hbar k < 2\hbar \quad . \tag{59}$$

Fine Structure

General Theory. Two important paramagnetic properties are the spectroscopic splitting factors (g-factors) and the zero-field splitting (when $S \geq 1$). Of the magnetic perturbations applied to the ion in a ligand field, the g-factors are determined by the spin-orbit interaction, while both the spin-orbit and spin-spin interactions determine the zero-field splittings. The effect of the spin-spin interaction will be considered qualitatively only because a) it is usually small compared with the spin-orbit interaction, b) it gives rise to no further splitting of the energy levels beyond the spin-orbit interaction, and c) it is especially difficult to determine when the total orbital angular momentum L is no longer a good quantum number.

Our method of handling the spin-orbit interaction depends on whether the orbital ground-state of the ion in a ligand field is non-degenerate or near-degenerate; i.e., whether the energy separation between the ground state and the next higher state is very large compared to the spin-orbit interaction ($E_1 - E_0 \gg \zeta$) or of the same order of magnitude as the spin-orbit interaction ($E_1 - E_0 \sim \zeta$). We will first consider the method of calculating the g-factor and zero-field splittings arising from spin-orbit coupling when the orbital ground-state of the metal ion is non-degenerate.

The method involving projection operators used by Pryce (32) is the more general and elegant procedure for obtaining the necessary relations, but the more straightforward method of Bleaney and Stevens (14) will be used here. We consider the magnetic perturbation Hamiltonian

$$\mathcal{H}' = \sum_i \zeta_i \underset{\sim}{l}_i \cdot \underset{\sim}{s}_i + |\beta| \sum_i (\underset{\sim}{l}_i + 2\underset{\sim}{s}_i) \cdot \underset{\sim}{H} \qquad (60)$$

The ionic states perturbed by the ligand field, including bonding, will be taken as our basis states. These states then represent the solutions of the Schrödinger equation containing only kinetic and electrostatic potential energies, both of which are real. Therefore the states $|n\rangle$ can be chosen real and independent of spin variables so the matrix elements of $\underset{\sim}{l}_i = -i\, \underset{\sim}{r} \times \frac{\partial}{\partial \underset{\sim}{r}}$ are purely imaginary. As $\underset{\sim}{l}_i$ is Hermitian, diagonal elements vanish and off-diagonal elements are antisymmetrical ($\langle m| \underset{\sim}{l}_i |n\rangle = - \langle n| \underset{\sim}{l}_i |m\rangle$). Denoting the ground state by $|0\rangle$, we have in first order

$$W^{(1)} = \langle 0| \mathcal{H}' |0\rangle = \langle 0| \sum_i \zeta_i \underset{\sim}{l}(i) \cdot \underset{\sim}{s}(i) + \sum_i (\underset{\sim}{l}(i) + 2\underset{\sim}{s}(i)) \cdot \underset{\sim}{H} |0\rangle \qquad (61)$$

$$= 2|\beta| \underset{\sim}{S} \cdot \underset{\sim}{H} \qquad (62)$$

where $\underset{\sim}{s}_{(i)}$ acts on the ith electron and $\underset{\sim}{S} = \sum_i \underset{\sim}{s}(i)$. (In the following we will reserve subscripts for denoting components of a vector.)

In second order,

$$W^{(2)} = - \sum_{n \neq o} \frac{\langle 0 | \mathcal{H}' | n \rangle \langle n | \mathcal{H}' | 0 \rangle}{E_n - E_o} \tag{63}$$

$$= - \sum_{\mu, \nu = x, y, z} \sum_{i,j} \sum_{n \neq o} \left\{ \frac{\langle 0 | \ell_\mu(i) | n \rangle \langle n | \ell_\nu(j) | 0 \rangle}{E_n - E_o} \right.$$

$$\left. \times (\zeta_i s_\mu(i) + |\beta| H_\mu)(\zeta_j s_\nu(j) + |\beta| H_\nu) \right\} . \tag{64}$$

It is sufficiently general for our purposes to take $\zeta_i = \zeta_j$ for all i and j because 3d, 4s, and 4p orbitals are not mixed under spin-orbit interaction; i.e., considering hydrogen-like orbitals $\psi_{n\ell m}$ and $\psi_{n'\ell'm'}$,

$$\int \psi^*_{n\ell m} \zeta \underset{\sim}{\ell \cdot s} \psi_{n'\ell'm'} \, d\tau = 0 \text{ if } \ell \neq \ell' . \tag{65}$$

Equation 64 can be simplified further. As $|0\rangle$ and $|n\rangle$ are products of one-electron orbitals, the matrix element $\langle 0 | \ell_\mu(i) | n \rangle$ vanishes if $|0\rangle$ and $|n\rangle$ differ in more than one orbital (33) --- $|0\rangle$ and $|n\rangle$ will differ by at least one orbital. Let us say that by permutation $|0\rangle$ and $|n\rangle$ differ in the jth orbital. Then

$$\langle 0 | \ell_\mu(j) | n \rangle = \langle 0 | \ell_\mu(i) | n \rangle \delta_{ij} . \tag{66}$$

Further, because the spin-orbit interaction is small it is a sufficiently good approximation to let $\underset{\sim}{s}_{(i)}$ operate on the manifold of spin functions characterized by the total spin S, and S will have the value of one-half times the number of unpaired electrons; that is, the ground state has maximum multiplicity. Then since

$$\left\langle S, m_s \right| s_\mu(i) \left| S, m_s' \right\rangle = \left\langle S, m_s \right| s_\mu(j) \left| S, m_s' \right\rangle \tag{67}$$

we obtain

$$\left\langle S, m_s \right| s_\mu(i) \left| S, m_s' \right\rangle = \frac{1}{2S} \left\langle S, m_s \right| S_\mu \left| S, m_s' \right\rangle . \tag{68}$$

Writing

$$\Lambda_{\mu\nu} \Lambda_{\nu\mu} = \sum_{n \neq o} \sum_{i} \frac{\left\langle 0 \right| \ell_\mu(i) \left| n \right\rangle \left\langle n \right| \ell_\nu(i) \left| 0 \right\rangle}{E_n - E_o} \tag{69}$$

equation 64 can be written

$$W^{(2)} = - \sum_{\mu, \nu = x, y, z} \left\{ \left(\frac{\zeta}{2S} \right)^2 \Lambda_{\mu\nu} S_\mu S_\nu \right.$$

$$\left. + 2|\beta| \frac{\zeta}{2S} \Lambda_{\mu\nu} S_\mu H_\nu + \beta^2 \Lambda_{\mu\nu} H_\mu H_\nu \right\} . \tag{70}$$

Combining with equation 62, to second order,

$$W^{(1)} + W^{(2)} = \sum_{\mu, \nu = x, y, z} \left\{ 2|\beta| \left(\delta_{\mu\nu} - \frac{\zeta}{2S} \Lambda_{\mu\nu} \right) S_\mu H_\nu \right.$$

$$\left. - \left(\frac{\zeta}{2S} \right)^2 \Lambda_{\mu\nu} S_\mu S_\nu - \beta^2 \Lambda_{\mu\nu} H_\mu H_\nu \right\} . \tag{71}$$

Equation 71 gives the energy in terms of the spin variables and the applied magnetic field. The coefficient $2(\delta_{\mu\nu} - \frac{\zeta}{2S}\Lambda_{\mu\nu})$ is the μ,ν dyad of the g-tensor, the terms involving $S_\mu S_\nu$ represent the contribution of spin-orbit interaction to the zero-field splitting, and the terms involving $H_\mu H_\nu$ correspond to a temperature-independent susceptibility.

If the orbital ground state of an ion in a ligand field can be approximated by an atomic term with total angular momentum L, then, as given by Pryce (32),

$$\Lambda_{\mu\nu} = \sum_{n\neq o}{}' \frac{\langle 0|L_\mu|n\rangle\langle n|L_\nu|0\rangle}{E_n - E_o} \tag{72}$$

and

$$W^{(1)} + W^{(2)} = \sum_{\mu,\nu=x,y,z} \Big\{ 2|\beta|(\delta_{\mu\nu} - \lambda\Lambda_{\mu\nu})S_\mu H_\nu - \lambda^2\Lambda_{\mu\nu}S_\mu S_\nu - \beta^2\Lambda_{\mu\nu}H_\mu H_\nu \Big\}. \tag{73}$$

Since $\Lambda_{\mu\nu}$ is a symmetric dyadic, it can be diagonalized. Therefore, we can write zero-field splitting terms as

$$\begin{aligned}\Lambda_{xx}S_x^2 + \Lambda_{yy}S_y^2 + \Lambda_{zz}S_z^2 = {} & \frac{1}{3}(\Lambda_{xx}+\Lambda_{yy}+\Lambda_{zz})S(S+1) \\ & + \frac{1}{2}(\Lambda_{xx}-\Lambda_{yy})(S_x^2 - S_y^2) \\ & + [\Lambda_{zz} - \frac{1}{2}(\Lambda_{xx}+\Lambda_{yy})][S_z^2 - \frac{1}{3}S(S+1)].\end{aligned} \tag{74}$$

Neglecting the first term on the right side of equation 74 because it gives rise to no splitting, we can write the spin-Hamiltonian for the g-factor and zero-field splitting as

$$\mathcal{H}' = |\beta| g_x H_x S_x + |\beta| g_y H_y S_y + |\beta| g_z H_z S_z$$
$$+ D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right) \qquad (75)$$

where

$$g_\mu = 2\left(1 - \frac{\zeta}{2S}\Lambda_{\mu\mu}\right) \qquad (76)$$

$$D = -\left(\frac{\zeta}{2S}\right)^2 \left[\Lambda_{zz} - \frac{1}{2}\left(\Lambda_{xx} + \Lambda_{yy}\right)\right] \qquad (77)$$

$$E = -\frac{1}{2}\left(\frac{\zeta}{2S}\right)^2 \left(\Lambda_{xx} - \Lambda_{yy}\right). \qquad (78)$$

If the molecule has axial symmetry, $\Lambda_{xx} = \Lambda_{yy}$ and

$$\mathcal{H} = g_{\parallel} |\beta| H_z S_z + g_{\perp} |\beta| \left(H_x S_x + H_y S_y\right)$$
$$+ D\left[S_z^2 - \frac{1}{3}S(S+1)\right]. \qquad (79)$$

When the orbital ground state of an ion under a ligand field is near-degenerate ($E_1 - E_0 \sim \zeta$), the g-value and zero-field splitting can be calculated to second order in the orbital by the preceding formulae. However, spin angular momentum is not approximately conserved. When the orbital ground state is near-degenerate it is

convenient to first apply W_{s-o} and consider the interaction with the magnetic field later. This leads to a secular equation that may be difficult to solve depending on the degree of the equation. However, the general form of the resulting states can be predicted. If the molecule has one electron or one hole (cf. $Ti(C_5H_5)_2^+$ and $Fe(C_5H_5)_2^+$ in the discussion below), the result of the ligand field and spin-orbit interaction is to leave a Kramer's doublet lying lowest. If the molecule has two unpaired electrons or holes (cf. $Cr(C_5H_5)_2$ below), the ligand field and spin-orbit interaction leaves a group of low-lying states: a singlet state separated from a doublet by the zero-field splitting. We cannot predict without a calculation whether the doublet or the singlet lies lower.

When W_{s-o} is applied to orbital states which are near-degenerate the resulting states are not eigenfunctions of S_z. Therefore, to continue to use the spin-Hamiltonian formalism we introduce a fictitious spin vector $\underset{\sim}{S}'$. The spin-Hamiltonian for the g-value is then

$$\mathcal{H}' = g_x H_x S_x' + g_y H_y S_y' + g_z H_z S_z' . \qquad (80)$$

With one electron or hole we use $S' = \frac{1}{2}$ and denote the states of the Kramer's doublet by $\left| \pm \frac{1}{2} \right\rangle$, and

$$g_x = \left\{\langle 1/2| + \langle -1/2|\right\} \ell_x + 2S_x \left\{|1/2\rangle + |-1/2\rangle\right\} \qquad (81)$$

$$g_y = \left\{\langle 1/2| - i\langle -1/2|\right\} \ell_y + 2S_y \left\{|1/2\rangle + i|-1/2\rangle\right\} \qquad (82)$$

$$g_z = 2\langle 1/2|\ell_z + 2S_z|1/2\rangle \qquad (83)$$

where $\frac{1}{\sqrt{2}}\left\{|1/2\rangle + |-1/2\rangle\right\}$ and $\frac{1}{\sqrt{2}}\left\{|1/2\rangle + i|-1/2\rangle\right\}$ are the diagonal representations of S_x' and S_y'. There is a complication which results if the x, y, z coordinates are not the principal coordinates, i.e., if the matrix elements such as $\langle 1/2|\ell_x + 2S_x|1/2\rangle$ do not vanish. These matrix elements will vanish if the x, y, z coordinates are symmetry coordinates. But if these non-diagonal elements are not zero, then we can transform to principal axes x', y', z', and equation 80 is written as

$$\mathcal{H}' = g_{x'}H_{x'}S_{x'}' + g_{y'}H_{y'}S_{y'}' + g_{z'}H_{z'}S_{z'}' \quad . \qquad (84)$$

Likewise, with two electrons or holes we let $S' = 1$ and

$$g_z = \langle +1|L_z + 2S_z|+1\rangle \quad . \qquad (85)$$

However, the calculation of g_x and g_y is complicated by the fact that in general $|\pm 1\rangle$ and $|0\rangle$ will be separated energetically by an amount which is not small compared to $2|\beta|H$; but the diagonal representation of S_x' is $\frac{1}{2}\left\{|+1\rangle + \sqrt{2}\,|0\rangle + |-1\rangle\right\}$.

Therefore, a secular equation involving the matrix elements of $|\beta|\ (\underset{\sim}{L} + 2\underset{\sim}{S}) \cdot \underset{\sim}{H}$ has to be solved. The g-factor is then obtained by operating on the energy solutions with $\partial/\partial H$. If $2A$ is the energy difference between $|\pm 1\rangle$ and $|0\rangle$ the energy solutions have the form $\pm A$ and $\pm\left(-A \pm \sqrt{A^2 + \alpha^2 \beta^2 H^2}\right)$ with $\alpha \sim 1$, so for $\beta H \ll A$, the g-factors vary linearly with H.

We have obtained the general formulae for calculating the g-factors and the zero-field splittings arising from spin-orbit interaction when the orbital levels are non-degenerate or near-degenerate in the absence of magnetic effects. The first-order spin-orbit interaction was assumed to vanish so we had to go to second-order in the orbital to obtain the preceding formulae. There is, however, the possibility that the ground orbital state is degenerate in the absence of magnetic effects. It may be recalled that in the section dealing with the covalent model the molecular orbitals that were constructed did not necessarily have zero expectation values for ℓ_z. It is thus possible to have first-order spin-orbit interaction which will split the orbital degeneracy. The spin-orbit interaction couples the electron spin with the orbital moment thus aligning the spin along the symmetry axis. We again use the fictitious spin variable $\underset{\sim}{s}'$ and because of the spin alignment $g_\perp = 0$ and $g_{\parallel}$ is given by

$$g_{\parallel} = \frac{\langle \ell_z + 2S_z \rangle}{\langle s'_z \rangle} \tag{86}$$

The overall g-factor is then

$$g = g_{\parallel} / \sqrt{3} \tag{87}$$

We can obtain a g-factor in this manner for each of the two doublet states into which the degenerate level is split by spin-orbit interaction. To obtain an effective g-factor with which we can compare the magnetic moments in table 2 we have to consider a Boltzmann average. Letting the lower state have g-value g_1 and the upper g_2 with respective energies E_1 and E_2 we obtain

$$g_{eff}^2 = \frac{g_1^2 + g_2^2 \, e^{-(E_2 - E_1)/kT}}{1 + e^{-(E_2 - E_1)/kT}} \tag{88}$$

Since both states have the same multiplicity we have dropped this factor.

The doublets resulting from spin-orbit interaction are "non-Kramers doublets" because transitions between the two levels do not occur in the usual magnetic resonance experiments. Since $g_{\perp}(g_x, g_y)$ is zero there is no magnetic moment perpendicular to the symmetry axis through which transitions can be induced by the rf-field. It is found that in several rare earth ions in a crystal field transitions

occur between the non-Kramers doublets if both the rf- and applied magnetic fields are parallel to the symmetry axis (34). Baker and Bleaney (34) give as the fine structure spin Hamiltonian

$$\mathcal{H} = g_z |\beta| s'_z H_z + \Delta_x s'_x + \Delta_y s'_y \qquad (89)$$

where $\underset{\sim}{s'}$ is the fictitious spin variable ($s' = \frac{1}{2}$) and Δ_x and Δ_y do not have unique values but have a distribution of values; they represent the effect of random local departures in the molecule from the normal symmetry. Transitions between the non-Kramers doublets occur at the energy

$$\hbar\omega = [(g_z |\beta| H_z)^2 + \Delta_x^2 + \Delta_y^2]^{1/2} \quad . \qquad (90)$$

Fine Structure of the Sandwich Molecules. To calculate the g-factors and zero-field splitting due to spin-orbit interaction we will use the methods of the preceding section based on the knowledge obtained from considerations of the ionic and covalent models and the experimental values of the magnetic susceptibility. Since detailed knowledge about the ground and low-lying excited states for the paramagnetic sandwich molecules is difficult to obtain from either the ionic or covalent models, we will use the experimental values of the magnetic susceptibility to decrease the number of possible orbital arrangements. That is, the greater the deviation between the experimental and "spin only" values of the magnetic moments given in table 2, the more orbital contribution to the magnetic moment. There is, however, an important difference between the g-factor one would obtain in a magnetic resonance experiment and the magnetic moment obtained from susceptibilities. This disparity results from the fact that most of the data in table 2 was obtained at room temperature (296° K), while magnetic resonance experiments need to be performed at low temperatures ($\sim$10° K) when there is an appreciable contribution of orbital magnetism to the total magnetic moment. Therefore, it is possible that most of the orbital magnetism is associated with a state that, although appreciably occupied at room temperature, is vacant at low temperatures. Then the apparent g-factor from susceptibility measurements could deviate considerably more from

g = 2.00 than the g-factor observed in a magnetic resonance experiment. The converse may also occur; the deviation of the observed values of the magnetic moments from "spin only" may be larger at low temperatures than at room temperature.

Since in our considerations of the g-factor and zero-field splittings we will not be able to distinguish between the compounds listed in table 2 with the same number of d-electrons, we will segregate the work below into groups depending on 1) the number of unpaired electrons and 2) whether we expect non-degenerate or near-degenerate ground states, i.e., whether or not the observed magnetic moment differs from spin-only or not. We will use the fact that within the three magnetic orbitals μ electrons correspond to $(6 - \mu)$ holes, reversing the sign of the spin-orbit coupling coefficient.

One Electron or Hole, Non-Degenerate Ground State. This situation is applicable to $V(C_6H_6)_2$, $Cr(C_6H_6)(C_5H_5)$, $Cr(C_6H_6)_2^+$, and possibly to $V(C_5H_5)_2^{++}$. With benzene as the ligands it appears from the results in table 2 that the sub-configuration $(d'_{\pm 2})^4(d'_0)$ lies considerably below $(d'_{\pm 2})^3(d'_0)^2$ because the observed magnetic moments are essentially the same as the spin only values. The possible reason for this has been discussed in the section dealing with the covalent model. The g-factors are expected to be near 2.00. The

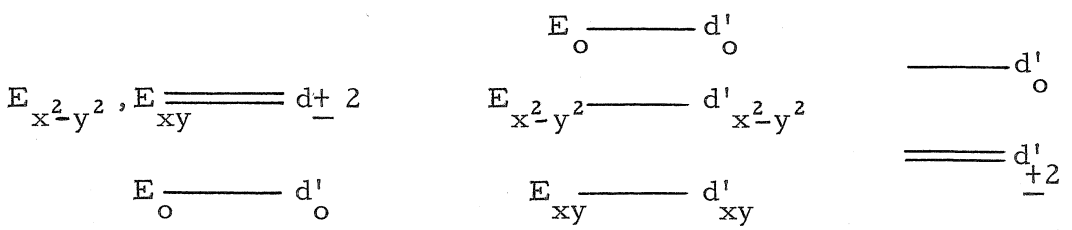
g-factor for $Cr(C_6H_6)_2^+$ has been found to be 1.99 (35, 36, 37). We will consider $V(C_5H_5)_2^{++}$ below.

$Co(C_5H_5)_2$ and $Ni(C_5H_5)_2^+$ each have one unpaired electron. Two orbital arrangements for these compounds can be considered. We can put the unpaired electron into the 4s' orbital giving $g \approx 2.0_0$, or we can put the electron into a d_{xz}^* or d_{yz}^* antibonding orbital. In this latter case we cannot use equation 71 to calculate the g-factor because this does not correspond to Hund's rule of maximum multiplicity. Since there is only one electron in the d_{xz}^* and d_{yz}^* orbitals, we take ζ positive and mix these orbitals with ℓ_z. This yields $g_{\parallel} < 2$. ℓ_x and ℓ_y mix d_{xz}^*, say, with the d_o', $d'_{x^2-y^2}$, and d'_{xy} orbitals (which are filled so ζ is taken to be negative) which yields $g_{\perp} > 2$. Since the energy difference between d_{xz}^* and d_o', $d'_{x^2-y^2}$, and d'_{xy} is probably considerably greater than that between d_{xz}^* and d_{yz}^*, the overall g-factor may be less than 2.

If the $d^*_{\pm 1}$ orbitals are degenerate in the absence of magnetic interactions we obtain with spin-orbit interaction two non-Kramers doublets. We take ζ positive and obtain $g_{\parallel} = 2(-k + 1) \sim 0$ for the lower doublet and $g_{\parallel} = 2(k + 1) \sim 4$ for the upper doublet. k is the orbital angular momentum reduction factor and is less than one. With equations 87 and 88 this leads to an effective g-factor considerably less than two. Since table 2 shows the effective g-factor to be

about two, the $d^{*}_{\pm 1}$-orbitals probably are not degenerate in the absence of magnetic effects.

<u>One Electron or Hole, Near-Degenerate Ground State.</u> This corresponds to $Ti(C_5H_5)_2^{+}$, $Fe(C_5H_5)_2^{+}$, and probably to $V(C_5H_5)_2^{++}$. The three types of energy level arrangements we need to consider are represented by (II), (III), and (IV) for one electron or one hole.



(II) (III) (IV)

The energy level diagram (II) can be distinguished experimentally from (III) and (IV) because of the difference discussed previously between magnetic susceptibility and magnetic resonance experiments. Since d'_o and $d_{\pm 2}$ do not mix in first order under $\underset{\sim}{\ell}$, the g-factor should be very close to 2.00 for the orbital arrangement (II). If the $d_{\pm 2}$ levels are slightly split due to molecular distortion, but d'_o still lies lowest,

$$g_x = 2 - 2\zeta\left[\frac{|a|^2}{E'_{xy} - E'_o} + \frac{|b|^2}{E_{x^2-y^2} - E_o}\right] \qquad (91)$$

$$g_y = 2 - 2\zeta\left[\frac{|c|^2}{E_{xy} - E_o} + \frac{|e|^2}{E_{x^2-y^2} - E_o}\right] \tag{92}$$

$$g_z = 2 - 2\zeta\left[\frac{|f|^2}{E_{xy} - E_o}\right] \tag{93}$$

where

$$a = (d'_o | \ell_x | d'_{xy}) \tag{94}$$

$$b = (d'_o | \ell_x | d'_{x^2-y^2}) \tag{95}$$

$$c = (d'_o | \ell_y | d'_{xy}) \tag{96}$$

$$e = (d'_o | \ell_y | d'_{x^2-y^2}) \tag{97}$$

$$f = (d'_o | \ell_z | d'_{xy}) \tag{98}$$

The matrix elements a, b, c, e, and f will be small, being dependent on the mixing of orbitals, equation 34.

When $d_{\pm 2}$ are split and d'_{xy} lies lowest, (III), we obtain

$$g_x = 2 - 2\zeta\frac{|a|^2}{E_o - E_{xy}} \tag{99}$$

$$g_y = 2 - 2\zeta\left[\frac{|g|^2}{E_{x^2-y^2} - E_{xy}} + \frac{|c|^2}{E_o - E_{xy}}\right] \tag{100}$$

$$g_z = 2 - 2\zeta\left[\frac{|k|^2}{E_{x^2-y^2} - E_{xy}} + \frac{|f|^2}{E_o - E_{xy}}\right] \tag{101}$$

where

$$g = (d'_{xy}|\ell_y|d'_{x^2-y^2}) \tag{102}$$

and

$$k = (d'_{xy}|\ell_z|d'_{x^2-y^2}) \tag{103}$$

While the matrix elements in a, b, c, e, f, and g will be small, k will be of the order of one. Comparing with the susceptibility measurements, table 2, we can expect

$V(C_5H_5)_2$: g is a little less than 2.0 (~ 1.9)

$Ti(C_5H_5)_2$: g is considerably less than 2.0 (~1.2-1.6)

$Fe(C_5H_5)_2$: g is greater than 2.0 (~ 2.1-2.3)

if d'_{xy} lies lowest.

These solutions for the g-factors (equations 91-93 and 99-101) are correct to second order only. We have used the distorted configuration in which the cyclopentadiene rings have been translated with respect to one another along the y-axis, keeping the x-axis as a two-fold symmetry axis. For a more exact formulation of the g-factors we would have to turn to a secular equation, but this is not warranted here because of the uncertainty in the mixing of orbitals.

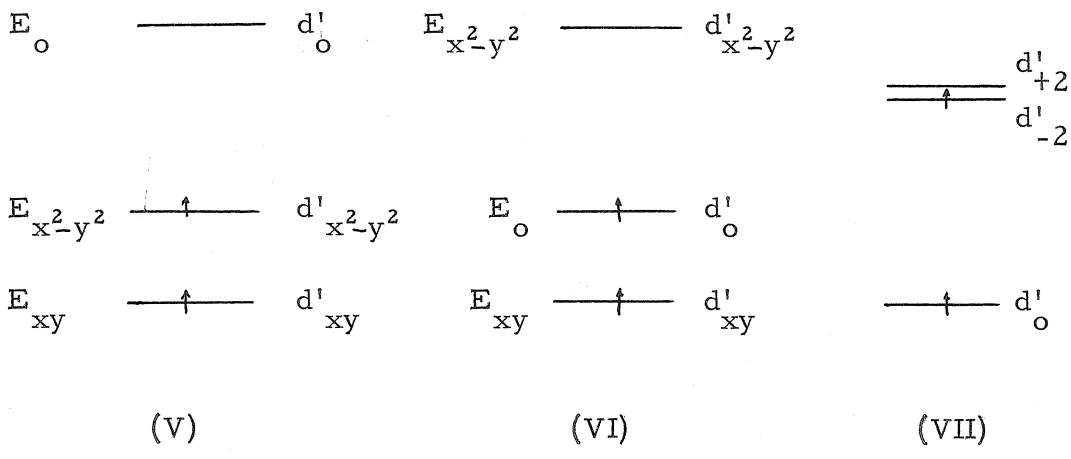
Also, we have neglected the contribution of the $d^*_{\pm 1}$ antibonding orbitals in calculating the g-factors.

(IV) represents an orbitally-degenerate ground state in the absence of magnetic interactions. Neglecting the orbital reduction factor (k=1), equations 86 and 87 give $g_1 = 3.46$ and $g_2 = -1.15$ for the two non-Kramers doublets. The doublet characterized by g_1 lies lowest in $Fe(cp)_2^+$ (ζ negative), while the doublet characterized by g_2 lies lowest in $Ti(cp)_2^+$ and $V(cp)_2^{++}$. In the absence of better data for the spin-orbit interaction in these ions we will assume the doublets to be split by 200 cm^{-1} in $Fe(cp)_2^+$. Using equation 88 at room temperature $g_{eff} = 3.0$ for $Fe(cp)_2^+$ which can be brought into agreement with the observed $g_{eff} = 2.7$ by letting $k < 1$. Even letting the energy difference between the doublets vanish yields $g_{eff} = 2.6$ for $Ti(cp)_2^+$ which is smaller than the observed $g_{eff} = 2.7$. If the observed magnetic moment is correct, energy diagram (IV) is untenable for $Ti(cp)_2^+$. Taking the energy difference between the doublet to be 100 cm^{-1} in $V(cp)_2^{++}$, $g_{eff} = 2.3$ which is in agreement with the observed $g_{eff} = 2.2$ with $k < 1$.

Two Electrons or Holes (S = 1), Non-Degenerate Ground State.

$V(C_5H_5)_2^+$ and $Ni(C_5H_5)_2$ are the examples of this category; we will discuss $V(C_5H_5)_2^+$ first. As was pointed out above, the matrix element $(d'_{xy} | \ell_z | d'_{x^2-y^2})$ leads to the greatest deviation from g = 2.

Therefore, we need consider only three energy level diagrams. We can put the two electrons in the d_{xy}' and $d'_{x^2-y^2}$ orbitals with the d'_o level considerably higher, (V). Or we can consider the d'_{xy} and $d'_{x^2-y^2}$ to be split by $\sim 10^4$ cm^{-1}, and put the two electrons into the low-lying d'_{xy} and d'_o orbitals, (VI). We will also consider the orbital degenerate case (VII).



The energy level arrangement (V) leads to

$$g_x = 2 - \zeta\left[\frac{|a|^2}{E_o - E_{xy}} + \frac{|b|^2}{E_o - E_{x^2-y^2}}\right] \tag{104}$$

$$g_y = 2 - \zeta\left[\frac{|c|^2}{E_o - E_{xy}} + \frac{|e|^2}{E_o - E_{x^2-y^2}}\right] \tag{105}$$

$$g_z = 2 - \zeta\frac{|f|^2}{E_o - E_{xy}} \tag{106}$$

using the matrix elements as defined by equation 94 to 98. Using equations 76-78,

$$D = \frac{1}{4}\zeta\left[g_z - \frac{1}{2}(g_x + g_y)\right] \tag{107}$$

and

$$E = \frac{1}{8}\zeta\left[g_x - g_y\right] \quad . \tag{108}$$

For the energy levels arranged as in (VI),

$$g_x = 2 - \zeta\frac{|b|^2}{E_{x^2-y^2} - E_o} \tag{109}$$

$$g_y = 2 - \zeta\left[\frac{|g|^2}{E_{x^2-y^2} - E_{xy}} + \frac{|e|^2}{E_{x^2-y^2} - E_o}\right] \tag{110}$$

$$g_z = 2 - \zeta\frac{|k|^2}{E_{x^2-y^2} - E_{xy}} \tag{111}$$

with the zero-field splitting given by equations 107 and 108.

Although we have considered the one-electron orbital approximation, it is possible to consider the ground state of V^{+2} in $V(C_5H_5)_2^+$ to arise from a ^3F state. The ligand field theory gives a degenerate ground state ($m_\ell = \pm 2$) under K. Therefore, the potential K + T has to be considered in first order. However, the fine structure parameters are essentially the same as obtained above with the one-electron approximation.

For the orbitally degenerate ground state (VII) spin-orbit interaction yields three non-Kramers doublets. The g-factors from equations 86 and 87 for the doublets are $g_1 = 0.58$, $g_2 = 1.15$ and $g_3 = 1.73$, if we set the orbital reduction factor equal to one. g_1 characterizes the lowest and g_3 the highes doublets for $V(cp)_2^+$. Even taking the energy differences between the doublets to be zero yields a g_{eff} smaller than the observed $g_{eff} = 2.0$. Therefore, (VII) cannot describe the orbital ground state of $V(cp)_2^+$. Moreover, (VII) cannot describe $Ni(cp)_2$ or $Cr(cp)_2$. Even though for these latter molecules g_3 characterizes the lowest and g_1 the highest doublet, the calculated g_{eff} is still less than the observed $g_{eff} = 2.0$ for $Ni(cp)_2$ and $g_{eff} = 2.25$ for $Cr(cp)_2$ regardless of the assumed energy separations between the doublets.

There are various possible fine structure parameters obtainable for $Ni(C_5H_5)_2$. First, Ni^{+2} in $Ni(C_5H_5)_2$ can be characterized as arising from a mixture of the ^3F and ^3P terms. In terms of one-electron orbitals for the holes, the ground state has the form

$$|0\rangle = \left\{a\, d_{+1}\, d_{-1} + b\, d_{+2}\, d_{-2}\right\} \tag{112}$$

with excited states

$$|1a\rangle = \left\{c\, d_{+1}\, d_{o} + e\, d_{+2}\, d_{-1}\right\} \tag{113}$$

$$|-1a\rangle = \left\{c\, d_{o}\, d_{-1} + e\, d_{+1}\, d_{-2}\right\} \tag{114}$$

$$|1b\rangle = \left\{c\ d_{+2}\, d_{-1} - e\ d_{+1}\, d_{o}\right\} \tag{115}$$

$$|-1b\rangle = \left\{c\ d_{+1}\, d_{-2} - e\ d_{o}\, d_{-1}\right\} . \tag{116}$$

This yields

$$g_{\parallel} = 2.00 \tag{117}$$

$$g_{\perp} = 2.00 + 2|\zeta|\left\{\frac{(ac\sqrt{\frac{3}{2}} + eb)^2}{E_{\pm 1a} - E_o} + \frac{(ae\sqrt{\frac{3}{2}} - bc)^2}{E_{\pm 1b} - E_o}\right\} \tag{118}$$

with the zero-field splitting parameter

$$D = \frac{1}{2}\zeta^2\left\{\frac{(ac\sqrt{\frac{3}{2}} - eb)^2}{E_{\pm 1a} - E_o} + \frac{(ae\sqrt{\frac{3}{2}} - bc)^2}{E_{\pm 1b} - E_o}\right\} . \tag{119}$$

These equations, when multiplied by a suitable reduction factor, correspond to putting the two unpaired electrons into the $d^*_{\pm 1}$ antibonding orbitals. There are still other possible aufbau schemes.

We can put the two unpaired electrons into the 4p-orbitals. Because of the small spin-orbit coupling coefficient for the 4p orbitals, the g-factor should be very nearly 2.00 --- possibly a little less. Finally, we could put one electron into a 4s' orbital and the other into a d^*_{xz} or d^*_{yz} antibonding orbitals; these antibonding orbitals probably split because of the Jahn-Teller effect. This latter case corresponds to $Ni(C_5H_5)_2^+$ and $Co(C_5H_5)_2$ as regards the g-factor.

Although we have disregarded the spin-spin contribution to the zero-field splitting, it gets progressively larger in proceeding from Ti^{+2} to Ni^{+2} (38), and thus may be important in $Ni(C_5H_5)_2$. Also, it may well enter with the opposite sign of D obtained from spin-orbit interaction.

Two Electrons or Holes (S = 1), Near-Degenerate Ground State. Susceptibility measurements indicate that $Cr(C_5H_5)_2$ is an example of this category. As a first orientation we can use the formulae for the g-factors and zero-field splittings obtained for $V(C_5H_5)_2^+$, equations 104 to 111. (ζ is negative for $Cr(C_5H_5)_2$.) However, the non-diagonal elements become important here, i.e., terms like Δ_{yz}, complicating even this approximate approach.

Experimentally, $Cr(C_5H_5)_2$ may be difficult to study because the zero-field splitting may be 0.3 cm^{-1} or larger.

Three Electrons (S = 3/2). $V(C_5H_5)_2$ and $Cr(C_5H_5)_2^+$ make up this category. We can view this case from two points. First we can consider the one-electron orbital approximation where the g-factors are determined by the distance between the d'_o, $d_{\pm 2}$-orbitals and the $d^*_{\pm 1}$ antibonding orbitals. Secondly we can consider the molecule to be essentially ionic, so that the metal ions are characterized by a mixture of the ^4F and ^4P terms. For this latter case we will write the orbital ground state as

$$|0\rangle = \left\{a\, d_{+2}\, d_{o}\, d_{-2} + b\, d_{+1}\, d_{o}\, d_{-1}\right\} \tag{120}$$

with the excited states as

$$|1a\rangle = \left\{c\, d_{+2}\, d_{o}\, d_{-1} + e\, d_{+2}\, d_{+1}\, d_{-2}\right\} \tag{121}$$

$$|-1a\rangle = \left\{c\, d_{+1}\, d_{o}\, d_{-2} + e\, d_{+2}\, d_{-1}\, d_{-2}\right\} \tag{122}$$

$$|1b\rangle = \left\{c\, d_{+2}\, d_{+1}\, d_{-2} - e\, d_{+2}\, d_{o}\, d_{-1}\right\} \tag{123}$$

$$|-1b\rangle = \left\{c\, d_{+2}\, d_{-1}\, d_{-2} - e\, d_{+1}\, d_{o}\, d_{-2}\right\} \tag{124}$$

This leads to

$$g_{\parallel} = 2.00 \tag{125}$$

$$g_{\perp} = 2 - \frac{4}{3}\zeta\left\{\frac{\left[a(c + \sqrt{\frac{3}{2}}\, e) + bc\right]^2}{E_{\pm 1a} - E_o} \quad \frac{\left[a(e - \sqrt{\frac{3}{2}}\, c) + be\right]^2}{E_{\pm 1b} - E_o}\right\} \tag{126}$$

and the zero-field splitting is

$$D = \frac{\zeta^2}{9}\left\{\frac{\left[a(c + \sqrt{\frac{3}{2}}\, e) + bc\right]^2}{E_{\pm 1a} - E_o} + \frac{\left[a(e - \sqrt{\frac{3}{2}}\, c) + be\right]^2}{E_{\pm 1b} - E_o}\right\} \tag{127}$$

The observed g-factor for $V(cp)_2$ is 2.00 in solution (39). Recent measurements (40) of D for diluted crystalline $V(cp)_2$ show it to be fairly large ($\sim$ 40 kMc). Such a large zero-field splitting is understandable, for a small difference between $g_{\parallel}$ and $g_{\perp}$ can lead to a large value of D because ζ is large.

Five Unpaired Electrons, $Mn(C_5H_5)_2$. All of the molecules we have considered thus far seem to have three low-lying orbitals which must be filled before electrons are added to higher orbitals. However, $Mn(C_5H_5)_2$ must be considered as an ionic molecule with the Mn^{+2} ion having five unpaired electrons characterized by the ^6S ground state term. The difference between $Mn(C_5H_5)_2$ and the other bis-cyclopentadiene metal molecules must be due to the especially great stability of the ^6S term. Although, since the ferric ion in $Fe(C_5H_5)_2^+$ (also with five d-electrons) is not characterized by a ^6S ground state, the ligand potential V in $Mn(cp)_2$ must be almost as strong as the correlation energy, $\sum_{i<j} \frac{e^2}{r_{ij}}$. Since $\sum_i \zeta_i \underset{\sim}{\ell}_i \cdot \underset{\sim}{S}_i$ does not affect the ^6S term, the g-factor is expected to be near 2 --- the observed values are between 1.99 and 2.01 (41).

The calculation of the zero-field splitting is different for Mn^{+2} than we have considered previously. Neither spin-orbit interaction alone nor the ligand field alone gives rise to a zero-field splitting, but the combined effects of the two do, by consideration of the excited states of the ion (42). Matrix elements of the spin-orbit interaction, $\zeta \sum_i \underset{\sim}{\ell}_i \cdot \underset{\sim}{S}_i$, vanish between two states unless

$$\Delta L = 0, \pm 1 \quad , \qquad \Delta S = 0, \pm 1 \, , \tag{128}$$

while matrix elements of the ligand field, K, vanish unless

$$\Delta S = 0. \tag{129}$$

The lowest order correction which does not vanish is the fourth order correction

$$W^{(4)} = \frac{\langle {}^6S | W_{s-o} | {}^4P \rangle \langle {}^4P | K | {}^4D \rangle \langle {}^4D | K | {}^4P \rangle \langle {}^4P | W_{s-o} | {}^6S \rangle}{(E_{{}^4P} - E_{{}^6S})^2 (E_{{}^4D} - E_{{}^6S})} \tag{130}$$

The third order correction vanishes because the matrix element $\langle {}^4P | K | {}^4P \rangle$ vanishes. It is the $Y_{2,0}(\vartheta, \varphi)$ term in K, V_2, which produces the splitting. Letting $V_2 \approx 5 \cdot 10^3$ cm^{-1}, $\zeta \approx 300$ cm^{-1}, and $(E_{{}^4P} - E_{{}^6S}) \approx (E_{{}^4D} - E_{{}^6S}) \approx \Delta E \approx 3 \cdot 10^4$ cm^{-1}

$$D \sim \frac{K^2 \zeta^2}{(\Delta E)^3} \sim 0.1 \text{ cm}^{-1} \tag{131}$$

As mentioned previously, besides the spin-orbit contribution to the zero-field splitting there is the magnetic dipole interaction between electron spins. In Mn^{+2} the spin-spin interaction deforms the otherwise spherical symmetry of the ion producing elliptical symmetry. Thus the combined effects of the spin-spin interaction and the axial field produce a zero-field splitting (43):

$$D \sim \frac{\beta^2 \langle r^{-3} \rangle K}{\Delta E} \sim 0.1 \text{ cm}^{-1} \tag{132}$$

In equation 132 ΔE is the energy difference between the $3d^4 4s\ ^6D$ and the $3d^5\ ^6S$ states, and K represents a matrix element of the form $\langle 3d | K | 4s \rangle$. Since the zero-field splitting term D in equation 132 usually enters with opposite sign from D in equation 131 (40), the zero-field splitting will probably be of the order of 0.01 cm^{-1}.

Hyperfine Structure

The interaction between the paramagnetic moment of the molecule and nuclear magnetic moments will produce a hyperfine structure in the paramagnetic resonance spectra. There are two types of nuclei that can produce hyperfine structure with the sandwich molecules; i.e., there are two nuclear species with non-zero magnetic moments. These are the protons of the hydrogen atoms bonded to the aromatic rings, and the metal nucleus.

Proton Hyperfine Structure. The Hamiltonian for the proton interaction is

$$W_p = 2|\beta|\gamma_p \hbar \sum_{\substack{j \\ \text{protons}}} \sum_{\substack{i \\ \text{electrons}}} \left\{ \frac{(\underset{\sim}{\ell}_i - \underset{\sim}{s}_i)\cdot \underset{\sim}{I}_j}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|^3} \right.$$

$$+ 3 \frac{[(\underset{\sim}{r}_i - \underset{\sim}{r}_j)\cdot \underset{\sim}{S}_i][(\underset{\sim}{r}_i - \underset{\sim}{r}_j)\cdot \underset{\sim}{I}_j]}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|^5}$$

$$\left. + \frac{8\pi}{3} \delta(\underset{\sim}{r}_i - \underset{\sim}{r}_j)\, \underset{\sim}{S}_i \cdot \underset{\sim}{I}_j \right\} . \qquad (133)$$

The dipole part of equation 133 is very difficult to calculate. Thus, as an approximation one might consider a paramagnetic dipole moment

fixed at the nucleus. This, however, tends to reduce the importance of the dipolar interaction to the hyperfine interaction because of the short-ranged nature of $1/r_j^3$.

The Fermi contact term can act in two ways. First, there is the direct overlap of the metal orbital containing an unpaired electron and the proton. This effect will be small when the metal orbital is made orthogonal to the 1s orbitals (strictly the C-H bond orbitals) of the hydrogen atoms as required by the Pauli principle (44, 45). Secondly, there is the indirect contribution which acts through the carbon atoms. This has been considered by McConnell and Chesnut (46), who give the formula

$$a_N \approx -22.5\ \rho_N \text{ gauss}, \tag{134}$$

where a_N is the proton hyperfine splitting and ρ_N is the unpaired electron density at the adjacent carbon atom (in a p-orbital). The numerical coefficient, 22.5, in equation 134 has been obtained from free aromatic molecules, but due to the influence of the metal atom we must expect a different coefficient for the sandwich molecule. This latter is presumably the principal source of hyperfine splitting in $Cr(C_6H_6)^+$ and related benzenoid molecules having phenyl substitution in the benzene rings. For these molecules $|a_N| = 3.5$ gauss (35, 36, 37).

Metal Nuclear Hyperfine Structure. The hyperfine structure in the sandwich compounds of Ti, Cr, Fe, and Ni will not arrest our attention because of the small natural abundance of the isotopes of these nuclei with non-zero spin and the small magnetic moments of these isotopes. Therefore, this section is principally of interest as regards the sandwich molecules of V, Mn, and Co.

The Hamiltonian for the metal nuclear interaction is that part of W_N, equation 5, which is linear in the nuclear spin vector $\underset{\sim}{I}$:

$$W_N' = 2|\beta|\gamma\hbar \sum_i \left\{ \frac{(\underset{\sim}{\ell}_i - \underset{\sim}{S}_i)\cdot\underset{\sim}{I}}{r_i^3} + 3\,\frac{(\underset{\sim}{r}_i\cdot\underset{\sim}{S}_i)(\underset{\sim}{r}_i\cdot\underset{\sim}{I})}{r_i^5} + \frac{8\pi}{3}\,\delta(\underset{\sim}{r}_i)(\underset{\sim}{S}_i\cdot\underset{\sim}{I}) \right\} . \qquad (135)$$

W_N' acts on the energy levels, split by the ligand field and modified by spin-orbit interaction. Therefore, we can also consider the perturbation

$$\mathcal{H}' = W_{s\text{-}o} + W_N' \qquad (136)$$

applied to an atom in a ligand field. When the ligand field produces a non-degenerate orbital ground state, it is convenient to consider the perturbation $\mathcal{H}'$. But when the orbital ground state is degenerate or near-degenerate, it is more convenient to let W_N' act on the ground state resulting from the combined effects of the ligand field

and spin-orbit interaction.

First we will consider nuclear interaction when the ligand field produces an orbital singlet ground state. Writing the ground and excited orbital states as $|0\rangle$ and $|n\rangle$, in first order,

$$\mathcal{H}' = \frac{8\pi}{3}(2|\beta|\gamma\hbar)\left\langle 0\left|\sum_i \delta(\underset{\sim}{r}_i)\,\underset{\sim}{S}_i\cdot\underset{\approx}{I}\right|0\right\rangle$$

$$+ 2|\beta|\gamma\hbar \sum_{\mu,\nu=x,y,z}\sum_i \left\langle 0\left|\left\{3\frac{r_\mu r_\nu}{r^5} - \frac{\delta_{\mu\nu}}{r^3}\right\}_i\right|0\right\rangle S_\mu(i)\,I_\nu \,. \tag{137}$$

If $|0\rangle$ and $|n\rangle$ are products of 3d orbitals only, then integration over the radial part of each orbital in equation 137 gives the common factor $\overline{1/r^3}$. Also, letting $\underset{\sim}{s}(i)$ operate within the manifold of states of total S, we can replace $\underset{\sim}{s}(i)$ by $(1/2S)\underset{\sim}{S}$. Therefore,

$$\mathcal{H}'^{(1)} = \frac{8\pi}{3S}(2|\beta|\gamma\hbar)\left\langle \sum_i \delta(\underset{\sim}{r}(i))\,S_z(i)\right\rangle_{m_s=S}\underset{\sim}{S}\cdot\underset{\approx}{I}$$

$$+ \frac{P}{2S}\sum_{\mu,\nu=x,y,z}\sum_i \left\langle\left\{3\frac{r_\mu r}{r^2} - \delta_{\mu\nu}\right\}_i\right\rangle_{\psi_i\,\varphi_i} S_\mu I_\nu \,, \tag{138}$$

where

$$P = 2|\beta|\gamma\hbar\,\overline{r^{-3}} \tag{139}$$

Then, in second order

$$\mathcal{H}'^{(2)} = -\sum_{n\neq o} \frac{\langle 0|W_{s-o}|n\rangle\langle n|W_N'|0\rangle}{E_n - E_o} - \sum_{n\neq o} \frac{\langle 0|W_N'|n\rangle\langle n|W_{s-o}|0\rangle}{E_n - E_o} \tag{140}$$

$$= -\frac{\zeta P}{S} \sum_{\mu,\nu=x,y,z} \Lambda_{\mu\nu} S_\mu I_\nu$$

$$-\frac{|\beta|\gamma\hbar\zeta}{S} \sum_{\omega,\mu,\nu=x,y,z}' \sum_{n\neq o} \sum_i \left\{ \frac{\langle 0|\ell_\omega(i)|n\rangle\langle n|\left[3\frac{r_\mu r_\nu}{r^5} - \frac{\delta_{\mu\nu}}{r^3}\right]_i|0\rangle}{E_n - E_o} \right\} S_\omega S_\mu I_\nu$$

$$-\frac{|\beta|\gamma\hbar\zeta}{S} \sum_{\omega,\mu,\nu=x,y,z}' \sum_{n\neq o} \sum_i \left\{ \frac{\langle 0|\left[3\frac{r_\mu r_\nu}{r^5} - \frac{\delta_{\mu\nu}}{r^3}\right]_i|n\rangle\langle n|\ell_\omega(i)|0\rangle}{E_n - E_o} \right\} S_\mu S_\omega I_\nu \tag{141}$$

where we have followed the considerations leading to equation 70 concerning the total spin S. Although the second and third lines of equation 141 do not appear to have the spin-dependence $S_\mu I_\nu$, they can be put into this form with the use of the commutator for spin angular momentum. However, since these terms are complicated and also probably small we will not consider them further. Then, using the first term in equation 141 with equation 138,

$$\mathcal{H}'^{(1)} + \mathcal{H}'^{(2)} = \frac{8\pi}{3S}(2|\beta|\gamma\hbar)\left\langle \sum_i{}' \delta(\underset{\sim}{r}(i))\, S_z(i)\right\rangle_{m_s = S} \underset{\sim}{S}\cdot\underset{\sim}{I}$$

$$+ \frac{P}{2S}\sum_{\mu=x,y,z}{}' \left\{ \sum_i \left\langle 3\frac{r'^2_\mu(i)}{r^2} - 1\right\rangle_{\vartheta_i,\varphi_i} - 2\zeta\Lambda_{\mu\mu}\right\} S_\mu I_\mu \tag{142}$$

where we have diagonalized the dyadic in the braces. This has the effect of shifting the coordinates r_μ to r_μ' if the molecule does not have axial symmetry. However, if the distortion is not too great, we can use r_μ in place of r_μ'. This we have done in table 4 where we give the values of $\left\langle 3\frac{r_\mu^2}{r^2} - 1\right\rangle_{\vartheta,\varphi}$ for d-orbitals. If we assume axial symmetry, the hyperfine spin Hamiltonian can be written as

$$A\, S_z I_z + B(S_x I_x + S_y I_y). \tag{143}$$

where

$$A = \frac{16\pi}{3S}\,|\beta|\gamma\hbar\left\langle \sum_i{}' \delta(\underset{\sim}{r}(i))\, s_z(i)\right\rangle_{m_s = S}$$

$$+ \frac{P}{2S}\left\{ \sum_i{}' \left\langle 3\frac{z_i^2}{r^2} - 1\right\rangle_{\vartheta_i,\varphi_i} - 2\zeta\Lambda_{zz}\right\}. \tag{144}$$

and

$$B = \frac{16\pi}{3S}\,|\beta|\gamma\hbar\left\langle \sum_i{}' (r(i))\, s_z(i)\right\rangle_{m_s = S}$$

$$+ \frac{P}{2S}\left\{ \sum_i{}' \left\langle 3\frac{x_i^2}{r^2} - 1\right\rangle_{\varphi_i,\vartheta_i} - 2\zeta\Lambda_{xx}\right\}. \tag{145}$$

Table 4

Values of $\left\langle 3\,\frac{r^2}{r^2}\,\mu - 1 \right\rangle_{\vartheta,\varphi}$ for d-Orbitals

ψ	$\int\psi^*(3\frac{x^2}{r^2}-1)\psi\,d\tau$	$\int\psi^*(3\frac{y^2}{r^2}-1)\psi\,d\tau$	$\int\psi^*(3\frac{z^2}{r^2}-1)\psi\,d\tau$
d_0	-2/7	-2/7	4/7
$d_{\pm 1}$	-1/7	-1/7	2/7
$d_{\pm 2}$	2/7	2/7	-4/7
d_{xz}	2/7	-4/7	2/7
d_{yz}	-4/7	2/7	2/7
d_{xy}	2/7	2/7	-4/7
$d_{x^2-y^2}$	2/7	2/7	-4/7

A useful experimental parameter is the hyperfine anisotropy given by

$$A - B = \frac{P}{2S}\left\{\sum_i \left[\left\langle 3\,\frac{z_i^2}{r^2} - 1\right\rangle_{\vartheta_i,\varphi_i} - \left\langle 3\,\frac{x_i^2}{r^2} - 1\right\rangle_{\vartheta_i,\varphi_i}\right] + (g_{\parallel} - g_{\perp})\right\} . \tag{146}$$

In $V(C_5H_5)_2$, for instance, we can consider the orbital ground state to have the form

$$\left\{a\ d_{+2}\, d_0\, d_{-2} + b\ d_{+1}\, d_0\, d_{-1}\right\} \tag{147}$$

with

$$a^2 + b^2 = 1. \tag{148}$$

Using table 3 we find

$$A - B = \frac{P}{2S}\left\{\frac{6}{7}(-a^2 + 2b^2) + (g_{\parallel} - g_{\perp})\right\} . \tag{149}$$

If, with the molecule in solution, the spin lattice relaxation time T_{1e} is long compared to τ_c, $T_{1e} \gg \tau_c$, which should be true for $V(C_5H_5)_2$ and with $g_{\parallel} \approx g_{\perp}$, then only the isotropic hyperfine splitting will be observable. Then,

$$A_{solid} - A_{solution} = \frac{P}{2S}\left\{\sum_i \left\langle 3\,\frac{z_i^2}{r^2} - 1\right\rangle_{\vartheta_i,\varphi_i} + (g_{\parallel} - 2)\right\} \tag{150}$$

$$= \frac{P}{2S}\left\{\frac{4}{7}(-a^2 + 2b^2) + (g_{\parallel} - 2)\right\} \tag{151}$$

Therefore, we can find a, b, and P from equations 149 and 151, using the condition of equation 148. It will be interesting to compare P for the $V(C_5H_5)_2$ with P for a free ion ($\sim$330 Mc) (47). As P varies as $1/r^3$, this is a sensitive measure of the degree the magnetic orbitals of $V(C_5H_5)_2$ are spread toward the cyclopentadiene rings, i.e., the amount of mixing between the 3d orbitals with the orbitals associated with the rings.

Similar considerations apply to the other sandwich molecules. Equations 149 and 151 also apply to $Cr(C_5H_5)_2^+$, although the small natural abundance of Cr^{53} (9.5%) coupled with its small magnetic moment may defy detection of nuclear hyperfine structure in this ion. In $Mn(C_5H_5)_2$ there will be little anisotropy because the metal ion is essentially spherically symmetrical. Because of the uncertain mixing of orbitals in $V(C_5H_5)_2^+$, $V(C_6H_6)_2$, $V(C_5H_5)_2^{++}$, and $Co(C_5H_5)_2$, general relations for the anisotropic hyperfine splitting are not particularly useful, so we need not record them. Before considering the Fermi contact term, we will point out that when the energy levels under the ligand field are degenerate or near-degenerate we treat

$$W_N'' = 2|\beta|\gamma\hbar \sum_i \left\{ \frac{(\underset{\sim}{\ell}_i - \underset{\sim}{S}_i)\cdot \underset{\sim}{I}}{r_i^3} + 3\,\frac{(\underset{\sim}{r}_i \cdot \underset{\sim}{S}_i)(\underset{\sim}{r}_i \cdot \underset{\sim}{I})}{r_i^5} \right\} \qquad (152)$$

in the same way we treated $|\beta|\,(\underset{\sim}{L} + 2\underset{\sim}{S}) \cdot \underset{\sim}{H}$ when we discussed the

fine structure for a near-degenerate orbital ground state.

The Fermi contact term in W_N', equation 135 or 152, is the principal source of hyperfine splitting, and for molecules with only a slightly anisotropic g-factor it is the only source of hyperfine splitting in solution. This splitting depends on the s-orbital spin density, which can arise in two ways. There can be a positive s-orbital spin density from the unpaired electrons having a certain probability of being in the 4s-orbital. Too, there can be a negative spin density resulting from the slight exchange polarization of the electron spins in the 1s, 2s, and 3s orbitals due to the paramagnetism of the ion (48, 49).

For an electron in an s-orbital the hyperfine splitting is given by a semi-empirical equation due to Goudsmit (50, 51):

$$a_s = \frac{8}{3} g(I) \frac{R \alpha^2 Z (1+z)^2}{n^{*3} 1838} K(\tfrac{1}{2}, Z) \quad cm^{-1} \qquad (153)$$

where g(I) is the magnetic moment of the nucleus in units of the nuclear magneton, R is the Rydberg constant ($1.09 \cdot 10^5$ cm^{-1}), α is the fine structure constant ($7.28 \cdot 10^{-3}$), Z is the nuclear charge, z is the degree of ionization, n* is the effective quantum number of the orbital, and $K(\frac{1}{2}, Z)$ is a relativistic correction which is near one for V, Mn, and Co. If the unpaired electron in $Co(C_5H_5)_2$ goes into

the 4s' orbital rather than into $3d^*_{xz}$ or $3d^*_{yz}$ antibonding orbitals, we expect a large hyperfine splitting, possibly as large as $\sim$ 4800 Mc, as would be expected for an electron in the 4s orbital of Co^{+2}. Also, as mentioned before, the 4s orbital can mix with the $3d_o$ orbital under the ligand field. This will contribute to the hyperfine splitting in $V(C_5H_5)_2$. Therefore, when due care is taken in correcting for the slight exchange polarization of the 1s, 2s, and 3s electron spins, the amount of mixing of the 4s and $3d_o$ orbitals in $V(C_5H_5)_2$ can be calculated from the hyperfine splitting.

By an exchange polarization of the electron spins in the 1, 2, and 3s-orbitals we mean that the electron with spin α is in a slightly different orbital than the corresponding electron with spin β. This is a result of the fact that when the ion has a net spin α, say, there is an exchange integral between this unpaired electron and the electrons with spin α in the 1s, 2s, and 3s orbitals, but none between the unpaired electron and the electrons with spin β. Doing a rough "unrestricted" Hartree-Fock calculation, Heine (48) found

$$\begin{aligned} &\text{from } 2s^2 && \Delta\chi \approx -8.6 \\ &\text{from } 3s^2 && \Delta\chi \approx 5.3 \end{aligned} \tag{154}$$

where χ is defined by

$$\chi = \frac{4\pi}{S} \left\langle \sum_i \delta(\underset{\sim}{r}(i))\, S_z(i) \right\rangle_{m_s = S} . \tag{155}$$

These results can be interpreted by thinking of the 3d exchange potential as attractive. This pulls the 2s orbital with α spin outward, pulling the 3s orbital with α spin inward. Neglecting $\Delta\chi$ from $1s^2$, χ for the ion is -3.3. Wood and Pratt (49), doing a more detailed calculation, found $\Delta\chi$ from $1s^2$ to be comparable and of the same sign as $\Delta\chi$ from $2s^2$. Then, for the ion they found $\chi = -2.4$. Therefore, the values in equation 154 may be somewhat in error, but both Heine and Wood and Pratt obtain values which agree fairly well with experiment. In table 5 are given the values of χ obtained experimentally for V^{+2}, Mn^{+2}, and Co^{+2}, along with the isotropic hyperfine constant, a, for these ions (47).

Table 5

Hyperfine Structure Parameters of Ions

ion	χ (a.u.)	a(Mc)
V^{+2}	-2.8	-264
Mn^{+2}	-3.1	-273
Co^{+2}	-2.5	-210

The observed hyperfine splitting in $V(C_5H_5)_2$ (39) of only 77 Mc in solution can be understood by assuming that there is about

$\frac{341 \text{ Mc}}{4600 \text{ Mc}}$ or about 7.4% 4s-orbital mixed with the $3d_o$ orbital because

$$+ 341 \text{ Mc} - 264 \text{ Mc} = + 77 \text{ Mc}, \tag{156}$$

although it is possible that the splitting is -77 Mc, meaning $\frac{187}{4600}$ = 4.1% 4s-orbital is mixed with the $3d_o$ orbital. The actual sign of the isotropic splitting will have to be obtained from the analysis of the anisotropic hyperfine structure.

Discussion

In the present work we have tried to estimate the paramagnetic parameters where feasible, but more, we have tried to lay a theoretical basis for understanding the experimental results as they become available. To establish what orbitals would contain the unpaired electrons we considered the ionic and covalent models; and the qualitative results of these models were compared with the observed magnetic moments. In addition, we noticed that orbital angular momentum about the symmetry axis was not necessarily zero. But first-order spin-orbit interaction seems to be important only in $Fe(cp)_2^+$ and $V(cp)_2^{++}$, and maybe not even in these molecules.

Although the great advantage of the ionic over the covalent model is that energy splittings can be calculated quite simply, we have not inserted the energy splittings into the expressions for the magnetic resonance properties because orbital mixing and the extent of distortion are unknown. In fact, we have stressed a fair degree of generality in obtaining these expressions rather than definite values so that a firmer comparison can be made with the experimentally derived values. It is possible to eliminate the energy level separations as parameters if they were known from optical spectra. The

intensities of the lines from optical spectra could also help establish the orbital mixing.

Our treatment of the hyperfine structure is rough and incomplete. However, it does contain the essence of what is presently known concerning the magnetic interaction between electron and nuclear spins.

APPENDIX

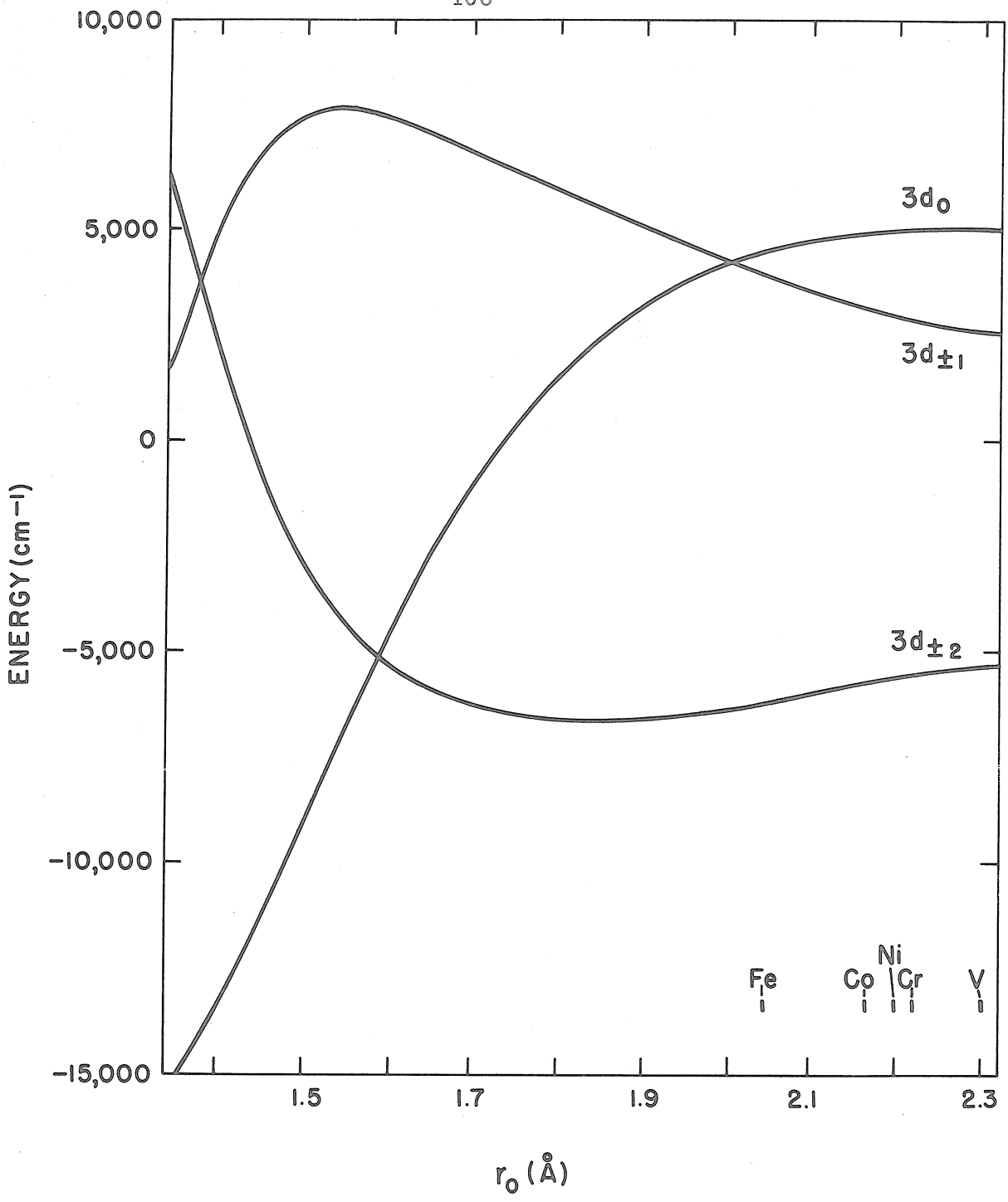


Fig. 1. Splitting of the 3d-orbitals under K. The energy units are for unit charge -e on each ring. r_o is the distance between the charged rings and the metal atom; and the lines marked V, Cr, Fe, Co, and Ni represent taking the charged ring at the normal position for the carbon atoms of the aromatic groups for the respective molecules.

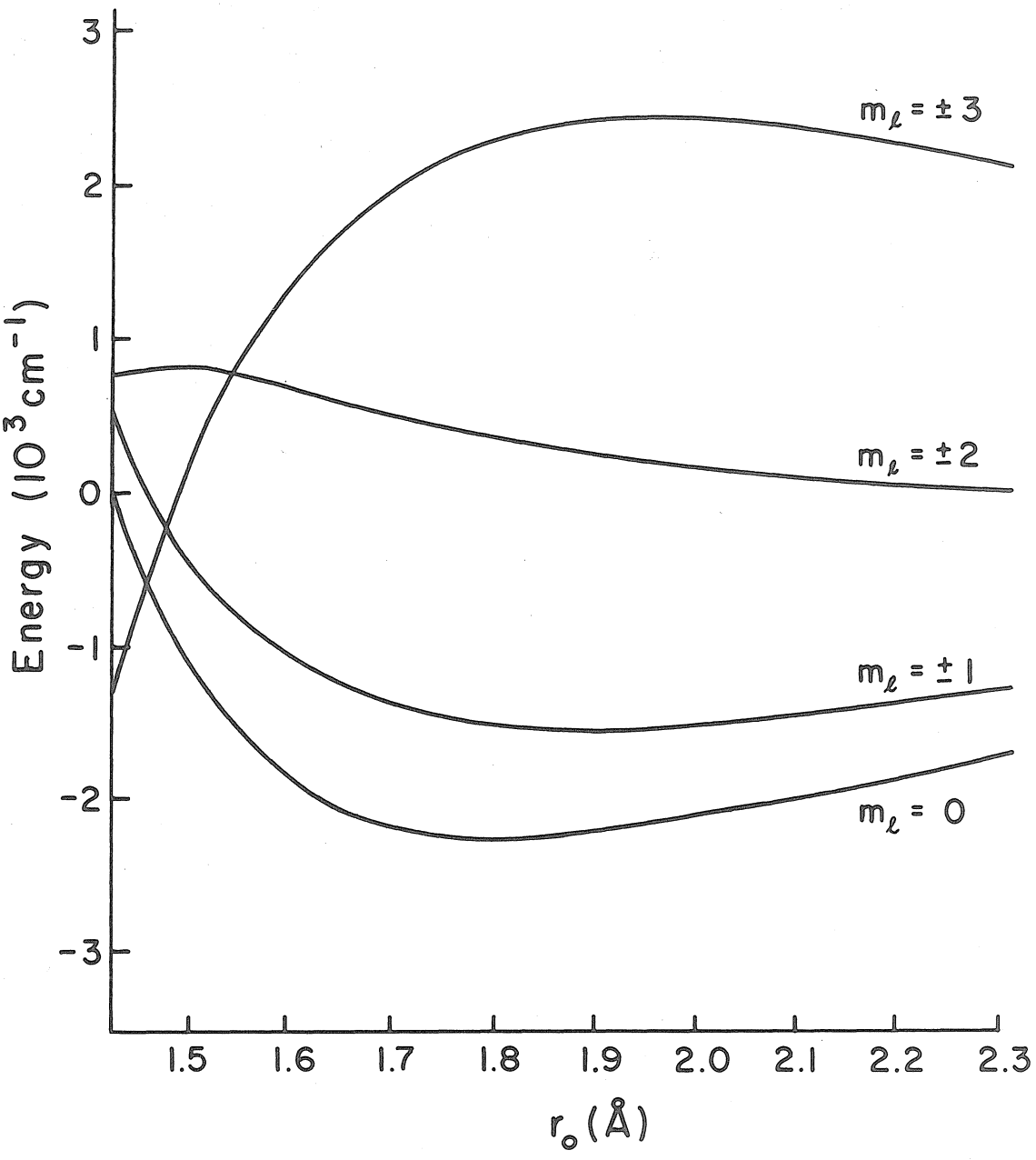


Fig. 2. Orbital splitting of $3d^3\ ^4F$ and $3d^8\ ^3F$ states under K. The energy units are for unit charge -e on each loop. r_o is the distance between the metal atom and the symmetrically placed charged loops.

References

1. J. D. Dunitz and L. E. Orgel, Nature 171, 121-122 (1953).

2. W. Moffitt, J. Am. Chem. Soc. 76, 3386-3392 (1954).

3. A. D. Liehr and C. J. Ballhausen, Acta Chem. Scand. 11, 207-218 (1957).

4. J. D. Dunitz and L. E. Orgel, J. Chem. Phys. 23, 954-958 (1955).

5. E. Kaurer, Z. physik. Chem. (Frankfurt) [N.F.] 6, 105-117 (1956).

6. G. Joos and K. H. Peter, Z. physik. Chem. (Frankfurt) [N.F.] 18, 74-79 (1958).

7. E. O. Fischer, G. Joos, E. Vogg, Z. physik. Chem. (Frankfurt) [N.F.] 18, 80-89 (1958).

8. D. A. Brown, J. Chem. Phys. 29, 1086-1090 (1958).

9. A. Abragam and M.H.L. Pryce, Proc. Roy. Soc. (London) A205, 135-153 (1950).

10. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press (1957), pp. 187-212.

11. D.J.E. Ingram, Spectroscopy at Radio and Microwave Frequencies, Butterworths Scientific Publications (1955), p. 149.

12. E. U. Condon and G. H. Shortley, op. cit., p. 174.

13. K.W.H. Stevens, Proc. Phys. Soc. (London) A65, 209-215 (1952).

14. B. Bleaney and K.W.H. Stevens, Reports of Progress in Physics 16, 108-159 (1953).

15. A. Abragam and M.H.L. Pryce, Proc. Roy. Soc. (London) A206, 173-191 (1951).

16. D. R. Hartree, The Calculation of Atomic Structures, John Wiley and Sons, Inc. (1957), pp. 166-173.

17. E. Weiss and E. O. Fischer, Z. anorg. allg. Chem. 284, 69-72 (1956).

18. J. O. Dunitz, L. E. Orgel, A. Rich, Acta Cryst. 9, 373-375 (1956).

19. A. F. Berndt, Ph. D. Thesis, California Institute of Technology (1957), p. 78.

20. W. Moffitt and A. D. Liehr, Phys. Rev. 106, 1195-1200 (1957).

21. G. Wilkinson and J. M. Birmingham, J. Am. Chem. Soc. 76, 4281-4284 (1954).

22. G. Wilkinson, P. L. Pauson, J. M. Birmingham, F. A. Cotton, J. Am. Chem. Soc. 75, 1011-1012 (1953).

23. A. K. Fischer and G. Wilkinson, J. Inorg. Nuclear Chem. 2, 149-152 (1956).

24. E. O. Fischer and W. Hafner, Z. Naturforsch. 9b, 503-504 (1954).

25. E. O. Fischer and U. Piesberger, Z. Naturforsch. 11b, 758-759 (1956).

26. F. Engelmann, Z. Naturforsch. 8b, 775-776 (1953).

27. E. O. Fischer, G. Joos, W. Meer, Z. Naturforsch. 13b, 456-457 (1958).

28. E. O. Fischer and H. P. Kogler, Z. Naturforsch. 13b, 197-198 (1958).

29. E. O. Fischer and W. Hafner, Z. Naturforsch. 10b, 665-668 (1958).

30. E. O. Fischer and H. Leipfinger, Z. Naturforsch. 10b, 353-355 (1955).

31. L. Pauling, Nature of the Chemical Bond, Cornell University Press, Ithaca, N.Y., (1948), p. 257.

32. M.H.L. Pryce, Proc. Phys. Soc. A63, 25-29 (1950).

33. E. U. Condon and G. H. Shortley, op. cit., pp. 164-171.

34. J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156-174 (1958).

35. R. D. Feltham, P. Sogo, M. Calvin, J. Chem. Phys. 26, 1354-1355 (1957).

36. B. Elschner and S. Herzog, Z. Naturforsch. 12a, 860-862 (1957).

37. Tsuetkov, Voevodsky, Razuvaev, Sorokin, Domrachev, Doklady Akad. Nauk. S.S.S.R. 115, 118-121 (1957).

38. M.H.L. Pryce, Phys. Rev. 80, 1107-1108 (1950).

39. H. M. McConnell, W. W. Porterfield, R. E. Robertson, J. Chem. Phys. 30, 442-44 (1959).

40. W. W. Porterfield and H. H. Dearman (private communication).

41. J. Voitländer and E. Schimitschek, Z. Elektrochem. Ber. Bunsenges. physik. Chem. 61, 941-943 (1957).

42. J. H. Van Vleck and W. G. Penney, Phil. Mag. 17, 961-987 (1934).

43. M.H.L. Pryce, Suppl. Nuovo Cimento 6, 817-856 (1957).

44. P.-O. Löwdin, J. Chem. Phys. 18, 365-375 (1950).

45. W. E. Blumberg and T. P. Das, J. Chem. Phys. 30, 251-256 (1959).

46. H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107-117 (1958).

47. A. Abragam, J. Horowitz, M.H.L. Pryce, Proc. Roy. Soc. (London) A230, 169-187 (1955).

48. V. Heine, Phys. Rev. 107, 1002-1003 (1957).

49. J. H. Wood and G. W. Pratt, Jr., Phys. Rev. 107, 995-1001 (1957).

50. S. Goudsmit, Phys. Rev. 43, 636-639 (1933).

51. H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. 8, 82-229 (1936), sec. 46.

PROPOSITIONS

1. The proton hyperfine splitting, a_H, for $Cr(C_6H_6)_2^+$ has been found to be $\pm$ 3.5 gauss (1). Such a large hyperfine splitting is rather surprising since from the study of the g-factor it appears that the unpaired electron is in the d_o-orbital of chromium and hence is in an orbital associated very little with the π-orbitals of the benzene rings. It is suggested that the hyperfine splitting results from the overlap between the d_o-orbital and the smaller lobe of the C-H σ-orbital.

2. The diamagnetic chemical shifts for N^{14} in urea and thiourea are 298×10^{-6} and 268×10^{-6}, respectively, compared to NO_3^- (2). Since the C=O group is more electronegative than the C=S group, it seemed surprising that the chemical shift in thiourea should be paramagnetic compared to urea. However, from the theory of the long-range chemical shift (3), it can be shown that to a good approximation there is a paramagnetic shift which varies inversely with the energy difference between the non-bonding orbitals of the oxygen or sulfur atom and the anti-bonding π-orbital. Assuming that the energy of the $\pi^* \longleftarrow$ n transitions of $CO_3^=$ and $CS_3^=$ of 46,000 cm^{-1} and 20,000 cm^{-1}, respectively (4), apply in the ureas, it has been estimated that the long-range shift accounts for at least 20% of the

paramagnetic shift of thiourea compared to urea.

3. Walsh and Bloembergen (5) found that the zero-field splitting D of nickel fluosilicate changed at the rate of $+8.9 \cdot 10^{-5}$ cm^{-1}/atm with the application of pressure. From the ionic model for the sandwich molecules it is likely that for some of these molecules D would change much more rapidly with pressure. For example, the zero-field splitting of $Cr(C_5H_5)_2$ at atmospheric pressure may be so large that the paramagnetic resonance will be impossible to detect except at extremely high fields. However, with moderately high pressures it may be possible to obtain the ground state

$$|0\rangle = \left\{a\, d_{+2} d_o \bar{d}_o d_{-2} + b\, d_{+1} d_o \bar{d}_o d_{-1}\right\}$$

which would easily yield a spectrum with standard magnetic resonance equipment.

4. The spin-orbit interaction in benzene negative ion is especially small so the g-factor is essentially that of the free spin value (g_{fs}). However, it may be possible to obtain a g-value different from g_{fs} by forming the negative ion with rubidium or cesium. It is envisioned that a bond, mostly ionic, but partially covalent, will be formed between the benzene molecule and the appropriate p- or d-orbitals of the alkali metal.

5. Matsen (6) calculated the d-orbital splitting in the sandwich molecules by assuming a potential expansion to the second power. This gave the $d_{\pm 2}$-orbitals highest, the d_o-orbital lowest, and the $d_{\pm 1}$-orbitals intermediate in energy. However, the fourth-power terms in the potential definitely are not negligible. Using a simple two-ring model, one can find that the $d_{\pm 1}$-orbitals lie highest and the $d_{\pm 2}$- and d_o-orbitals lie below in energy and are closely spaced. Inclusion of the fourth-power terms gives considerably better agreement with magnetic susceptibility measurements.

6. It is proposed that the first step in polarographic reduction of many halogenated hydrocarbons is the addition of an electron to an antibonding orbital. Thus, $E_{\frac{1}{2}}$ is dependent upon a) the energy of the antibonding orbital, b) the overlap between the antibonding orbital and the electron cloud surrounding the mercury drop, and c) the electric field in the immediate vicinity of the mercury drop. It is suggested that $(Et)_4$ NBr is a better electrolyte than $(Bu)_4$ Ni (7) because the region where the potential drops most rapidly is smaller with the first electrolyte. The reason for this smaller region may be as stated by Lambert and Kobayashi (7), however.

7. The diamagnetic nuclear resonance shift of H_2O^{17} in the presence of Gd^{+3} ion has been described as arising from the preferential transfer from the oxygen to the Gd^{+3} ion of an electron with spin parallel to the paramagnetic moment of the ion (8, 9). However, I wish to stress a description which is more general and more intuitive (10).

Assuming the ground state of Gd^{+3} to be $S = 7/2$, $m_S = 7/2$, there will be exchange integrals between the unpaired electrons and the electrons with spin α of the ligands. As an exchange integral acts in some ways as an attractive potential, the α-spin in s-orbitals of the ligands will be drawn toward the metal atom while the β-spins are unaffected. There is thus left a net β-spin at the nuclei of the oxygen atoms. This description does not imply that the electrons associated with the ligands are to be found part of the time in orbitals associated with the metal atom so much as that the orbitals of the α-spins of the ligands are just drawn closer toward the metal atom.

8. Venkataraman, et al. (11) found that the half-widths of the paramagnetic resonance spectra of p-benzosemiquinones increased from about 0.06 gauss with unsubstituted p-benzosemiquinones to about 0.46 gauss with trichlorosemiquinone. It is proposed that the

explanation lies in the increasing anisotropy of the g-value as more chlorine atoms are added (12).

9. I propose that the molecule $Ti(C_5H_5)_2$ tends to form bonds between neighboring Ti atoms in the crystal. It is found that solid $Ti(C_5H_5)_2$ is diamagnetic (13) while Ti^{+3} in $Ti(C_5H_5)_2^+$ appears to have a near-degenerate orbital ground state with a magnetic moment 2.3β (14) compared to the spin only value of 1.73β. Therefore, it seems somewhat unreasonable to ascribe the diamagnetism of $Ti(C_5H_5)_2$ to Ti^{+2} having two electrons in an orbital which lies considerably below any others. Also $V(C_5H_5)_2^+$ which is iso-electronic with titanocene has spin 1 (14). The tendency to form Ti-Ti bonds would show up in the crystal structure determination of titanocene.

10. Evans (15,16) has shown that the $T \leftarrow S$ transition of aromatic hydrocarbons can be induced by paramagnetic molecules. Letting $\underset{\sim}{T}$ be the dipole-dipole tensor $(3\underset{\sim}{rr}-\underset{\sim}{I})/r^3$, φ_1 the highest filled orbital and φ_2 the lowest unfilled orbital of the aromatic molecule, the energy of interaction between the aromatic and paramagnetic molecules giving rise to the allowedness of the $T \leftarrow S$ transition is

$$W' = \beta^2 \frac{1}{2} \left\{ (\varphi_1 | T_{zz} | \varphi_1) - (\varphi_2 | T_{zz} | \varphi_2) \right\} .$$

In order that W' be large it is necessary for either φ_1 or φ_2 to extend far into the region occupied by the paramagnetic molecule. It is suggested that the orbital of the unpaired electron is of the form $(a\chi + b\varphi_2)$ where χ is the orbital of the paramagnetic molecule and the triplet state is formed by the promotion of an electron in φ_1 to $(b^*\chi - a^*\varphi_2)$.

REFERENCES TO PROPOSITIONS

1. R. D. Feltham, P. Sogo, M. Calvin, J. Chem. Phys. 26, 1354-1355 (1957).

2. B. M. Schmidt, L. C. Brown, D. Williams, J. Mol. Spect. 3, 30-35 (1959).

3. H. M. McConnell, J. Chem. Phys. 27, 226-229 (1957).

4. H. M. McConnell, J. Chem. Phys. 20, 700-704 (1952).

5. W. M. Walsh, Jr. and N. Bloembergen, Phys. Rev. 107, 904-905 (1957).

6. F. A. Matsen, J. Am. Chem. Soc. 81, 2123 (1959).

7. F. L. Lambert and K. Kobayashi, J. Org. Chem. 23, 773-774 (1958).

8. R. G. Shulman and B. J. Wyluda, J. Chem. Phys. 30, 335-336 (1959).

9. L. E. Orgel, J. Chem. Phys. 30, 1617-1618 (1959).

10. V. Heine, Phys. Rev. 107, 1002-1003 (1957).

11. B. Venkataraman, B. G. Segal, G. K. Fraenkel, J. Chem. Phys. 30, 1006-1016 (1959).

12. H. M. McConnell and R. E. Robertson, J. Phys. Chem. 61, 1018 (1957).

13. A. K. Fischer and G. Wilkinson, J. Inorg. Nuc. Chem. 2, 149-152 (1956).

14. G. Wilkinson, P. L. Pauson, J. M. Birmingham, F. A. Cotton, J. Am. Chem. Soc. 75, 1011-1012 (1953).

15. D. F. Evans, J. Chem. Soc. (London) (1957), 1351-1357.

16. D. F. Evans, J. Chem. Soc. (London) (1957), 3885-3888.