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Electronic Structure of Metal Aromatic Complexes

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A semi-quantitative theory of the electronic structure of aromatic complexes formed by the *cyclo*pentadienyl radical and by benzene is presented. The theory utilizes the wavefunctions given by the molecular-orbital theory, and on the basis of a simple scheme for evaluating the necessary integrals gives an internally consistent treatment of the bonding in metal aromatic complexes. The magnetic properties of these compounds are correlated by means of the given theory. A comparison between the treatment here presented and those of previous authors is given.

All of the theories of "sandwich" bonding thus far proposed have made use of the molecular orbital theory of valence.[1-4] The various treatments differ solely in the methods of determining the relative locations of the sundry molecular energy levels.

The most general mixing of the available *cyclo*pentadienyl radical and metal orbitals to form appropriate molecular orbitals has been performed by Jaffé [1] and by Ruch [4]. The approach of both of these authors is open to some criticism. Whereas Jaffé's treatment is too indefinite as to the relative positions of the molecular energy levels, Ruch's treatment is governed too much by a predisposition to obtain a rare gas configuration about the metal atom. Because of these objections neither Jaffé nor Ruch is able to give a satisfactory physical picture of the bonding in di-π-*cyclo*pentadienyl compounds.

The first physically appealing treatment of the problem was given by Dunitz and Orgel [2a]. These authors assumed that the *cyclo*pentadienyl orbital $\psi_{cp}(a_{1g})$ was too tightly bound to mix with any of the available metal orbitals of symmetry a_{1g}, such as $3d(a_{1g})$ and $4s(a_{1g})$. They likewise assumed that the empty 4p levels of the metal atom were too far removed energetically to interact with the filled *cyclo*pentadienyl orbitals $\psi_{cp}(a_{1u})$ and $\psi_{cp}(e_{1u})$. Further, they proposed that the bonding consisted mainly of two "covalent-ionic" bonds between the half-filled *cyclo*pentadienyl orbitals $\psi_{cp}(e_{1g})$ and the metal orbitals $3d(e_{1g})$. It was also supposed that the bonding could take place *via*

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two "donor" bonds formed by the mixing of the empty *cyclo*pentadienyl orbitals $\psi_{cp}(e_{2g})$ with the metal orbitals $3d(e_{2g})$.

However, as more experimental data became available, it was found that the bonding scheme as first proposed by Dunitz and Orgel was not adequate to explain the magnetic properties of all the newly prepared *cyclo*pentadienyl-metal compounds. This led Moffitt [3] to propose a modification of the Dunitz and Orgel model. He assumed that the large difference in energy between the $3d(e_{2g})$ and the $\psi_{cp}(e_{2g})$ orbitals precluded any interaction of these orbitals, and thus eliminated the "donor" bonds of Dunitz and Orgel. He also assumed that the $4s(a_{1g})$ and $3d(a_{1g})$ metal orbitals interact under the molecular force fields to produce one orbital lying in the vicinity of the 4p metal orbitals, and one in the vicinity of the $3d(e_{2g})$ orbitals. Moreover, he placed the antibonding orbital of symmetry e_{1g} above the 4p metal orbitals. This model will explain satisfactorily the magnetic properties of the di-π-*cyclo*pentadienyl compounds, but is admittedly of a qualitative nature.

The first and only other semi-quantitative treatment has been recently published by Dunitz and Orgel [2b]. They have retained the major portion of their own previous theory [2a], but have also included some of the modifications given by Moffitt. They differ from Moffitt in placing the antibonding levels of symmetry e_{1g} below the 4p levels of the metal. This calculation of Dunitz and Orgel is based on the heuristic principle which states that the interaction energy is proportional to the overlap, the overlap being computed according to the prescriptions of Craig, Maccoll, Nyholm, Orgel and Sutton [5]. This means of evaluating the molecular integrals seems to the present authors to be less satisfactory than that utilized in this paper.

1. ENERGY LEVELS FOR THE DI-π-*CYCLO*PENTADIENYL COMPOUNDS

The di-π-*cyclo*pentadienyl compounds have the structure depicted in Fig. 1[2a]. Thus, calling one *cyclo*pentadienyl ring CpA and the other CpB, we have the following wave functions for the *cyclo*pentadienyl ring systems [3],

$$\begin{aligned}
&\mathrm{Cp}S(a_2'') = (5)^{-\frac{1}{2}}\sum_r \varphi_r^{(s)} && (S = \mathrm{A, B}).\\
&\mathrm{Cp}S(e_{1\pm}'') = (5)^{-\frac{1}{2}}\sum_r (\omega^{\pm 1})^r \varphi_r^{(s)} && \omega = \exp(2\pi i/5)\\
&\mathrm{Cp}S(e_{2\pm}'') = (5)^{-\frac{1}{2}}\sum_r (\omega^{\pm 2})^r \varphi_r^{(s)}. && (1)
\end{aligned}$$

In eqn (1) we have given in parenthesis the symmetry designations of the wave functions CpS (S = A, B) in the point group D_{5h}. Combining the wave functions given in (1) to form molecular orbitals of symmetry D_{5d} we have

$$\begin{aligned}
\psi_{cp}(a_{1g}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(a_2'') - \mathrm{CpB}(a_2'')\}\\
\psi_{cp}(a_{1u}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(a_2'') + \mathrm{CpB}(a_2'')\}\\
\psi_{cp}(e_{1g}^{\pm}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(e_{1\pm}'') - \mathrm{CpB}(e_{1\pm}'')\}\\
\psi_{cp}(e_{1u}^{\pm}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(e_{1\pm}'') + \mathrm{CpB}(e_{1\pm}'')\}\\
\psi_{cp}(e_{2g}^{\pm}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(e_{2\pm}'') - \mathrm{CpB}(e_{2\pm}'')\}\\
\psi_{cp}(e_{2u}^{\pm}) &= (2)^{-\frac{1}{2}}\{\mathrm{CpA}(e_{2\pm}'') + \mathrm{CpB}(e_{2\pm}'')\} \quad . \qquad (2)
\end{aligned}$$

The wave functions of eqn. (2) represent the appropriate molecular orbitals for the di-π-*cyclo*pentadienyl ring system.

We must now construct wave functions for the metal atoms having the proper symmetry in D_{5d}. We shall assume that only the 3d and 4s orbitals of the metal are significantly involved in the bonding. In section 5 we shall discuss the validity of this assumption. Thus, the appropriate wave functions are *

$$\begin{aligned} \mathrm{s}(a_{1g}) &= R_{4s}(r)\Theta_{00}\,(2\pi)^{-\frac{1}{2}} \\ \mathrm{d}(a_{1g}) &= R_{3d}(r)\Theta_{20}\,(2\pi)^{-\frac{1}{2}} \\ \mathrm{d}(e^{\pm}_{1g}) &= R_{3d}(r)\Theta_{2\pm1}\,(2\pi)^{-\frac{1}{2}}\,\exp\,(\pm i\varphi) \\ \mathrm{d}(e^{\pm}_{2g}) &= R_{3d}(r)\Theta_{2\pm2}\,(2\pi)^{-\frac{1}{2}}\,\exp\,(\pm 2i\varphi) \end{aligned} \tag{3}$$

The molecular orbitals for the entire molecule are then formed by functions of the type

$$\chi(e^{\pm}_{1g}) = \sin\xi\cdot\psi_{cp}(e^{\pm}_{1g}) + \cos\xi\ \mathrm{d}\ (e^{\pm}_{1g}). \tag{4}$$

Following Moffitt [3], we shall assume that the bonding takes place primarily through the $e^{\pm}_{1g}$ orbitals, the remaining molecular orbitals being of the non-bonding variety. To determine the energies of these orbitals, we shall employ a new type of approximation scheme which combines the most appealing parts of the molecular orbital and crystal field theories of chemical valence.

Under the assumptions mentioned above, we may write the single electron *molecular orbitals* for the valence electrons as

$$\begin{aligned} \chi(e^{\pm}_{1g}) &= \sin\xi\cdot\psi_{cp}(e^{\pm}_{1g}) + \cos\xi\,\mathrm{d}(e^{\pm}_{1g}) \\ \check{\mathrm{d}}(a_{1g}) &= \cos\eta\ \mathrm{d}(a_{1g}) + \sin\eta\ \mathrm{s}(a_{1g}) \\ \check{\mathrm{s}}(a_{1g}) &= \sin\eta\ \mathrm{d}(a_{1g}) - \cos\eta\ \mathrm{s}(a_{1g}) \\ \check{\mathrm{d}}(e_{2g}) &= \mathrm{d}(e_{2g}) \end{aligned} \tag{5}$$

And, according to molecular orbital theory, we may determine the corresponding single electron energies as

$$\begin{aligned} \mathrm{h}(e_{1g})\chi(e^{\pm}_{1g}) &= E[\chi(e^{\pm}_{1g})]\chi(e^{\pm}_{1g}) \\ \mathrm{h}(a_{1g})\check{\mathrm{d}}(a_{1g}) &= E[\check{\mathrm{d}}(a_{1g})]\check{\mathrm{d}}(a_{1g}) \\ \mathrm{h}(a_{1g})\check{\mathrm{s}}(a_{1g}) &= E[\check{\mathrm{s}}(a_{1g})]\check{\mathrm{s}}(a_{1g}) \\ \mathrm{h}(e_{2g})\check{\mathrm{d}}(e^{\pm}_{2g}) &= E[\check{\mathrm{d}}(e^{\pm}_{2g})]\check{\mathrm{d}}(e^{\pm}_{2g})\ , \end{aligned} \tag{6}$$

where h is the appropriate single electron Hamiltonian.

Substituting eqns. (5) into eqns. (6), and performing the usual variational treatment, we obtain the following results:

* For the definition of $R_{3d}(r)$, $R_{4s}(r)$, and Θ_{lm} see Pauling, L. and Wilson, E. B. *Introduction to Quantum Mechanics*, McGraw-Hill, 1935, pp. 132–9.

$$E[\chi(e_{1g}^{\pm})] = \tfrac{1}{2}\{E[\psi_{cp}(e_{1g}^{\pm})] + E[d(e_{1g}^{\pm})]\} \pm \tfrac{1}{2}\{(E[\psi_{cp}(e_{1g}^{\pm})] - E[d(e_{1g}^{\pm})])^2 + 4(\mathrm{Rl.}\int \psi_{cp}^{*}(e_{1g}^{\pm})h(e_{1g})d(e_{1g}^{\pm}))^2\}^{\frac{1}{2}}$$

$$E[\tilde{d}(a_{1g})] = \tfrac{1}{2}\{E[d(a_{1g})] + E[s(a_{1g})]\} + \tfrac{1}{2}\{(E[d(a_{1g})] - E[s(a_{1g})])^2 + 4(\int d^{*}(a_{1g})h(a_{1g})s(a_{1g}))^2\}^{\frac{1}{2}}$$

$$E[\tilde{s}(a_{1g})] = \tfrac{1}{2}\{E[d(a_{1g})] + E[s(a_{1g})]\} - \tfrac{1}{2}\{(E[d(a_{1g})] - E[s(a_{1g})])^2 + 4(\int d^{*}(a_{1g})h(a_{1g})s(a_{1g}))^2\}^{\frac{1}{2}}$$

$$E[\tilde{d}(e_{2g})] = \int d^{*}(e_{2g}^{\pm})h(e_{2g})d(e_{2g}^{\pm})$$

$$\tan 2\xi = \frac{2\ \mathrm{Rl.}\{\int \psi_{cp}^{*}(e_{1g}^{\pm})h(e_{1g})d(e_{1g}^{\pm})\}}{E[d(e_{1g}^{\pm})] - E[\psi_{cp}(e_{1g}^{\pm})]}$$

$$\tan 2\eta = \frac{2\int d^{*}(a_{1g})h(a_{1g})s(a_{1g})}{E[d(a_{1g})] - E[s(a_{1g})]} \quad , \tag{7}$$

where Rl. = "real part of".
For convenience, we have set the overlap integral between the metal orbitals and the ring orbitals equal to zero in eqn. (7).

Since it is observed that the di-π-*cyclo*pentadienyl compounds are fairly stable, one would naturally wish to maximize the binding strength of the $\chi(e_{1g}^{\pm})$ orbitals. To accomplish this, we assume that the $\psi_{cp}(e_{1g}^{\pm})$ and $d(e_{1g}^{\pm})$ electrons have approximately the same energy. That is, we set

$$E[\psi_{cp}(e_{1g}^{\pm})] = E[d(e_{1g}^{\pm})]. \tag{8}$$

From (7) we see that the $\chi(e_{1g}^{\pm})$ energy is then given by (since this condition makes $2\xi = \pm\frac{\pi}{2}$)

$$E[\chi(e_{1g}^{\pm})] = E[d(e_{1g}^{\pm})] \pm \mathrm{Rl.}\{\int \psi_{cp}^{*}(e_{1g}^{\pm})h(e_{1g})d(e_{1g}^{\pm})\} \quad , \tag{9}$$

and the corresponding wave functions are

$$\chi_b(e_{1g}^{\pm}) = (2)^{-\frac{1}{2}}\{d(e_{1g}^{\pm}) + \psi_{cp}(e_{1g}^{\pm})\}$$
$$\chi_a(e_{1g}^{\pm}) = (2)^{-\frac{1}{2}}\{d(e_{1g}^{\pm}) - \psi_{cp}(e_{1g}^{\pm})\}. \tag{10}$$

In (9) and (10) the plus sign corresponds to the bonding orbital and the minus sign to the antibonding orbital.

We have yet to evaluate the integrals occurring in eqns. (7) and (9). In general, the evaluation of such integrals involves insuperable difficulties. However, there does exist a consistent approximation scheme for evaluating them. The procedure is the following:

For the electrons involved primarily in the bonding, the $e_{1g}^{\pm}$ electrons, we shall consider the effect of compound formation to be a strong attraction of the $d(e_{1g}^{\pm})$ electrons of the metal to the rings, with a similar attraction of the ring electrons to the metal atom. Thus, we *replace* the true expression for the energy of the $\chi_b(e_{1g}^{\pm})$ state, $E[\chi_b(e_{1g}^{\pm})]$, by an *estimate* obtained by considering the energy of attraction to be given by a set of *positive* point charges, $+qe_{1g}$,

situated on the carbon atoms of the two *cyclo*pentadienyl rings and interacting with the electrons, metal plus ring, which are moving in $d(e_{1g}^{\pm})$ orbitals. We hence assume that the energy of the *bonding* $e_{1g}^{\pm}$ orbitals is given by

$$E[\chi_b(e_{1g}^{\pm})] = E_d^0 + \int d(e_{1g}^{\pm})^* V_c(+ qe_{1g}) d(e_{1g}^{\pm}) \quad , \tag{11}$$

where E_d^0 is the energy of a d-electron in the normal atom and $V_c(+ qe_{1g})$ is the crystal field potential produced by the ten point charges $+ qe_{1g}$ of the two *cyclo*pentadienyl rings.

For the *antibonding* $\chi_a(e_{1g}^{\pm})$ electrons we replace the true $\chi_a(e_{1g}^{\pm})$ energy, $E[\chi_a(e_{1g}^{\pm})]$, by an estimate obtained by considering the energy of repulsion to be given by a set of *negative* point charges, $-qe_{1g}$, situated on the carbon atoms of the two *cyclo*pentadienyl rings and interacting with the electrons, metal plus ring, which are moving in $d(e_{1g}^{\pm})$ orbitals. That is,

$$E[\chi_a(e_{1g}^{\pm})] = E_d^0 + \int d(e_{1g}^{\pm})^* V_c(-qe_{1g}) d(e_{1g}^{\pm}) \tag{12}$$

For the *nonbonding* electrons, *i.e.*, those not primarily involved in the bonding, such as the $\tilde{d}(e_{2g}^{\pm})$, $\tilde{d}(a_{1g})$, and $\tilde{s}(a_{1g})$ electrons, the situation is conceptually simpler. Here we assume that the sole effect of compound formation is to *repel* these electrons from the region of the *cyclo*pentadienyl rings. We shall consider this repulsion to be represented by the effect of a set of ten negative point charges, $-qe_{2g}$ or $-qa_{1g}$, situated on the carbon atoms and interacting with the electrons moving in $d(a_{1g})$, $s(a_{1g})$, and $d(e_{2g}^{\pm})$ orbitals. Thus we can finally write

$$\begin{aligned}
&E[\chi_{(b)}^{(a)}(e_{1g}^{\pm})] \approx E_d^0 \pm \int d(e_{1g}^{\pm})^* V_c(qe_{1g})\, d(e_{1g}^{\pm}) \\
&E[\tilde{d}(e_{2g}^{\pm})] \approx E_d^0 + \int d(e_{2g}^{\pm})^* V_c(-qe_{2g}) d(e_{2g}^{\pm}) \\
&E[d(a_{1g})] \approx E_d^0 + \int d(a_{1g})^* V_c(-qa_{1g}) d(a_{1g}) \\
&E[s(a_{1g})] \approx E_s^0 + \int s(a_{1g})^* V_c(-qa_{1g}) s(a_{1g}) \\
&\int d(a_{1g})^* h(a_{1g}) s(a_{1g}) \approx \int d(a_{1g})^* V_c(-qa_{1g}) s(a_{1g})
\end{aligned} \tag{13}$$

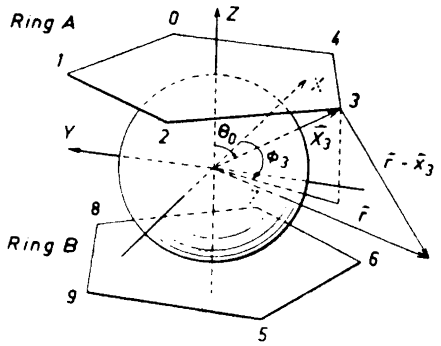

Fig. 1. Model of the compounds.

We next wish to consider the explicit evaluation of the integrals occurring in eqn. (13). Now by making use of Fig. 1, we see

$$V_c(\pm q) = \pm \frac{(-e)q}{a_0} \sum_{j=0}^{9} \frac{1}{|\vec{r}-\vec{x}_j|} \tag{14}$$

In eqn. (14) $\vec{r}$ and $\vec{x}_j$ are measured in units of the Bohr radius a_0. Expanding $|\vec{r}-\vec{x}_j|^{-1}$ in terms of the associated Legendre polynomials of the first kind and carrying out the sum over all the atoms occurring in (14) we obtain

$$V_c(\pm q) = \frac{\mp 10qe}{a_0 r_>} \sum_{l \geq 5m}^{\infty} \left(\frac{r_<}{r_>}\right)^l \sum_{5m=-l}^{l} \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\vartheta) P_l^{|m|}(\cos\vartheta_0) \exp.[5im(\varphi-\varphi_0)] \tag{15}$$

Substituting the wave functions of eqn. (3) together with the expansion of $V_c(\pm q)$ of eqn. (15) into eqn. (13) we have

$$\begin{aligned}
E[\chi_{(a)}^{(b)}(e_{1g}^{\pm})] &\approx E_d^0 \mp 10qe_{1g} \cdot e\{G_{0d} + \frac{1}{7} P_2(\cos\vartheta_0)\, G_{2d} - \frac{4}{21} P_4(\cos\vartheta_0)\, G_{4d}\} \\
E[\tilde{d}(e_{2g}^{\pm})] &\approx E_d^0 + 10qe_{1g} \cdot e\{G_{0d} - \frac{2}{7} P_2(\cos\vartheta_0) G_{2d} + \frac{1}{21} P_4(\cos\vartheta_0) G_{4d}\} \\
E[d(a_{1g})] &\approx E_d^0 + 10qa_{1g} \cdot e\{G_{0d} + \frac{2}{7} P_2(\cos\vartheta_0) G_{2d} + \frac{2}{7} P_4(\cos\vartheta_0) G_{4d}\} \\
E[s(a_{1g})] &\approx E_s^0 + 10qa_{1g} \cdot eG_{0s},
\end{aligned} \tag{16}$$

where

$$\begin{aligned}
G_{kd}(x) &= \frac{1}{a_0} \int_0^x \frac{r^k}{x^{k+1}} R_{3d}^2(r) r^2 dr + \frac{1}{a_0} \int_x^{\infty} \frac{x^k}{r^{k+1}} R_{3d}^2(r) r^2 dr \\
G_{ks}(x) &= \frac{1}{a_0} \int_0^x \frac{r^k}{x^{k+1}} R_{4s}^2(r) r^2 dr + \frac{1}{a_0} \int_x^{\infty} \frac{x^k}{r^{k+1}} R_{4s}^2(r) r^2 dr
\end{aligned} \tag{17}$$

Using [6-8] a carbon-carbon distance equal to 1.41 Å, a metal carbon distance of 2 Å, and the angle ϑ_0 equal to arc cos (0.80338) in the formulae given above we obtain the results tabulated in Tables 1 and 2. These results are also plotted

Table 1.

Z_{3d}	Units of $\frac{10}{a_0} qe_{1g} \cdot e$ $E[\tilde{d}(a_{1g})] - E_d^0$	Units of $\pm \frac{10}{a_0} qe_{1g} \cdot e$ $E(e_{1g}^{\pm}) - E_d^0$	Units of $\frac{10}{a_0} qe_{2g} \cdot e$ $E[\tilde{d}(e_{2g}^{\pm})] - E_d^0$
2.9780	0.25746	0.25834	0.22417
3.5736	0.26829	0.26853	0.23710
4.3677	0.27273	0.27196	0.24694
5.1618	0.27276	0.27130	0.25235
5.9560	0.27166	0.26993	0.25558
6.7501	0.27051	0.26875	0.25767
7.5442	0.26954	0.26788	0.25911

Energy Values

Table 2.

Z_{4s}	Units of $\frac{10}{a_0}$ $qa_{1g}e$ $E[\tilde{s}(a_{1g})]-E^0_{4s}$
1.58826	0.0807
2.11768	0.1039
2.64710	0.1260
2.91181	0.1360
3.17652	0.1455
3.70594	0.1630
4.23536	0.1801
4.76478	0.1970
5.29420	0.2131

Energy Values.

in Figure 2a. Since the computations for a wide range of values of Z_{3d} and Z_{4s} showed that the interaction integral, $\int d(a_{1g})^* h(a_{1g}) s(a_{1g})$, is only of the order of 10^{-2} times the diagonal terms $E[d(a_{1g})]$ and $E[s(a_{1g})]$, this term was neglected in computing the values given in Tables 1 and 2.

In the following section we shall use Tables 1 and 2 as well as Figures 2a and 2b to explain the magnetic properties of the di-π-*cyclo*pentadienyl compounds.

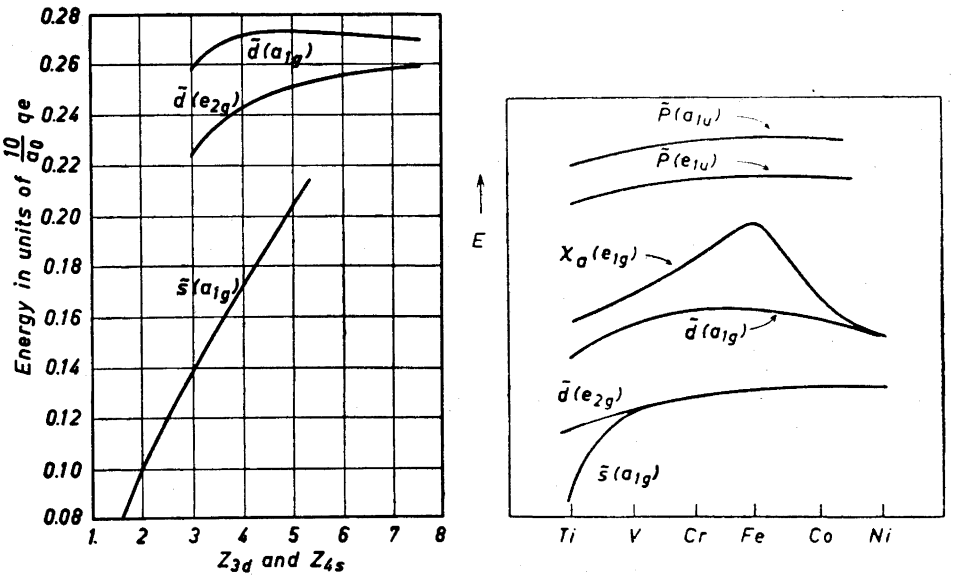

Fig. 2 a, b. A qualitative plot of the energy levels for the di-π-*cyclo*pentadienyl compounds of the first transition series. The energy spacings are distorted for illustrative clarity. Manganese is omitted from the plot for reasons stated in the text.

2. DISCUSSION OF THE MAGNETIC PROPERTIES OF THE DI-π-*CYCLO*-PENTADIENYL COMPOUNDS

Titanium. The compound $(C_5H_5)_2Ti$ is diamagnetic [9]. Hence, on our energy level diagram we must have the electronic structure * $[A]cp(a_{1g})^2cp(a_{1u})^2cp(e_{1u})^4 \chi_b(e_{1g})^4\tilde{s}(a_{1g})^2$. Since $E_s^0-E_d^0$ for Ti(II) is about $9\times10^{-2}\times\frac{10}{a_0}qa_{1g}e$, we see from Figure 2a that any value of $Z_{4s}\sim2.5$ and $Z_{3d}\sim4.5$ will ensure that the $\tilde{s}(a_{1g})$ level is well below the $\tilde{d}(e_{2g})$ level (if $qa_{1g}=1/5\ e$ it is $\sim16\ 000\ cm^{-1}$ below it) [10]. These values, in addition to yielding a diamagnetic molecule, are very reasonable physically for the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ *molecular orbitals* of the *molecule* $(C_5H_5)_2Ti$. Ionization of the *molecule* to form $[(C_5H_5)_2Ti]^{+1}$ and $[(C_5H_5)_2Ti]^{+2}$ then takes place by the removal of first one and then the other $\tilde{s}(a_{1g})$ electron. This makes $[(C_5H_5)_2Ti]^{+1}$ paramagnetic with one unpaired electron and makes $[(C_5H_5)_2Ti]^{+2}$ diamagnetic.

Vanadium. The compound $(C_5H_5)_2V$ is paramagnetic with three unpaired electrons [11,12]. This implies that the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ levels must be nearly degenerate. Thus the electronic structure is $[A]cp(a_{1g})^2cp(a_{1u})^2cp(e_{1u})^4 \chi_b(e_{1g})^4\tilde{s}(a_{1g})^1\tilde{d}(e_{2g})^2$. This will be the case if $Z_{4s}\sim3.3$ and $Z_{3d}\sim4.8$ for then the observed value of $E_s^0-E_d^0$ for V (II) will bring the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ levels into near degeneracy (if $qa_{1g}=qe_{2g}\sim\frac{1}{5}e$ then $E_s^0-E_d^0=1\times10^{-1}\times\frac{10}{a_0}qa_{1g}e$). *The above choices of Z_{4s} and Z_{3d} are not critical. All that is required is that they be slightly higher than those occurring in $(C_5H_5)_2Ti$, as they must be on physical grounds.* Having determined the best values of Z to use for the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ *molecular orbitals*, we would predict that $[(C_5H_5)_2V]^{+1}$ and $[(C_5H_5)_2V]^{+2}$ would be paramagnetic with two unpaired and one unpaired electrons, respectively.

Chromium. The additional electron introduced into the *cyclo*pentadienyl-metal electronic system upon replacement of vanadium by chromium will probably not introduce too great a change in the energy level scheme present in vanadium. Thus we might expect chromium to have the electronic structure:

$$[A]cp(a_{1g})^2cp(a_{1u})^2cp(e_{1u})^4\chi_b(e_{1g})^4[\tilde{s}(a_{1g})\tilde{d}(e_{2g})]^4.$$

This structure predicts that $(C_5H_5)_2Cr$ is paramagnetic with two unpaired electrons. The energy level scheme $(\tilde{d}(e_{2g}))^4(\tilde{s}(a_{1g}))^0$ is eliminated on the grounds that it would require larger values of Z_{4s} than are reasonable. We therefore have two possibilities: (a) The $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ levels are nearly degenerate as in vanadium, so that $[(C_5H_5)_2Cr]^{+1}$ and $[(C_5H_5)_2Cr]^{+2}$ are paramagnetic with three and two unpaired electrons, respectively; (b) the $\tilde{s}(a_{1g})$ level is lower than the $\tilde{d}(e_{2g})$ level as in titanium, so that $[(C_5H_5)_2Cr]^{+1}$ is paramagnetic with one unpaired electron and $[(C_5H_5)_2Cr)]^{+2}$ is diamagnetic. The investigations of the German school [13–15] indicate that $[(C_5H_5)_2Cr)^{+1}$ has three unpaired electrons

* The symbol [A] is used to designate the Argon core which is common to all of the metals of the first transition series.

and thus case (a) is the one actually occurring. The relative instability of $(C_5H_5)_2Cr$ indicates [16] that the binding parameter of qe_{1g} is not very large.

Manganese. The compound $(C_5H_5)_2Mn$ is known from experiment to be "ionic", and therefore has no $\chi_b(e_{1g})$ bonding orbital. In the crystal the ions $C_5H_5^-$ Mn^{++} $C_5H_5^-$ are probably arranged in a lattice having D_{5d} symmetry at the manganese sites.[16,17] Hence, the energy levels are given by a pure crystal field perturbation of the Mn^{+2} ion by the $C_5H_5^-$ rings. Since the ground state of Mn^{+2} is a ^6S state, which will not be split by a crystal field, the $(C_5H_5)_2Mn$ molecule will have five unpaired electrons [unless the crystal field is strong enough to depress one of the higher states, such as ^4G, ^4P, etc., below the ^6S state). Since it is observed that $(C_5H_5)_2Mn$ has five unpaired electrons [16], we see that the latter possibility is not realized.*

Iron. Here we have an extremely stable covalent compound having the formula $(C_5H_5)_2Fe$. Since iron has enough electrons to fill both the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ shells, the relative location of these shells with respect to one another is immaterial from the magnetic viewpoint. Since the $\tilde{d}(a_{2g})$ level is significantly higher than the $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ levels, all possible assignments of the electrons will yield a diamagnetic $(C_5H_5)_2Fe$ molecule and a paramagnetic $[(C_5H_5)_2Fe]^{+1}$ ion having one unpaired electron. The degree of stability of this compound indicates a large positive value for qe_{1g}. The $\tilde{s}(a_{1g})$ and $\tilde{d}(e_{2g})$ levels are probably equi-energetic as in the case of vanadium.

Cobalt. It is likely that for $(C_5H_5)_2Co$, the $\tilde{s}(a_{1g})$ and $d(e_{2g})$ levels are, as in vanadium, nearly degenerate. The electrons are then placed in the molecule as $[A]cp(a_{1g})^2cp(a_{1u})^2cp(e_{1u})^4\chi_b(e_{1g})^4[\tilde{s}(a_{1g})\tilde{d}(e_{2g})]^6(\tilde{d}(a_{1g}))^1$, yielding a paramagnetic molecule with one unpaired electron. The cobalticinium ion, $[(C_5H_5)_2Co]^{+1}$, is then diamagnetic.

Nickel. This compound is relatively unstable thermally, in contrast to ferrocene.[18] Hence, we expect that qe_{1g} is not too large. This is further confirmed by the fact that the molecule is paramagnetic with two unpaired electrons. This paramagnetism implies that the antibonding orbital, $\chi_a(e_{1g})$, is nearly degenerate with the $\tilde{d}(a_{1g})$ nonbonding orbital. We see from Table 1 that the choice $q_{e_{1g}} = q_{a_{1g}}$ will bring about this degeneracy. Hence, we may assign to nickelocene the following electronic structure:

$$[A]cp(a_{1g})^2cp(a_{1u})^2cp(e_{1u})^4\chi_b(e_{1g})^4[\tilde{s}(a_{1g})\tilde{d}(e_{2g})]^6[\tilde{d}(a_{1g})\chi_a(e_{1g})]^2.$$

This structure gives nickelocene two unpaired electrons. We also see that this electronic assignment for $(C_5H_5)_2Ni$ implies that the nickelocinium ion is paramagnetic with one unpaired electron.

Miscellaneous Di-π-cyclopentadienyl Compounds. A number of other di-π-*cyclo*pentadienyl compounds have also been prepared, and a discussion of these follows much the same pattern as that given for the first transition series. For example, $[(C_5H_5)_2Zr]^{+2}$, $[(C_5H_5)_2Nb]^{+3}$, and $[(C_5H_5)_2Ta]^{+3}$ are formed exactly as is $[(C_5H_5)_2Ti]^{+2}$; $(C_5H_5)_2Ru$, $[(C_5H_5)_2Rh]^{+1}$, and $[(C_5H_5)_2Ir]^{+1}$ are similar to ferrocene; $[(C_5H_5)_2Ru]^{+1}$ is analogous to the ferricinium ion.

* In the solid state the five unpaired electrons interact to form an antiferromagnetic crystal. See Ref.[16]

The compounds $[(C_5H_5)_2Mo]^{+3}$ and $[(C_5H_5)_2W]^{+3}$ are completely analogous to the similar electronic systems $[(C_5H_5)_2V]^{+2}$ and $[(C_5H_5)_2Ti]^{+1}$. Preliminary investigations by Piper and Wilkinson [19] indicate that $(C_5H_5)_2Mo$ is analogous to $(C_5H_5)_2Cr$. However, $[(C_5H_5)_2Mo]^{+2}$ behaves quite differently from $[(C_5H_5)_2Cr]^{+2}$, being diamagnetic instead of paramagnetic [20]. Reference to the discussion of $(C_5H_5)_2Cr$ shows that for molybdenum we must thus have the $\tilde{s}(a_{1g})$ level below the $\tilde{d}(e_{2g})$ level. Hence, $[(C_5H_5)_2Mo]^{+2}$ resembles its neutral titanium analogue rather than its chromium and vanadium analogues.*

3. DISCUSSION OF THE MAGNETIC PROPERTIES OF THE *CYCLO*PENTADIENIDES OF THE GROUP III METALS AND THE ACTINIDES.

The group III metals form ionic compounds of the general formula $(C_5H_5)_3M$ (M = Sc, Y, and the rare earths).[21] Both the spectra and the magnetic properties are very similar to those of the normal triply ionized metals in solution. Thus, one is led to assume that, as in the case of manganese, the crystal field acting on the trivalent metal ions is of the same order of magnitude as that found in the normal salts of these metals. One then has the ordinary weak crystal field splitting of the trivalent ion which gives rise to the well-known magnetic properties of these ions [22].

Recently there have been reported [23] the stable ions $[(C_5H_5)_3U]^{+1}$ and $[(C_5H_5)_2Th]^{+2}$ (the latter ion has not as yet been fully characterized). The bonding in these ions would involve, in general, the low lying 5f, 6d, and 7s orbitals. A treatment similar to that given in sections 1 and 2 for the first series of transition elements could also be applied here. However, the uncertainty in geometry and the intrinsic complexity of the atomic systems involved makes a treatment of this sort impracticable.

4. DISCUSSION OF THE MAGNETIC PROPERTIES OF THE DI-π-BENZENE CHROMIUM COMPOUNDS

Fischer and Hafner [24] have recently reported the covalent diamagnetic compound $(C_6H_6)_2Cr$, and have, because of its great similarity to ferrocene, proposed a "sandwich" type bonding. ** They have also reported the stable ion $[(C_6H_6)_2Cr]^{+1}$ which they found to be chemically analogous to the ferricinium ion. As the theory of section 1 is completely general, it applies equally well to these di-π-benzene systems. To adapt section 2 to the di-π-benzene chromium compounds all one need to do is alter the geometrical parameters slightly and run all summations over twelve point charges rather than ten. Hence one would obtain exactly the same results for $(C_6H_6)_2Cr$ and $[(C_6H_6)_2Cr]^{+1}$ as were obtained for the isoelectronic systems $(C_5H_5)_2Fe$ and $[(C_5H_5)_2Fe]^{+1}$. These conclusions agree with the experimental findings [24].

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* In an earlier paragraph we have shown that the hypothetical $[(C_5H_5)_2Cr]^{+2}$ ion must be paramagnetic.

** Previously Zeiss and Tsutsui had proposed a "sandwich" type bonding for several of the polyphenyl chromium compounds. See the review article by Cotton [25].

5. DISCUSSION

On the basis of a simple scheme for evaluating the necessary interaction integrals, we have been able to give an internally consistent semi-quantitative treatment of the bonding in metal aromatic complexes. This treatment has preserved those parts of the previous theories of Jaffé, Dunitz and Orgel, Moffitt, and Ruch which are most appealing physically. For example, we have followed Moffitt [3] in assuming that the only *cyclo*pentadienyl orbitals intimately involved in the bonding are the $\psi_{cp}(e_{1g})$ orbitals. However, as a calculation based on the *molecular orbital-crystal field* formalism employed in this paper shows that the p levels lie higher than the antibonding levels $\chi_a(e_{1g})$, we have followed Dunitz and Orgel [2b] rather than Moffitt in the ordering of these levels.

Of course, the explanation of the magnetic properties of the metal aromatic complexes is not alone sufficient proof of the validity of any given energy level scheme. A further test of the various theories concerning the electronic structure of these compounds could be obtained by a study of their absorption spectra. However, considerations of this kind have so far only been presented by Jaffé. In view of these facts, we plan next to apply the theory set forth in this paper to the problem of explaining the visible spectrum of the metal aromatic complexes.*

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* Note added in proof: M. Yamazaki has recently performed a simplified SCF-LCAO-MO computation for both the D_{5h} and D_{5d} structures of ferrocene, obtaining essentially the same electronic level ordering as all other workers in this field. Also, using the results of his calculations, he has presented an explanation of the absorption spectrum of ferrocene. See *J. Chem. Phys.* **24**, (1956) 1260.

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