Ligand field model for di-π-(1)2,3-dicarbollyl, π-cyclopentadienyl-π-(1)2,3-dicarbollyl, and π-arene-π-(1)2,3-dicarbollyl metal sandwich complexes

The recent reports[1] of the synthesis of metal complexes involving the $B_9C_2H_{11}^{2-}$ (DCB) and $C_5H_5^-$ (Cp) ions and the confirmation of the sandwich structure of the π-cyclopentadienyl-π-(1)2,3-dicarbollyliron(III), (Cp)(DCB)Fe(III), complex by X-ray diffraction studies[2] has led us to suggest an axial ($C_{\infty v}$) ligand field model which should be useful for prediction and correlation of the properties of these complexes, *e.g.* stabilities and gross magnetic properties, as well as more quantitative properties such as assignment of optical and ESR spectra and electronic ground and excited states. At the present time it does not appear feasible to carry out a molecular orbital calculation on these complexes due to the complexity of the carborane ligands. Even if this were to be accomplished, such results are often not quantitatively or, in some cases, even qualitatively correct. For example, it has been found[3] that even self-consistent field computations on the simpler metallocenes are grossly in error. For these reasons the present ligand field approach seems to be a useful and appropriate model.

Although the (Cp)(DCB)Fe(III) complex was found[2] to have only C_s symmetry (one reflection plane), the di-π-DCB metal complexes should have C_{2v} (carbon atoms *cis*) or C_{2h} (carbon atoms *trans*) for eclipsed conformations and perhaps C_{2v} or C_1 symmetry for staggered conformations. Assuming sandwich structures for both the di-π-DCB and π-DCB-π-Cp complexes as well as effective five fold rotational symmetry about the z axis passing through the metal atom and the opposite apex of the carborane icosahedron; *effective* point groups of D_{5h} or D_{5d} are appropriate for the di-π-DCB complexes and C_{5v} for the π-Cp-π-DCB complexes.

The one-electron ligand field potential for a purely axial field ($C_{\infty v}$) can be expressed as:

$$V_{LF} = \lambda_1 V_0^0 + \lambda_2 V_0^2 + \lambda_3 V_0^4$$

where the λ_i are expansion coefficients and the V_q^k are spherical harmonics. If one considers only d orbitals, it can be proved[4] that the same ligand field potential also occurs for symmetries of C_n, C_{nh}, C_{nv}, D_{nd}, and D_{nh} for $n > 4$[*]. The only difference between the purely axial field potential and that for the aforementioned symmetries is in the values of the λ_i which are determined by the type (point charge, dipole, etc.) and geometrical parameters of the charge distributions. However, these may be absorbed into the splitting parameters, Ds and Dt, yielding the same axial ligand field potential for all these symmetries. Compounds for which the ligand field potential may be expressed as a sum of coaxial potentials of differing symmetry, each of which individually has a rotational axis of $n > 4$, also have an axial ($C_{\infty v}$) ligand field. An example is π-(C_6H_6)(π-Cp)Mn which could have C_s overall symmetry at most, but which has an effective axial ligand field[**]. Since the carborane complexes being

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[*] This has been mentioned previously in Ref. 5 for $n = 5$ but has not been proved in general for $n > 5$.

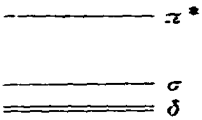
[**] It should be emphasized that it is not just approximately true, but exactly true. As long as only the d configurations are involved, no additional splitting of the d levels can be produced by the symmetries mentioned above. The splittings and eigenvalues are given by those for a purely axial field ($C_{\infty v}$).

considered have *approximate* D_{5h}, D_{5d}, or C_{5v} symmetry, their properties should be adequately described by an *approximate* axial field model.

In an axial field the *d* orbitals split into three sets, denoted $\sigma(d_{z^2}; d_0)$; $\pi(d_{xz}, d_{yz}; d_{\pm 1})$; and $\delta(d_{x^2-y^2}, d_{x\pm y}; d_{2})$, with one-electron energies[4,6] where *Ds* and *Dt* are ligand

$$E(\sigma) = 2Ds - 6Dt \qquad E(\pi) = Ds + 4Dt \qquad E(\delta) = -2Ds - Dt$$

field splitting parameters defined by Piper and Carlin[6]. From qualitative arguments concerning the relative overlaps of the various *d* and ligand orbitals as well as naive electrostatic arguments, the splitting of the *d* levels is expected to be as shown:



This is the order found for ferrocene[3] and other metallocenes[7], but the relative positions of the σ and δ orbitals are variable*.

Since Cp and presumably DCB are strong field ligands (due to strong π-bonding), all of these complexes should be "spin-paired". Furthermore, since the highest energy *d*-orbital (π^*) would be correlated with an antibonding molecular orbital in a full molecular orbital scheme, "closed shell" complexes will have six "*d*" electrons with a ground state electronic configuration $\sigma^2\delta^4[^1\Sigma^+]$. These complexes will be diamagnetic, relatively stable to oxidation–reduction, and possess maximum ligand field stabilization energies. Their chemical properties should be very similar since they are primarily determined by the "chemical electrons" (σ and δ) and by the nature of the lowest unfilled orbital (π^*). Since the π-DCB and π-Cp ligands are assigned formal charges of -2 and -1 respectively, "d^6" complexes of the types, $[(\pi\text{-DCB})_2\text{M(II)}]^{2-}$, $[(\pi\text{-DCB})_2\text{M(III)}]^{-}$, $[(\pi\text{-Cp})(\pi\text{-DCB})\text{M(II)}]^{-}$ and $[(\pi\text{-Cp})(\pi\text{-DCB})\text{M(III)}]$ are feasible, where M is a transition metal. Mixed π-arene-π-DCB metal complexes of the types $(\pi\text{-benzene})(\pi\text{-DCB})\text{M(II)}$ and $[(\pi\text{-benzene})(\pi\text{-DCB})\text{M(III)}]^{-1}$ are also feasible.

The "d^6" complexes known thus far[1] are $[(\pi\text{-DCB})_2\text{Fe(II)}]^{2-}$, $[(\pi\text{-Cp})(\pi\text{-DCB})\text{Fe(II)}]^{-}$, $[(\pi\text{-DCB})_2\text{Co(III)}]^{-}$, and $(\pi\text{-Cp})(\pi\text{-DCB})\text{Co(III)}$. The first two have been found experimentally to be diamagnetic as expected from the axial field model, and the latter two should also be diamagnetic. Analogous Ru, Os, Ir, and Rh complexes are predicted as well as $[(\pi\text{-arene})(\pi\text{-DCB})\text{M(I)}]^{-}$ complexes where M is Mn or Re.

The "d^5" complexes known[1] at the present time are $[(\pi\text{-DCB})_2\text{Fe(III)}]^{-}$ and $(\pi\text{-Cp})(\pi\text{-DCB})\text{Fe(III)}$. These complexes have $[\sigma\delta]^5$ ground state configurations with one unpaired electron and $^2\Sigma^-$ or $^2\Delta$ ground states, depending upon the relative energies of the σ and δ orbitals and the electron repulsion energies. Both of these complexes are found to be paramagnetic from experimental studies. No experimental investigation of the temperature dependence of the magnetic susceptibility has been attempted, but the axial ligand field model should provide at least a first-order model for calculations of this property. In a recent[9] paramagnetic resonance study of the $(\pi\text{-Cp})(\pi\text{-DCB})\text{Fe(III)}$ and $[(\pi\text{-DCB})_2\text{Fe(III)}]^{-}$ complexes it was found that the

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* For ferrocene and dibenzenechromous cation the order is $\pi^* > \sigma > \delta$ (refs. 3 and 8). For ferricenium cation the order is $\pi^* > \delta > \sigma$ (ref. 8).

observed line shapes of polycrystalline samples could be fitted with an axial g-tensor. The observed g factors were $g_\perp = 1.53$, $g_\parallel = 3.94$ for $[(\pi\text{-DCB})_2\text{Fe(III)}]^-$, and $g_\perp = 1.78$; $g_\parallel = 3.58$ for $(\pi\text{-Cp})(\pi\text{-DCB})\text{Fe(III)}$.

Although a detailed explanation of these results must necessarily include the effects of the actual ligand field potential, it is possible to interpret them semi-quantitatively via the axial field model and to determine the electronic ground states of these complexes. Assuming pure d orbitals and excluding any spin-orbit coupling between the σ and δ orbitals and the π^* orbitals, the axial field results for a $\sigma^2\delta^3[^2\Delta]$ configuration are[9] $g_\parallel = 6.0$ and $g_\perp = 0.0$. For the $\sigma^1\delta^4[^2\Sigma^+]$ configuration the results are an isotropic g-tensor, $g_\parallel = 2.00$ and $g_\perp = 2.00$. By including spin-orbit coupling of the σ and π^* orbitals, these become[10] $g_\parallel = 2.00$ and $g_\perp \cong 2[1 - 3\lambda/(E_\pi - E_\sigma)]$. Since $\lambda \sim -0.05$ ev and $E_\pi - E_\sigma \sim 3$–4 ev, the corrected values are $g_\parallel = 2.00$ and $g_\perp = 2.10$. Even after correction for the effects of lower symmetry interactions the g-factor for this configuration remain practically unchanged[9]. Since the experimental $g_\parallel$ values are much greater than 2.00, the electronic ground states of both complexes are clearly $^2\Delta(\sigma^2\delta^3)$*. The results of the axial field model are not in very good quantitative agreement with the experimental values, and the effects of the lower symmetry fields and molecular orbital formation must be included to obtain better agreement[9].

The electronic absorption spectra of these complexes may also be interpreted via the axial field model. None of the absorption spectra have been reported in detail, but the "d^5" complex, $[(\pi\text{-DCB})_2\text{Fe(III)}]^-$ is reported[1] to have weak absorption bands at 4440 Å and 5200 Å. Assuming that no other bands occur beyond 5200 Å, this band can be assigned as the $\sigma \rightarrow \delta$ ($^2\Delta \rightarrow {}^2\Sigma^+$) transition. The same band in ferricenium cation is at 6170 Å[7,8]. Using the arguments previously applied to ferricenium cation[7], it can be shown that

$$E(\delta) - E(\sigma) = 19.2 \text{ kK } (5200 \text{ Å}) - 20\,\beta B \text{ (free ion)}$$

where β = nephelauxetic parameter and B is the Racah electron interaction parameter. Taking $B(\text{Fe}^{3+}) = 1.09$ kK and $\beta = 0.5$**, it is found that the δ orbital lies about 8300 cm^{-1} *above* the σ orbital in the $[(\pi\text{-DCB})_2\text{Fe(III)}]^{-1}$ complex. In ferricenium cation this same interval is about 5300 cm^{-1} (ref. 8).

The "d^6" complexes should have ligand field spectra similar to that of ferrocene[3,7] since both types of complexes may be discussed via an axial field model. There will be three spin-allowed bands due to the one-electron jumps $\sigma \rightarrow \pi^*$ (excited state: $^1\Pi$) and $\delta \rightarrow \pi^*$ (excited states: $^1\Pi$, $^1\Phi$). The two Π states interact to yield Π^+ (higher energy) and Π^- (lower energy) states. The reported[1] spectrum of $(\pi\text{-DCB})(\pi\text{-Cp})\text{Co(III)}$ is very similar to that of ferrocene with weak bands at 3200 Å and 4220 Å. The first band is assigned to the $^1\Sigma^+ \rightarrow {}^1\Pi^+$ transition, and the second to the almost degenerate $^1\Sigma^+ \rightarrow {}^1\Pi^-$, $^1\Phi$ transitions.

Without a detailed experimental study of the absorption spectra of these complexes, definite determination of the energies of the d orbitals is not possible. However, by making reasonable approximation for some of the required parameters, approximate results may be obtained. In the axial field model, the transition energies

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* This is in agreement with the ground state of ferricenium cation[8].

** $\beta = 0.4$ for ferrocene[3].

are expressed in terms of the splitting parameters, *Ds* and *Dt*, and the electron repulsion parameters, F_2 and F_4:

$$^1\Sigma^+ \rightarrow {}^1\Pi^+ :\quad Ds + 7.5Dt + 6F_2 - 65F_4 + X \qquad (1)$$

$$^1\Pi^- :\quad Ds + 7.5Dt + 6F_2 - 65F_4 - X \qquad (2)$$

$$^1\Delta \ :\quad 3Ds + 5Dt - 9F_2 + 10F_4 \qquad (3)$$

where $X = 1/2[(-4Ds + 5Dt + 6F_2 - 30F_4)^2 + 384(F_2 - 5F_4)^2]^{1/2}$.

For (π-DCB)(π-Cp)Co(III), we set

$F_2 = 0.923$ kK and $F_4 = 0.103$ kK (values previously found for ferrocene[3]).

eqn. (1) to 31.25 kK (3200 Å), (2) and (3) to 23.70 kK (4220 Å); and solve (1) + (2) and (3) simultaneously. Values of $Ds = 5090$ and $Dt = 3140$ cm^{-1} are obtained. Using the same values of F_2 and F_4 and the experimental[11] data for [(π-Cp)$_2$Co(III)]$^+$, 4100 Å and 3330 Å, we obtained $Ds = 5470$ and $Dt = 3050$ cm^{-1}. We now have splitting parameters for two π-Cp ligands and for the combined effect of one π-Cp and one π-DCB group. Since the splitting parameters for the (π-Cp)(π-DCB)Co(III) complex may be divided into individual contributions for each ligand within the ligand field model, we may obtain the *Ds* and *Dt* values for two π-DCB ligands from the data above:

$$Ds = 2[Ds(\text{DCB} + \text{Cp}) - 1/2Ds(\text{Cp} + \text{Cp})] = 4710 \text{ cm}^{-1}$$

$$Dt = 2[Dt(\text{DCB} + \text{Cp}) - 1/2Dt(\text{Cp} + \text{Cp})] = 3230$$

The ligand field bands of [(π-DCB)$_2$Co(III)]$^-$ are then predicted to occur at 4350 and 4200 Å ($^1\Sigma^+ \rightarrow {}^1\Delta$, $^1\Pi$) and 3140 Å ($^1\Sigma^+ \rightarrow {}^1\Pi^+$). Experimentally[1] these bands occur at 4450 Å ($\varepsilon = 440$) and 345 ($\varepsilon = 2200$). Considering the approximations made for F_2 and F_4, the results should be regarded as good. Much better agreement is expected after a detailed spectral study is made.

Approximate energy differences between the one electron orbitals may now be obtained from the derived *Ds* and *Dt* values. The derived values are listed below with those of ferrocene[3] for comparison:

(π-Cp)(π-DCB)Co (III):	$E(\pi) - E(\sigma) \sim 26.3$ kK
	$E(\sigma) - E(\delta) \sim 4.7$
[(π-DCB)$_2$Co (III)]$^-$:	$E(\pi) - E(\sigma) \sim 27.6$ kK
	$E(\sigma) - E(\delta) \sim 2.7$
(π-Cp)$_2$Fe(II):	$E(\pi) - E(\sigma) = 25.5$ kK
	$E(\sigma) - E(\delta) = 4.6$

These applications of the axial field model to the various properties of the new carborane complexes illustrate its usefulness. This model should serve as a predictive tool for the preparation of new carborane complexes and as a model for the calculation of their properties. The previously mentioned analogy[1] between the metallocenes and the new carborane metal complexes may now be explained since both types of complexes are "axial field" complexes.

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Department of Chemistry, Texas Technological College, Lubbock, Texas (U.S.A.) DONALD R. SCOTT

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1,4-Dilithiooctafluorobutane*

Perfluoro-n-propyllithium[1], perfluoroisopropyllithium[2], and perfluoro-n-heptyllithium[3] are useful intermediates despite some restrictions arising from their instability. The first dilithioperfluoroalkane, 1,4-dilithiooctafluorobutane, has now been prepared by metal–halogen exchange in ether at −80°, and characterised by its reaction with acetaldehyde to give 2,7-dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane in at least 18% yield. This diol, which readily yielded a bis(*p*-nitrobenzoate) derivative, was also obtained from diethyl octafluoroadipate and a mixture of methylmagnesium iodide and isopropylmagnesium bromide (a reaction reported[4] for monofunctional esters). One pure crystalline form of the diol, and two of the bis(*p*-nitrobenzoate), were isolated by fractional crystallisation.

Although the stability of 1,4-dilithiooctafluorobutane is limited even at −80°, dilithioperfluoroalkanes should prove, using simultaneous or alternating addition techniques, as useful intermediates as the perfluoroalkyllithiums.

Experimental

2,7-Dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane from diethyl octafluoroadipate. To a stirred solution of the mixed Grignard reagents[4] from magnesium (8.4 g, 0.35 g-atom), methyl iodide (18.0 g, 0.13 mole), and isopropylmagnesium bromide (23.0 g, 0.19 mole) in ether (175 ml), diethyl octafluoroadipate (20.0 g, 0.058 mole) in ether (10 ml) was added under nitrogen at 5–10° during 1 h. After being allowed to stand overnight, the mixture was refluxed for 1 h, and then hydrolysed with 6 *N* hydrochloric acid (100 ml). The ethereal layer, and two 50 ml ether extracts, were dried ($MgSO_4$). Removal of solvent afforded a very viscous liquid fraction (6.9 g), b.p. 152°/50 mm,

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