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**LIGAND FIELD MODEL
FOR BENT (C_{2v}) d^1 METALLOCENE COMPLEXES**

Ivan PAVLÍK¹, Josef FIEDLER, Jaromír VINKLÁREK
and Martin PAVLIŠTA
Department of General and Inorganic Chemistry, University of Pardubice,
CZ-532 10 Pardubice

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Ligand field calculations, excluding spin-orbit coupling, have been carried out for bent d^1 metallocene complexes in C_{2v} symmetry. The application of the results to the interpretation of the $d-d$ electronic spectrum of the representative d^1 complex vanadocene dichloride is discussed with particular reference to the relative energy of the five d orbitals.

Introduction

The nature of the bonding in bent d^N metallocene complexes of the type Cp_2ML_n ($Cp = \eta^5-C_5H_5$; $M =$ early transition metal; $L =$ ligand, e.g. halide, pseudohalide etc.; $N = 1 - 4$; $n = 1$ or 2) has been a matter of great interest. Various

¹ To whom correspondence should be addressed.

theoretical molecular orbital (MO) calculations on such complexes [1–5] have led to different orders of the frontier d orbitals. One very sensitive test of these calculations is a check of the calculated d orbital energy order against the order deduced by analysis of the $d-d$ electronic spectrum using an appropriate theoretical model. The model employed for this purpose is one which had been used for a number of linear d^x ($x = 2-8$) metallocenes [6–11], namely the ligand field (LF) model. In the framework of this model, the splitting of the d^1 M(IV) free-ion level by a ligand field of C_{2v} symmetry is investigated. It is our subject to test such a LF model by making assignment for the $d-d$ bands in the electronic spectrum of the representative d^1 bent metallocene complex, *viz.* vanadocene dichloride, Cp_2VCl_2 , and to determine the relative energy order of the V(IV) d orbitals. We follow the traditional approach expressing the ligand field in terms of one-electron splitting or LF parameters which are determined from experimental data, mostly $d-d$ transition energies.

Theory

Figure 1 depicts a bent metallocene Cp_2ML_2 molecule of the idealised C_{2v} symmetry, its structural parameters and the coordinate system (identical to that used by Lauher and Hoffmann [3]). The one-electron LF potential (spin-orbit being neglected) experienced by a single d electron in the ligand field can be expressed as follows

$$V_{LF} = \sum_K \sum_Q A_K^Q Y_K^Q \frac{r_{<}^K}{r_{>}^{K+1}} \quad (1)$$

where A_K^Q are expansion coefficients, the Y_K^Q are spherical harmonics, and $r_{<}$ ($r_{>}$) is the lesser (greater) of the two distances, r , the distance of the electron from the metal ion nucleus, and $r_{M-ligand}$, the metal ion-ligand distance. Since V_{LF} represents the ligand field, it must be invariant to all symmetry operations \hat{O}_R of the appertaining point symmetry group G so that $\hat{O}_R V_{LF} = V_{LF}$ for all $\hat{O}_R \in G$. In the case of the C_{2v} point group, the invariance requirement is satisfied when $K = 0, 2, 4$; $Q = 0, 2, 4$ ($\hat{O}_R = \hat{C}_2$) and $A_2^2 = A_2^{-2}$, $A_4^2 = A_4^{-2}$, $A_4^4 = A_4^{-4}$ ($\hat{O}_R = \hat{\sigma}_{xz}, \hat{\sigma}_{yz}$). The effective and exact one-electron potential for the C_{2v} field is (neglecting term Y_0^0 , which contributes nothing to the splitting of the d level):

$$V_{LF} = A_2^0 Y_2^0 \frac{r_{<}^2}{r_{>}^3} + A_2^2 (Y_2^2 + Y_2^{-2}) \frac{r_{<}^2}{r_{>}^3} + A_4^0 Y_4^0 \frac{r_{<}^4}{r_{>}^5} + A_4^2 (Y_4^2 + Y_4^{-2}) \frac{r_{<}^4}{r_{>}^5} + A_4^4 (Y_4^4 + Y_4^{-4}) \frac{r_{<}^4}{r_{>}^5} \quad (2)$$

In order to calculate A_K^Q coefficients, the ligands are usually approximated by point charges. In the case of linear MCp₂ metallocenes, this approximation was realized by replacing each Cp ring by circular line unit charge [9,13,14]. The same approximation simplifying the calculation of coefficients has been also adopted for the case of bent metallocenes (see Fig. 1; here γ is the angle subtended at the central metal M between carbon atoms of the rings and the ring centroid-M axis). The individual A_K^Q coefficients involved in V_{LF} (2) for the C_{2v} Cp₂ML_n ($n = 1$ or 2) complexes are given in Table I (see also Appendix).

Table I The A_K^Q coefficients for C_{2v} Cp₂ML₂ complex^a

Coefficients	C _{2v} fragments	
	MCp ₂	ML ₂
A_0^0	$-4\sqrt{\pi}q$	$-4\sqrt{\pi}q$
A_2^0	$\sqrt{\pi/5}(3a-2)(3c-1)q$	$2\sqrt{\pi/5}(3b-2)q$
A_2^2	$-\sqrt{3\pi/10}a(3c-1)q$	$2\sqrt{3\pi/10}bq$
A_4^0	$-(\sqrt{\pi}/48)(8-40a+35a^2)(3-30c+35c^2)q$	$-(\sqrt{\pi}/6)(8-40b+35b^2)q$
A_4^2	$(\sqrt{10\pi}/48)a(7a-6)(3-30c+35c^2)q$	$-(\sqrt{10\pi}/6)b(7b-6)q$
A_4^4	$-(\sqrt{35\pi/2}/48)a^2(3-30c+35c^2)q$	$-\sqrt{70\pi}/12)b^2q$

^a $a = \sin^2(\alpha/2)$; $b = \sin^2(\beta/2)$; $c = \cos^2(\gamma)$; $q =$ unit charge

In the C_{2v} ligand field, the d orbital set is split into five sublevels $a_1(d_{z^2})$, $a_1(d_{x^2-y^2})$, $a_2(d_{xy})$, $b_1(d_{xz})$ and $b_2(d_{yz})$ where both a_1 orbitals are mixed (designated as $1a_1$ and $2a_1$ in accordance with [3]), with one-electron energies (for Cp₂ML₂)

$$E(1a_1) = \frac{1}{2} \left\{ H_{11} + H_{22} - \left[(H_{11} - H_{22})^2 + (2H_{12})^2 \right]^{1/2} \right\}$$

$$E(2a_1) = \frac{1}{2} \left\{ H_{11} + H_{22} + \left[(H_{11} - H_{22})^2 + (2H_{12})^2 \right]^{1/2} \right\}$$

$$H_{11} = -(3a - 2)Ds - \frac{3}{4}(8 - 40a + 35a^2)Dt +$$

$$+ \frac{3}{4}(8 - 40b + 35b^2)Dq - (3b - 2)Dr$$

$$H_{22} = (3a - 2)Ds - \frac{1}{4}(4 - 20a + 35a^2)Dt +$$

$$+ \frac{1}{4}(4 - 20b + 35b^2)Dq + (3b - 2)Dr \quad (3)$$

$$H_{12} = 3^{1/2} \left[-aDs + \frac{5}{4}a(7a - 6)Dt + \frac{5}{4}b(7b - 6)Dq + bDr \right]$$

$$E(a_2) = (3a - 2)Ds + (5a - 1)Dt - (5b - 1)Dq + (3b - 2)Dr$$

$$E(b_1) = Ds + (4 - 35a + 35a^2)Dt - (4 - 5b)Dq - (3b - 1)Dr$$

$$E(b_2) = -(3a - 1)Ds + (4 - 5a)Dt - (4 - 35b + 35b^2)Dq + Dr$$

with four one-electron splitting parameters defined as

$$Ds = \frac{1}{7}(3c - 1) \left\langle \frac{r_{<}^2}{r_{>}^3} \right\rangle_{\text{Cp}}$$

$$Dt = -\frac{1}{84}(35c^2 - 30c + 3) \left\langle \frac{r_{<}^4}{r_{>}^5} \right\rangle_{\text{Cp}}$$

$$Dq = \frac{2}{21} \left\langle \frac{r_{<}^4}{r_{>}^5} \right\rangle_{\text{L}}$$

$$Dr = \frac{2}{7} \left\langle \frac{r^2}{r^3} \right\rangle_L$$

where $a = \sin^2(\alpha/2)$, $b = \sin^2(\beta/2)$, $c = \cos^2\gamma$ (see Fig. 1)

As the definitions of the Ds and Dt parameters are identical to those for linear MCp_2 metallocenes [8,9,12,13], the acceptable basis results for comparing Cp_2ML_2 complexes with linear metallocenes. For the Dq parameter being quite analogous to that for octahedral or tetrahedral complexes [15,16] it holds

$$Dq(\text{C}_{2v}) = \frac{4}{7}Dq(\text{O}_h) = \frac{9}{7}Dq(\text{T}_d) \quad (4)$$

Thus, the comparison of Cp_2ML_2 species with octahedral ML_6 -type or tetrahedral ML_4 -type complexes is possible.

The correctness of Eqs (3) can be verified in several ways

- (i) It holds $E(1a_1) + E(2a_1) + E(a_2) + E(b_1) + E(b_2) = 0$ (centre of gravity conservation rule)
- (ii) For $Dq = Dr = 0$ (i.e. $R_L \rightarrow \infty$) and $\alpha = 180^\circ$ one obtains

$$\left. \begin{aligned} E(a_2) = E(b_1) = Ds + 4Dt &\equiv E(e_{1g}) = E(\pi) \\ E(2a_1) = 2Ds - 6Dt &\equiv E(a_{1g}) = E(\sigma) \\ E(1a_1) = E(b_2) = -2Ds - Dt &\equiv E(e_{2g}) = E(\delta) \end{aligned} \right\} \begin{array}{l} \text{one-electron energies} \\ \text{for linear MCp}_2 \\ \text{metallocenes (pseudo-axial)} \\ \text{LF [6,13]} \end{array}$$

- (iii) When $\gamma = 0^\circ$, ring centroid = R_L , $a = b = 2/3$, then Cp_2ML_2 complex transforms into a ML_4 complex. If the equalities $Ds = Dr$ and $Dq = -Dt$ are used, it results from (3) and (4)

$$\left. \begin{aligned} E(2a_1) = E(b_1) = E(b_2) &= \frac{28}{9}Dq(\text{C}_{2v}) = 4Dq(\text{T}_d) \equiv E(t_2) \\ E(1a_1) = E(a_2) &= -\frac{14}{3}Dq(\text{C}_{2v}) = -6Dq(\text{T}_d) \equiv E(e) \end{aligned} \right\} \begin{array}{l} \text{one-electron} \\ d\text{-orbital} \\ \text{energies for} \\ \text{tetrahedral} \\ \text{ML}_4 \end{array}$$

It should be noted that the one-electron energies of the $1a_1$, $2a_1$, a_2 , b_1 and b_2 orbitals for a Cp_2ML (C_{2v}) complex can simply be derived from Eq. (3) in the following way: first, one sets $\beta = 0^\circ$ into coefficients at Dq and Dr ; second, the residual coefficients are divided by two, e.g.

$$H_{11}(\text{Cp}_2\text{ML}) = -(3a - 2)Ds - \frac{3}{4}(8 - 40a + 35a^2)Dt + 3Dq + Dr$$

Results and Discussion

The applicability of this LF model was tested on the d^1 complex vanadocene dichloride. For any d^1 C_{2v} bent metallocene complex, four $d-d$ transitions (one of which is symmetry forbidden) are expected irrespective of the actual electronic ground state. If no *a priori* presumptions are made regarding both the nature of the lowest singly occupied d orbital and the relative energy order of remaining four d orbitals, there are 120 possible assignments of the experimental $d-d$ transition energies. The visible and near infrared spectrum of vanadocene dichloride (in chloroform) shows weak bands at ν_{max} [cm^{-1}] (ϵ_{max} [$\text{m}^2 \text{mol}^{-1}$]) 10920 (5.0), 12860 (5.5), 15790 (4.3), and 19790 (2.5) (the ν_{max} and ϵ_{max} values of the four bands reported were obtained by a Gaussian analysis of the experimental absorption curve). These bands may reasonably be assigned as $d-d$ or LF bands involving transitions within V(IV) d level split by the perturbing field of the Cp and Cl ligands. The only acceptable assignment (from the total number of 120 assignments tested) appears to be that involving the electronic ground state ${}^2A_{1g}$ ($1a_1$) and the relative d orbital energy order $1a_1 < b_1 < b_2 < 2a_1 < a_2$. The values of the four LF parameters deduced from the $d-d$ spectrum using equations (3) are (cm^{-1}): $Ds = 5230$, $Dt = 3042$, $Dq = 780$, $Dr = 5587$ ($Ds/Dt = 1.72$, $Dr/Dq = 7.17$) (for the α and β angles, the mean values from the X-ray study [17] were used). Therefore, the assignments of the $d-d$ bands are: ${}^2A_1 \rightarrow {}^2B_1$ (10920 cm^{-1}), ${}^2A_1 \rightarrow {}^2B_2$ (12860 cm^{-1}), ${}^2A_1 \rightarrow {}^2A_1$ (15790 cm^{-1}) and ${}^2A_1 \rightarrow {}^2A_2$ (19790 cm^{-1}). In fact, the highest energy band of lowest intensity corresponds to the symmetry forbidden $d-d$ transition $1a_1 \rightarrow a_2$. The obtained values of the Ds and Dt parameters as well as the value of their ratio Ds/Dt correlate well with the corresponding values for the linear V(II) metallocene vanadocene VCp_2 , where $Ds = 3756 \text{ cm}^{-1}$, $Dt = 2018 \text{ cm}^{-1}$, $Ds/Dt = 1.88$ [9] if one takes into consideration the well-known fact that the LF parameter(s) of any transition metal complex increase(s) with increasing central metal oxidation state. The Dq value found for Cp_2VCl_2 compares reasonably with the value $Dq(C_{2v}) \approx 850 \text{ cm}^{-1}$ deduced from the $Dq(T_d) = 660 \text{ cm}^{-1}$ for VCl_4 [18] or with $Dq(C_{2v}) \approx 880 \text{ cm}^{-1}$ from the $Dq(O_h) = 1540 \text{ cm}^{-1}$ for VCl_6^{2-} [19]. The same ${}^2A_1(1a_1)$ ground state has also been found by the analysis of EPR spectrum [4,20]. The EHT MO calculation on Cp_2VCl_2 [4] leads to the same relative d orbital order (note the interchange of x and y axes in our coordinate system in Fig. 1 in comparison with that by Stewart and Porte [4], leading to the interchange of b_1 and b_2 symmetry labels, too). The MO calculated $d-d$ transition energies agree reasonably with our

experimental energies. The additional d^1 bent metallocenes and the more detailed analysis, including spin-orbit coupling, of the LF problem will be presented in the next paper.

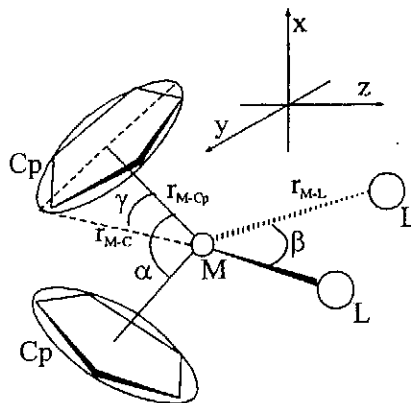


Fig. 1 Bent metallocene Cp_2ML_2 complex

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Appendix

The Calculation of the A_K^Q Coefficients

The calculation of the coefficients

$$A_K^Q = \frac{4\pi}{2k+1} \int \frac{\rho(\vec{R})}{4\pi\epsilon_0} Y_K^Q(\Theta, \Phi) d\tau_{\vec{R}} \quad (\text{A-1})$$

is based on a ligand system geometry and the coordinate system shown in Figs 1 and A-1.

In calculating A_K^Q , the ligands are usually approximated by point charges reducing the integral (A-1) to simple summation over single point charges. If we denote $\rho(\vec{R}) = -e$ or $q = e/(4\pi\epsilon_0)$, then it holds, e.g.,

$$A_2^0 = -q \frac{4\pi}{5} \left[\frac{1}{5} \sum_{i=1}^5 Y_2^{0*}(\Theta_i, \Phi_i) + \frac{1}{5} \sum_{i'=1}^5 Y_2^{0*}(\Theta_{i'}, \Phi_{i'}) + \sum_{j=L, L'}^5 Y_2^{0*}(\Theta_j, \Phi_j) \right] \quad (\text{A-2})$$

$$Y_2^0(\Theta, \Phi) = \sqrt{\frac{5}{16\pi}} (2 - 3\sin^2\Theta)$$

In order to calculate the expression (A-2) it is necessary to know the spherical coordinates Θ and Φ for all the twelve points charges ($i, i' = 1 - 5$ bearing the charge $-e/5$ or $j = L, L'$ bearing the charge $-e$).

On the basis of Figs 1 and A-1 the following expressions for the Cartesian coordinates of single point charges could be found, where $\xi_i = (i - 1)2\pi/5$, and $i = 1, 2, \dots, 5$

$$\left. \begin{array}{l} C_{cp,i} \\ (C_{cp',i}) \end{array} \right\} \begin{array}{l} x_i = R_C (\cos\gamma \sin\frac{\alpha}{2} + \sin\gamma \cos\frac{\alpha}{2} \cos\xi_i) \\ y_i = R_C \sin\gamma \sin\xi_i \\ z_i = R_C (-\cos\gamma \cos\frac{\alpha}{2} + \sin\gamma \sin\frac{\alpha}{2} \cos\xi_i) \end{array} \quad (\text{A-3})$$

$$L(L') \quad x = 0, y = R_L \sin\frac{\beta}{2}, z = R_L \cos\frac{\beta}{2}$$

Using the well-known relations between the Cartesian (x, y, z) coordinates and the spherical (r, ϑ, φ) ones

$$\begin{aligned} \sin\vartheta &= \frac{1}{r} \sqrt{x^2 + y^2}, & \cos\vartheta &= \frac{z}{r} \\ \sin\varphi &= \frac{y}{\sqrt{x^2 + y^2}}, & \cos\varphi &= \frac{x}{\sqrt{x^2 + y^2}} \end{aligned} \quad (\text{A-4})$$

in principle it would be possible to express, for example, A_2^0 by substituting (A-3) into (A-4) and subsequently (A-4) into (A-2), but the resulting A_K^Q coefficients would not be very clearly arranged. However, in the latter treatment the members

$$\frac{1}{5} \sum_{i=1}^5 f(\cos, \sin\xi_i), \quad \xi_i = (i - 1) \frac{2\pi}{5}$$

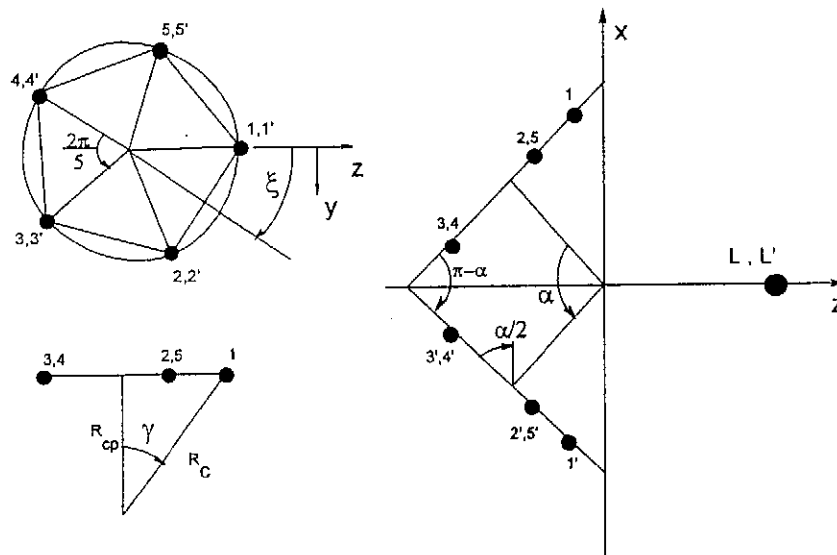


Fig. A-1 Geometry parameters for Cp_2ML_2 complex

are appearing. Reminding now the definition of the Riemann integral, namely

$$S = \frac{1}{5} \sum_{i=1}^5 (x_i - x_{i-1}) f(\xi_i), \quad x_{i-1} \leq \xi_i \leq x_i$$

and

$$\lim_{n \rightarrow \infty} \sum_{i=1}^n \frac{b-a}{n} f(\xi_i) = \int_a^b f(x) dx, \quad \text{respectively}$$

the following two generalizations can be written

– for replacement of the pentagon by N -gon

$$\frac{1}{5} \sum_{i=1}^5 f(\sin, \cos \xi_i) \rightarrow \frac{1}{N} \sum_{i=1}^N f(\sin, \cos \xi_i) \quad \text{and} \quad \xi_i = (i-1) \frac{2\pi}{N}$$

– for extension of the N -gon to a circle ($\xi \in \langle 0; 2\pi \rangle$)

$$\lim_{N \rightarrow \infty} \left\{ \frac{1}{2\pi} \sum_{i=1}^n \frac{2\pi}{n} f(\cos, \sin \xi'_i) \right\} = \frac{1}{2\pi} \int_0^{2\pi} f(\sin, \cos \xi) d\xi$$

For example, it follows for A_2^0 from (A-2) with respect to (A-2) – (A-5)

$$\begin{aligned}
 A_2^0 = & -q\sqrt{\frac{\pi}{5}} \left\{ \frac{1}{2\pi} \int_0^{2\pi} \left[2 - 3\cos^2\gamma \sin^2\frac{\alpha}{2} + \frac{1}{2}\sin 2\gamma \sin\alpha \cos\xi + \right. \right. \\
 & \left. \left. + \sin^2\gamma \cos^2\frac{\alpha}{2} \cos^2\xi + \sin^2\gamma \sin^2\xi \right] d\xi + \frac{1}{2\pi} \int_0^{2\pi} \left[2 - 3\cos^2\gamma \sin^2\frac{\alpha}{2} + \right. \right. \\
 & \left. \left. + \frac{1}{2}\sin 2\gamma \sin\alpha \cos\xi + \sin^2\gamma \cos^2\frac{\alpha}{2} \cos^2\xi + \sin^2\gamma \sin^2\xi \right] d\xi + \right. \\
 & \left. + 2\left(2 - 3\sin^2\frac{\beta}{2}\right) \right\} \quad (\text{A-5})
 \end{aligned}$$

The integration over ξ and several algebraic treatments afford for the example chosen

$$\begin{aligned}
 A_2^0 &= -q\sqrt{\frac{\pi}{5}} \left\{ (3\cos^2\gamma - 1) \left(2 - 3\sin^2\frac{\alpha}{2} \right) + 2 \left(2 - 3\sin^2\frac{\beta}{2} \right) \right\} = \\
 &= A_2^0(\text{MCp}_2) + A_2^0(\text{ML}_2)
 \end{aligned}$$