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SPLITTINGS OF d^n-CONFIGURATIONS IN PENTAGONAL AND HEXAGONAL LIGAND FIELDS. COMMENTS ON THE MAGNETIC PROPERTIES AND ABSORPTION SPECTRA OF SANDWICH MOLECULES

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Most of the workers who studied the electronic structure of the sandwich molecules[1-6] used the covalent model as a starting point whilst few of them[7-9] used the ionic model. We have tried to get to some qualitative conclusions concerning the magnetic properties and spectral behaviour of di-π-cyclopentadiene and dibenzene compounds of transition metals, on the basis of the purely ionic model assuming ligand fields of D_{5d} or D_{5h} and D_{6h} symmetries.

First we assume that the central ion in the sandwich molecules consists of a point-like ionic core and one d-electron, and the five- and six-membered rings are regular pentagons (C–C bond distance is 1.46 Å) and hexagons (C–C bond distance is 1.39 Å) in which the apices represent ligands of an effective point charge $Z > 0$. It was in these systems that the energies of the single d-electron have been calculated. The electron has an energy in the field of the free central ion to which contributes the effect of the ligands represented by a potential:

$$V_s = -\sum_j \frac{Z \cdot e^2}{|\vec{R}_j - \vec{r}|} \tag{1}$$

where $\vec{R}_j$ is the position vector of the j-th ligand and $\vec{r}$ that of the d-electron. The energy contributions are then given by integrals of the type

$$\langle \psi \mid V_s \mid \psi \rangle$$

where ψ is a linear combination of the five d-orbitals. Disregarding the factor $-Z \cdot e^2$ the forms of V_s in D_{5d} or D_{5h} and in D_{6h} are

$$V_5 = 10\frac{r_<^0}{r_>^1} + 10\frac{r_<^2}{r_>^3}P_2(\cos\vartheta_0)P_2(\cos\vartheta) + 10\frac{r_<^4}{r_>^5}P_4(\cos\vartheta_0)P_4(\cos\vartheta) \tag{2a}$$

and

$$V_6 = 12\frac{r_<^0}{r_>^1} + 12\frac{r_<^2}{r_>^3}P_2(\cos\vartheta_0)P_2(\cos\vartheta) + 12\frac{r_<^4}{r_>^5}P_4(\cos\vartheta_0)P_4(\cos\vartheta) \tag{2b}$$

and the corresponding one-electron integrals

$$\langle \pm 2 \mid V_5 \mid \pm 2 \rangle = \frac{80}{45} f G(0) - \frac{160}{315} f G(2) P_2(\cos \vartheta_0) + \frac{80}{945} f G(4) P_4(\cos \vartheta_0) \tag{3a}$$

$$\langle \pm 1 \mid V_5 \mid \pm 1 \rangle = \frac{80}{45} f G(0) + \frac{80}{315} f G(2) P_2(\cos \vartheta_0) - \frac{320}{945} f G(4) P_4(\cos \vartheta_0) \tag{3b}$$

$$\langle 0 \mid V_5 \mid 0 \rangle = \frac{80}{45} f G(0) + \frac{160}{315} f G(2) P_2(\cos \vartheta_0) + \frac{480}{945} f G(4) P_4(\cos \vartheta_0) \tag{3c}$$

and

$$\langle \pm 2 \mid V_6 \mid \pm 2 \rangle = \frac{96}{45} f G(0) - \frac{192}{315} f G(2) P_2(\cos \vartheta_0) + \frac{96}{945} f G(4) P_4(\cos \vartheta_0) \tag{4a}$$

$$\langle \pm 1 \mid V_6 \mid \pm 1 \rangle = \frac{96}{45} f G(0) + \frac{96}{315} f G(2) P_2(\cos \vartheta_0) - \frac{384}{945} f G(4) P_4(\cos \vartheta_0) \tag{4b}$$

$$\langle 0 \mid V_6 \mid 0 \rangle = \frac{96}{45} f G(0) + \frac{192}{315} f G(2) P_2(\cos \vartheta_0) + \frac{576}{945} f G(4) P_4(\cos \vartheta_0) \tag{4c}$$

in which

$$f = \frac{Z_c}{3 \cdot a_0}, \tag{5}$$

Z_c is the effective charge of the central ion, ϑ_0 the polar angle of the ligands determined at a given R by the sizes of the cyclopentadiene or benzene rings (Fig. 1), and

$$G(n) = \int_0^R (fr)^6 \frac{r^n}{R^{n+1}} e^{-2fr} \, dr + \int_R^\infty (fr)^6 \frac{R^n}{r^{n+1}} e^{-2fr} \, dr \tag{6}$$

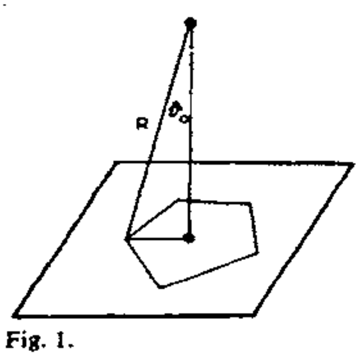

Fig. 1.

where r is the distance between the electron and the central ion and R that between the ligand and the central ion, and $n = 0$, 2 or 4.

Introducing the following notations

$$D_0(5) = \frac{80}{45} fG(0) \tag{7a}$$

$$D_2(5) = \frac{80}{315} fG(2)P_2(\cos \vartheta_0) \tag{7b}$$

$$D_4(5) = \frac{80}{945} fG(4)P_4(\cos \vartheta_0) \tag{7c}$$

and

$$D_0(6) = \frac{96}{45} fG(0) \tag{8a}$$

$$D_2(6) = \frac{96}{315} fG(2)P_2(\cos \vartheta_0) \tag{8b}$$

$$D_4(6) = \frac{96}{945} fG(4)P_4(\cos \vartheta_0) \tag{8c}$$

respectively, we get formally the same expressions for both symmetries:

$$\langle 2 \mid V_s \mid 2 \rangle = D_0(s) - 2D_2(s) + D_4(s), \tag{9a}$$

$$\langle 1 \mid V_s \mid 1 \rangle = D_0(s) + D_2(s) - 4D_4(s), \tag{9b}$$

$$\langle 0 \mid V_s \mid 0 \rangle = D_0(s) + 2D_2(s) + 6D_4(s). \tag{9c}$$

This result, of course, agrees with that of other authors[10-12] who investigated problems of axial symmetries.

Since in D_5 or D_6 symmetries* the d-orbitals split in the form:

$$\Gamma = A_1 + E_1 + E_2 \tag{10}$$

and since

d_0 transforms like A_1
$d_{\pm 1}$ like E_1 and
$d_{\pm 2}$ like E_2

the expressions (9a, 9b, 9c) actually give the energies belonging to the corresponding irreducible representations.

The numerical evaluation of the one-electron energies does not cause much trouble. By using the substitution

$$a = f \cdot R$$

* For simplicity we deal with D_5 and D_6 symmetries instead of D_{5d} or D_{5h} and D_{6h} symmetries.

we get for $G(n)$ that

$$G(n) = a^6 \left\{ \frac{(n+6)!}{(2a)^{n+7}} - A_{n+6}(2a) + A_{5-n}(2a) \right\} \tag{11}$$

where

$$A_m(\alpha) = \int_1^{\infty} e^{-\alpha x} \cdot x^m \, dx \tag{12}$$

For the probable values of f and R (f = 1–3 au and R = 4–6 au*) we calculated the one-electron energies and found that, as a rule, the sequence of the energies—regarding the minus sign in the factor $-Z \cdot e^2$—is

$$a_1 < e_1 < e_2$$

In the Tables 1 and 2 the energy differences Δ_1 ($= E(a_1) - E(e_1)$) and Δ_2 ($= E(e_1) - E(e_2)$) are given. It can be seen from the Tables that, in general, Δ_1 and Δ_2 are of the same order of magnitude and the larger is R or $Z_e(f)$ the smaller is the difference between them.

TABLE 1

D_5		f		
R		1	2	3
4	Δ_2	0.3221	0.1215	0.0527
	Δ_1	0.0047	0.0195	0.0129
5	Δ_2	0.2489	0.0789	0.0346
	Δ_1	0.1168	0.0298	0.0127
6	Δ_2	0.1742	0.0520	0.0232
	Δ_1	0.1164	0.0220	0.0089

TABLE 2

D_4		f		
R		1	2	3
4	Δ_2	0.3323	0.1164	0.0479
	Δ_1	−0.0969	−0.0032	0.0078
5	Δ_2	0.2841	0.0856	0.0370
	Δ_1	0.0772	0.0262	0.0120
6	Δ_2	0.2025	0.0585	0.0268
	Δ_1	0.1095	0.0230	0.0101

It can also be pointed out that by increasing R or Z_e both the absolute values of the energies and the energy differences Δ_1 and Δ_2 are decreased.

On the basis of the above considerations two cases can be distinguished. In the first case the separations Δ_1 and Δ_2 (Fig. 2) are relatively large. By increasing R or Z_e, or both of them, the first case turns into the second one where the separations Δ_1 and Δ_2 are small.

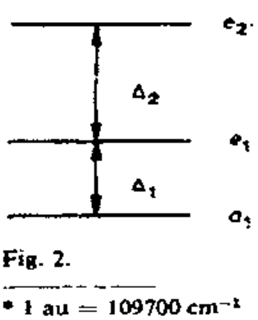

Fig. 2.

* 1 au = 109700 cm^{-1}

TABLE 3[a]

No. of	*Electron configuration*		*Ground*	*Excited*		*Examples*
electrons	*Ion*	*Molecule*	*state*	*Configurations*	*States*	
0	d^2	$(a_1)^2$	$^1A_1$	$(a_1)(e_1)$ $(a_1)(e_2)$	$^1E_1$ $^1E_2$	$Ti(cp)_2$ $Mo(cp)_2^{2+}$
1	d^3	$(a_1)^2(e_1)$	$^2E_1$	$(a_1)(e_1)(e_2)$ $(a_1)(e_1)^2$ $(a_1)^2(e_2)$	$2\,^2E_1, 2\,^2E_2$ $^2A_1, ^2A_2, ^2E_2$ $^2E_2$	—
2	d^4	$(a_1)^2(e_1)^2$	$^3A_2$	$(a_1)(e_1)^3$ $(a_1)(e_1)^2(e_2)$ $(a_1)^2(e_1)(e_2)$	$^3E_1$ $^3A_1, ^3A_2, ^3E_1, 3\,^3E_2$ $^3E_1, ^3E_2$	$Cr(cp)_2$
1	d^5	$(a_1)^2(e_1)^3$	$^2E_1$	$(a_1)(e_1)^4$ $(a_1)(e_1)^3(e_2)$ $(a_1)^2(e_1)^2(e_2)$	$^2A_1$ $2\,^2E_1, 2\,^2E_2$ $^2A_1, ^2A_2, ^2E_1$ $2\,^2E_2$	$Fe(cp)_2^+$ $(V(bz)_2)$ $(Cr(bz)_2^+)$
0	d^6	$(a_1)^2(e_1)^4$	$^1A_1$	$(a_1)^2(e_1)^3(e_2)$ $(a_1)(e_1)^4(e_2)$	$^1E_1, ^1E_2$ $^1E_2$	$Fe(cp)_2$ $Co(cp)_2^+$ $Rh(cp)_2^+$ $Ru(cp)_2$ $Ir(cp)_2^+$ $(Cr(bz)_2)$
1	d^7	$(a_1)^2(e_1)^4(e_2)$	$^2E_2$	$(a_1)(e_1)^4(e_2)^2$ $(a_1)^2(e_1)^3(e_2)^2$	$^2A_1, ^2A_2, ^2E_1$ $^2A_1, ^2A_2, 2\,^2E_1, ^2E_2$	$Co(cp)_2$ $Ni(cp)_2^+$

[a] The data of Tables 3 and 4 are those for D_5 symmetry, therefore, they are only valid for the cyclopentadiene compounds. Minor deviations in the (excited) many-electron states occur for D_6 symmetry (see Ref. 13).

In order to interpret the magnetic properties of the sandwich molecules, let us fill up one-by-one the one-electron states with electrons. It is obvious that the energy distribution related with the first case is favourable to the so called "low spin case" and the second, to the "high spin case". The electron configurations corresponding to these cases are given in the third columns of the Tables 3 and 4. As it can be seen, for a number of cyclopentadiene and for a few benzene compounds (last columns) the numbers of unpaired electrons (first columns) agree with those corresponding to the electron configurations in the normal states. If one found that for a given case the calculated and observed energy distribution or electron configuration were different, it would mean (i) that the presented ionic model could not be applied to that particular case, or (ii) that the sandwich rings suffered distortion and as a consequence one should have different $\vartheta_{\pm}$ polar angles at a given constant R.

To be able to explain, at least qualitatively, the spectral behaviour of these molecules, the many-electron states arising from the splittings, in fields of D_5 and D_6 symmetries, of electron configurations[13] have to be considered. The fourth columns of Tables 3 and 4 show the ground states corresponding to the electron

TABLE 4

No. of electrons	Electron configuration: ion	Electron configuration: Molecule	Ground state	Excited: Configurations	Excited: States	Examples
2	d^2	$(a_1)(e_1)$	$^3E_1$	$(e_1)^2$ $(e_1)(e_2)$ $(a_1)(e_2)$	$^3A_2$ $^3E_1$, $^3E_2$ $^3E_2$	$V(cp)_2^+$
3	d^3	$(a_1)(e_1)^2$	$^4A_2$	$(e_1)^3$ $(e_1)^2(e_2)$ $(a_1)(e_1)(e_2)$	— $^4E_2$ $^4E_1$, $^4E_2$	$V(cp)_2$ $Cr(cp)_2^+$
4	d^4	$(a_1)(e_1)^2(e_2)$	$^5E_2$	$(e_1)^3(e_2)$ $(e_1)^2(e_2)^2$ $(a_1)(e_1)(e_2)^2$	— $^5A_1$ $^5E_1$	—
5	d^5	$(a_1)(e_1)^2(e_2)^2$	$^6A_1$	—	—	$Mn(cp)_2$
4	d^6	$(a_1)^2(e_1)^2(e_2)^2$	$^5A_1$	$(a_1)(e_1)^3(e_2)^2$ $(a_1)(e_1)^2(e_2)^3$ $(a_1)^2(e_1)(e_2)^3$	$^5E_1$ $^5E_2$ —	—
3	d^7	$(a_1)^2(e_1)^3(e_2)^2$	$^4E_1$	$(a_1)(e_1)^4(e_2)^2$ $(a_1)(e_1)^3(e_2)^3$ $(a_1)^2(e_1)^2(e_2)^3$	$^4A_2$ $^4E_1$, $^4E_2$ $^4E_2$	—
1	d^1	(a_1)	$^2A_1$	(e_1) (e_2)	$^2E_1$ $^2E_2$	$Ti(cp)_2^+$ $V(cp)_2^{2+}$
2	d^8	$(a_1)^2(e_1)^4(e_2)^2$	$^3A_2$	$(a_1)(e_1)^4(e_2)^3$ $(a_1)^2(e_1)^3(e_2)^3$	$^3E_2$ $^3E_1$, $^3E_2$	$Ni(cp)_2$
1	d^9	$(a_1)^2(e_1)^4(e_2)^3$	$^2E_2$	$(a_1)^2(e_1)^3(e_2)^4$ $(a_1)(e_1)^4(e_2)^4$	$^2E_1$ $^2A_1$	—

configurations in the normal states as well as the excited levels (sixth columns), considering only one-electron jumps (fifth columns) from the ground electron configurations.

Finally, we would like to touch upon a few examples to compare these qualitative results with experimental data from the literature (Table 5).

TABLE 5[a]

Molecule	Probable d–d bands in Å		Reference (14)
$Ni(cp)_2$	5700	4400	a
$Fe(cp)_2$	4400	(3200)	b
$Ru(cp)_2$	3300	2700	c
$Co(cp)_2^+$	4200	3200	d
$Rh(cp)_2^+$	3200		
$Ir(cp)_2^+$	3000		e[b]

[a] Spectral data for other compounds are rather scarce, *e.g.* for $Cr(bz)_2$ and $Cr(bz)_2^+$ see Refs. 15 and 16.

[b] The broad tail, in the absorption spectra, towards the longer wavelengths may cover several bands.

Theoretically, in all the cases given in Table 5 three transitions are possible (see Tables 3 and 4) and one can expect certain similarity in the absorption spectra of low spin d^6 (Table 3) and d^8 (Table 4) systems seeing that for both systems a non-degenerate (A) state is the ground level and the three excited levels are doubly degenerate (E) states. To select the true transitions from the possible ones, calculation of interelectronic repulsions should be carried out but considering that the presented model is a rather rough and simple approach to the real problem there would have been no much point in doing it.

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