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Ligand Field Transitions in $M(CO)_5L$ (M = Cr, Mo, W)

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The energy diagram of the metal d-orbitals in $M(CO)_5L$ complexes is described taking into account both mutual electron repulsion and ligand field effects. The various parameters governing the diagram are estimated from absorption and photoelectron spectra. The LF transitions are assigned in detail and the shifts by replacement of L are discussed. The results show that the lowest excited state has mainly σ_z^*-character.

Introduction

The electronic absorption spectra of the group VI B metal hexacarbonyls and of a large number of monosubstituted complexes have been published and assigned in literature [1, 2]. The absorption spectrum of amine metal pentacarbonyl complexes does not change appreciably on going from one to another amine ligand L. In the absorption spectra of these complexes the first band at about 25 kK has been assigned to a LF transition ($^1E \leftarrow {}^1A_1$). In the tungsten complexes the singlet–triplet transition ($^3E \leftarrow {}^1A_1$) is observed at the low energy site. All complexes exhibit an intense CO←M charge transfer band at about 39 kK obscuring all other bands at higher energy. The weak bands in between these two bands at 25 and 39 kK have not been assigned in detail before.

Besides, the assignment of the first LF band in the spectra of the monosubstituted complexes is subject to some controversy. The photochemistry of $M(CO)_5L$ demonstrated a wavelength dependent quantum yield [3–5]. The preferential loss of the axial ligand L by irradiation at low energy and of the carbonyls by irradiation at higher energy has been rationalized by the assumption that the $\sigma_z^*(d_{z^2})$ orbital has a lower energy than $\sigma_{xy}^*(d_{x^2-y^2})$.

Another approach starts from the energy diagram of the hexacarbonyls and describes the changes that occur when a carbonyl is replaced by a ligand with poorer π-acceptor and stronger σ-donor properties [6]. The t_{2g}-orbital of the hexacarbonyls is stabilized by π-back bonding with the π^*-orbitals of the carbonyls. Substitution will reduce π-interaction along the z-axis and cause a destabilization of d_{xz} and d_{yz} orbitals with respect to the d_{xy}. The stronger σ-donation along the z-axis will split the σ-antibonding e_g in such a way that d_{z^2} has a higher energy than $d_{x^2-y^2}$. This is the situation normally described in the literature without taking into account electron repulsion.

In this article we will describe an energy diagram of $M(CO)_5L$ in which both ligand field effects and electron repulsion are accounted for. The results will be compared with the absorption spectra of several of these compounds.

Results and Discussion

In the description of the energy diagram three interactions are taken into account:

1. Ligand field splitting Δ in an octahedral symmetry.
2. Deviations from octahedral symmetry in mono substituted complexes in terms of differences in σ-donor ($\delta\sigma$) and π-acceptor ($\delta\pi$) properties of the ligand L and CO.
3. Mutual electron repulsion of d-electrons expressed in Racah parameters B and C.

1. The splitting Δ of the d-orbitals in the octahedral field is deduced from the u.v.-absorption spectra of the hexacarbonyls and is estimated at about 32.2 kK [1]. For mono-substituted amine pentacarbonyl complexes the lower limit of Δ, the splitting between σ-antibonding and π-bonding d-orbitals, is 25 kK as determined from the first LF transition.

2. Because of the difference in π-acceptor properties between the carbonyl group and an amine group the t_{2g}-level is split upon substitution. According to photoelectron spectroscopic measurements this splitting $\delta\pi$ is about 2.4 kK [7]. No measurements concerning $\delta\sigma$ are available. However, $\delta\sigma$ is assumed

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TABLE Ia. Energy States (Electron Repulsion > Deviation from O_h-symmetry).

Electronic State		Eigenfunction	Energy		
			Octahedral Field	Electron Repulsion	Deviation from O_h-sym.
O_h	C_{4v}				
A_{1g}	A_1	$d_{xy}^2 d_{xz}^2 d_{yz}^2$	–	–	–
T_{1g}	A_2	$d_{x^2-y^2}^1 d_{xy}^1 d_{xz}^2 d_{yz}^2$	Δ	–C	–
	E_a	$-\frac{1}{2}(d_{x^2-y^2} - \sqrt{3}\, d_{z^2})^1 d_{xz}^1 d_{xy}^2 d_{yz}^2$	Δ	–C	$+\frac{3}{4}\delta\sigma - \delta\pi$
		$-\frac{1}{2}(d_{x^2-y^2} + \sqrt{3}\, d_{z^2})^1 d_{yz}^1 d_{xy}^2 d_{xz}^2$	Δ	–C	$+\frac{3}{4}\delta\sigma - \delta\pi$
T_{2g}	B_2	$d_{z^2}^1 d_{xy}^1 d_{xz}^2 d_{yz}^2$	Δ	+16B – C	$\delta\sigma$
	E_b	$\frac{1}{2}(\sqrt{3}\, d_{x^2-y^2} + d_{z^2})^1 d_{xz}^1 d_{xy}^2 d_{yz}^2$	Δ	+16B – C	$\frac{1}{4}\delta\sigma - \delta\pi$
		$\frac{1}{2}(\sqrt{3}\, d_{x^2-y^2} - d_{z^2})^1 d_{yz}^1 d_{xy}^2 d_{xz}^2$	Δ	+16B – C	$\frac{1}{4}\delta\sigma - \delta\pi$

TABLE Ib. Energy States (Deviation from O_h-symmetry > Electron Repulsion).

Electronic State		Eigenfunction	Energy		
			Octahedral Field	Deviation from O_h-sym.	Electron Repulsion
O_h	C_{4v}				
A_{1g}	A_1	$d_{xy}^2 d_{xz}^2 d_{yz}^2$	–	–	–
T_{1g}	A_2	$d_{x^2-y^2}^1 d_{xy}^1 d_{xz}^2 d_{yz}^2$	Δ	–	–C
	E_a	$d_{z^2}^1 d_{xz}^1 d_{xy}^2 d_{yz}^2$	Δ	$+\delta\sigma - \delta\pi$	+4B – C
		$d_{z^2}^1 d_{yz}^1 d_{xy}^2 d_{xz}^2$	Δ	$+\delta\sigma - \delta\pi$	+4B – C
T_{2g}	B_2	$d_{z^2}^1 d_{xy}^1 d_{xz}^2 d_{yz}^2$	Δ	$+\delta\sigma$	+16B – C
	E_b	$d_{x^2-y^2}^1 d_{xz}^1 d_{xy}^2 d_{yz}^2$	Δ	$-\delta\pi$	+12B – C
		$d_{x^2-y^2}^1 d_{yz}^1 d_{xy}^2 d_{xz}^2$	Δ	$-\delta\pi$	+12B – C

to be proportional to the stabilization of the ligand lone pair upon complexation. $\delta\sigma$ is assumed to be of the same order of magnitude as $\delta\pi$, which seems quite realistic considering the changes that occur in the absorption spectrum of a hexacarbonyl upon monosubstitution. So the stabilization of the piperidine lone pair (15kK) is arbitrarily estimated to correspond to a $\delta\sigma$ of 2.4 kK. The consequences of this estimation are discussed below.

3. Mutual electron repulsion parameters [8, 9] can be determined from absorption spectra. For the hexacarbonyls B varies from 0.3 to 0.5 kK and C is 1.1–1.7 kK [1]. For monosubstituted W-species the magnitude of C is estimated from the difference in energy between $^1E \leftarrow {}^1A_1$ and $^3E \leftarrow {}^1A_1$ LF transitions which is about 1.0–1.3 kK. Using then the assumption that C = 4B [9] a value for B of about 0.3 kK is obtained. This points to the view that repulsion parameters do not change appreciably upon substitution, despite the increased electron density on the metal.

Now we can distinguish two limiting cases in a strong field approximation, one belonging to the hexacarbonyls with octahedral symmetry for which mutual electron repulsion is taken into account. This case is shown at the right in Figure 1. The eigenfunc-

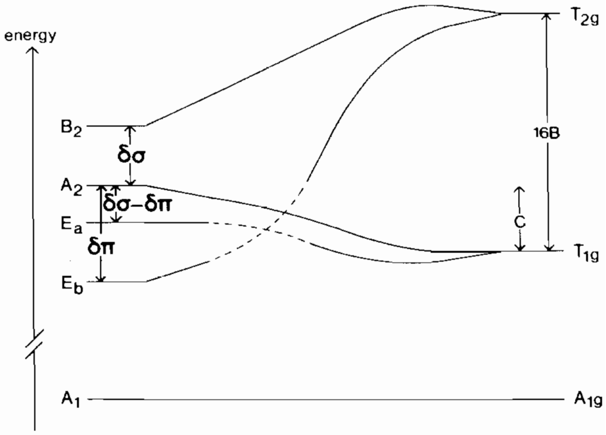

Figure 1. Correlation diagram of $M(CO)_5L$. Deviations from octahedral field ($\delta\sigma$, $\delta\pi$) increase from right to left whereas mutual electron repulsion (B, C) increases from left to right.

TABLE II. A Comparison of the Energy^a of the LF Transitions Calculated According to the Two Limiting Cases as shown in Table Ia–Ib^b and Observed in the Absorption Spectrum of W(CO)$_5$ Piperidine.

	$^1E_a \leftarrow {}^1A_1$	$^1A_2 \leftarrow {}^1A_1$	$^1E_b \leftarrow {}^1A_1$	$^1B_2 \leftarrow {}^1A_1$
Experimental [11]	24.8	29.4	34.2	–
Calculated as in Table Ia	30.6	30.9	34.6	38.5
Calculated as in Table Ib	32.5	30.9	32.7	38.5

^{a}In kK. ^{b}Parameters: Δ = 32.2 kK, 4B = C = 1.3 kK [1], $\delta\pi$ = 2.1 kK [7] and $\delta\sigma$ = 2.4 kK.

TABLE III. A Comparison of the Energy^a of the $^1E_a \leftarrow {}^1A_1$ Transition Calculated According to the Two Limiting Cases as Shown in Table Ia–Ib and Observed in the Absorption Spectrum of Cr(CO)$_5$L.

Ligand L		$\delta\sigma^b$	$\delta\pi^b$	$^1E_a \leftarrow {}^1A_1$ as In Table Ia	$^1E_a \leftarrow {}^1A_1$ as In Table Ib	$^1E_a \leftarrow {}^1A_1$ from Absorption Spectra
$C_5H_{11}N$	[7]	2.4	2.4	29.9	32.2	23.8
C_5H_5N	[7]	2.3	2.6	29.6	31.9	25.7
$S(C_2H_5)_2$	[12, 13]	1.0	1.8	29.5	31.4	25.4
PCl_3	[14, 15]	0.7	0	31.0	32.9	27.6
$P(C_6H_{11})_3$	[16]	2.0	1.4	30.6	32.8	29.4

^{a}In kK. ^{b}Other parameters: Δ = 32.2 kK and 4B = C = 1.7 kK for all complexes.

tions are linear combinations of atomic d-orbitals [10] and the energies are expressed in terms of Δ, B and C. The second case, shown at the left in Figure 1, represents the hypothetical case of a M(CO)$_5$L with symmetry C_{4v} for which mutual electron repulsion is neglected with respect to ligand field effects. In this case the correct eigenfunctions are the usual atomic d-orbitals and the corresponding eigenvalues are expressed in Δ, $\delta\sigma$ and $\delta\pi$.

Going from right to left in Figure 1 small deviations from octahedral symmetry can be treated as perturbations (Table 1a) where $\langle d_{z^2}|H'|d_{z^2}\rangle = \delta\sigma$ and $\langle d_{xz}|H'|d_{xz}\rangle = \langle d_{yz}|H'|d_{yz}\rangle = \delta\pi$. Going from left to right small mutual electron repulsions can be treated as a perturbation (Table Ib). It was not possible, however, to calculate the situation of a M(CO)$_5$L complex which is in between these two limiting cases by taking into account simultaneously a deviation from octahedral symmetry and mutual electron repulsion. The calculated perturbations can, however, be used to give a qualitative picture (shown in Figure 1) of the correlations which exist between the two limiting cases.

The energy diagram will be influenced by configuration interaction between both states with symmetry E, which is not taken into account. These states are not allowed to cross.

From the magnitude of the parameters for the deviation from octahedral field and the mutual electron repulsion it is clear that reality is in between the two extremes of Figure 1. Because no proper description can be made, taking both interactions in an equivalent way into account, an assignment has to be based on the calculation of both extremes as presented in Table Ia and b. The magnitude of the parameters was selected as described above.

In Table II the results are compared with the energies of the LF transitions from the absorption spectrum of W(CO)$_5$piperidine, which may be regarded as a typical example of an amine metal pentacarbonyl [11]. The $^1A_2 \leftarrow {}^1A_1$ transition is symmetry forbidden and possesses indeed a smaller intensity in the absorption spectrum. The $^1B_2 \leftarrow {}^1A_1$ is obscured by the strong metal-to-carbonyl charge transfer transition. Whatever the magnitude of $\delta\sigma$ may be, the energy of the first LF transition is much lower than the calculated energy. In agreement with the proximity of two excited E-states configuration interaction may lead to considerable stabilization of the $^1E_a \leftarrow {}^1A_1$ transition.

Upon replacement of an amine by another donor ligand the first LF transition in the absorption spectrum may shift considerably. For a number of Cr(CO)$_5$L complexes the $^1E_a \leftarrow {}^1A_1$ transition has been calculated and compared with the absorption spectrum (Table III). The parameters B and C are assumed to remain essentially unaltered upon replacement. This is confirmed by the constancy of the energy difference between the $^3E_a \leftarrow {}^1A_1$ and $^1E_a \leftarrow {}^1A_1$ transition in the absorption spectrum of the analogous W(CO)$_5$L complexes. $\delta\pi$ is directly determined from photoelectron spectroscopic measurements as described above.

The estimated value of $\delta\sigma$ will determine the energy of the different excited states to a large extent. Since configuration interaction distorts the proposed diagram this has no essential meaning. The changes of $\delta\sigma$ may influence the resulting energy trend of the LF transitions. The shift to higher energy of the lowest LF transition going from a N-donor to a P-donor is reproduced, when the different π-interactions of the ligands are taken into account and the different σ-interactions are considered to be of minor importance.

In general it may be stated that the lowest LF transition will shift to higher energy when σ-donor and π-acceptor properties increase and mutual electron repulsion reduces. The lowest excited state is calculated to be the E_a with predominant σ_z^*-character (see Table I). Contrary to previous publications [4–6], however, a mixing of σ_z^* and σ_{xy}^* in this state due to mutual electron repulsion of the d-electrons is present. The results also show that an additional configuration interaction must be involved.

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