M.C.D. Spectra of $Cr(CO)_5L$ (L = Piperidine, Trimethylamine, Pyridine, and Pyrazine). Evidence for the Nature of the Lowest Excited Ligand Field State and for Steric and Electronic Influences of L on the Symmetry of the Complexes

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Summary With the use of m.c.d. spectra the nature of the lowest ligand field (LF) excited state of $Cr(CO)_5L$ complexes (L = N-donor ligand) is characterized for the first time, which is of importance for understanding the photochemical behaviour of these complexes.

RECENT investigations of the photochemistry, both in rare gas matrices at 10 K and in solutions at 298 K, of $Cr(CO)_5L$ complexes (L = N-donor ligand) have shown the release of CO at high energy excitation and loss of L after irradiation within the lowest LF band.[1] This behaviour has been explained in terms of a one-electron *d* orbital diagram with two unoccupied LF orbitals, $d_{x^2-y^2}$ and d_{z^2}, of which d_{z^2} was assumed to have the lower energy. The photochemical results for these particular complexes excluded a fast non radiative decay between states in which these orbitals were involved.

In order to test that d_{z^2} is lower in energy than $d_{x^2-y^2}$ which is in contrast to the order assumed by others,[2] we investigated the m.c.d. spectra of a series of $Cr(CO)_5L$ complexes in n-hexane at room temperature and here report the results for L = piperidine, NMe_3, pyridine, and pyrazine. According to vibrational results for the $Cr(CO)_5L$ complexes, the $Cr(CO)_5$ group possesses local C_{4v} symmetry. If it is assumed that this symmetry applies, then the metallic 3*d* orbitals will be split, going from O_h to C_{4v} symmetry, into the unoccupied a_1 (d_{z^2}) and b_1 ($d_{x^2-y^2}$) orbitals and the occupied e (d_{xz},d_{yz}), and b_2 (d_{xy}) levels, the e level being of higher energy than the b_2 level[3] (Figure 1).

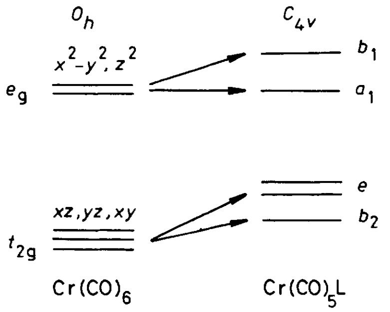

FIGURE 1. *d*-Orbital energy diagram for $Cr(CO)_6$ and $Cr(CO)_5L$ (L=N-donor) complexes.

For the lowest LF transition two different electronic transitions are possible, $^1E_a(b_2^2e^3a_1) \leftarrow {}^1A_1(b_2^2e^4)$ or $^1E_b(b_2^2e^3b_1) \leftarrow {}^1A_1(b_2^2e^4)$, depending on the relative positions of the a_1 and b_1 orbitals. Both transitions will give rise to an m.c.d. *A*-term.[4] The sign of the *A*-term is determined by symmetry and thus may be used to distinguish the two possibilities. If complex basis orbitals are considered, the e level consists of an $e(+1)$ and $e(-1)$ component. If the orbitals are pure metallic 3*d* orbitals they bear an orbital angular momentum of $+1\hbar$ and $-\hbar$, respectively. With the help of the tabulated *V* coefficients for point group C_{4v}[5] the relationship between the molecular excited state *E* and the one-electron excitations is easily shown (Table). Moreover the polarization of the transitions can also be inferred from the *V* coefficients. The polarization direction $\frac{1}{\sqrt{2}}(\vec{i} + i\vec{j})$ corresponds to left handed circularly (LHC) polarized light and a photon of angular momentum $+\hbar$ is absorbed; the direction $\frac{1}{\sqrt{2}}(\vec{i} - i\vec{j})$ corresponds to right-handed circularly (RHC) polarized light and absorption of a photon of $-\hbar$ angular momentum is observed.

Table

One-electron transition	Excited state component	Polarization	A/D[a]
$e(+1)\rightarrow a_1$	$E(+1)$	RHC	$+0{\cdot}5\beta$
$e(-1)\rightarrow a_1$	$E(-1)$	LHC	
$e(+1)\rightarrow b_1$	$E(-1)$	LHC	$-0{\cdot}5\beta$
$e(-1)\rightarrow b_1$	$E(+1)$	RHC	

[a] A/D for $3d(e)$ orbitals, $\beta = 1\ \mu_B$.

An electron in either of the orbitals a_1 or b_1 has no orbital angular momentum so excitation from the $e(+1)$ level leaves a hole of positive magnetic moment along the z-axis and excitation from the $e(-1)$ level a negative magnetic moment. In the magnetic field of the m.c.d. experiment the component with positive magnetic moment is lower in energy than the one with negative magnetic moment, so in the case of the $e\rightarrow a_1$ transition we obtain the RHC polarized transition at lower energy, resulting in a positive A-term, whereas in the case of the $e\rightarrow b_1$ transition the opposite is true giving a negative A-term. The A-term is[4] related to the magnetic moment of the excited state by the dipole strength D of the transition; $A/D = \mu/2$. Thus in the case where the e orbitals are pure metallic $3d$ orbitals we readily find $A/D = +0{\cdot}5\beta$ for ${}^1E_a(b_2^2e^3a_1) \leftarrow {}^1A_1(b_2^2e^4)$ and $A/D = -0{\cdot}5\beta$ for ${}^1E_b(b_2^2e^3b_1) \leftarrow {}^1A_1(b_2^2e^4)$. Now, in the m.c.d. spectra of all compounds a positive A-term is observed for the lowest LF transition, thus supporting our assignment ${}^1E_a(b_2^2e^3a_1) \leftarrow {}^1A_1(b_2^2e^4)$ for this transition. All spectra show a positive B-term at 280—310 nm (for L = pyridine at 285 nm), the nature of which is not yet clear. A negative A-term corresponding to the ${}^1E_b(b_2^2e^3b_1) \leftarrow {}^1A_1(b_2^2e^4)$ LF transition is not observed at 500—200 nm although the shape of the m.c.d. spectra between 300 and 350 nm suggests another m.c.d. term which might correspond to this transition.

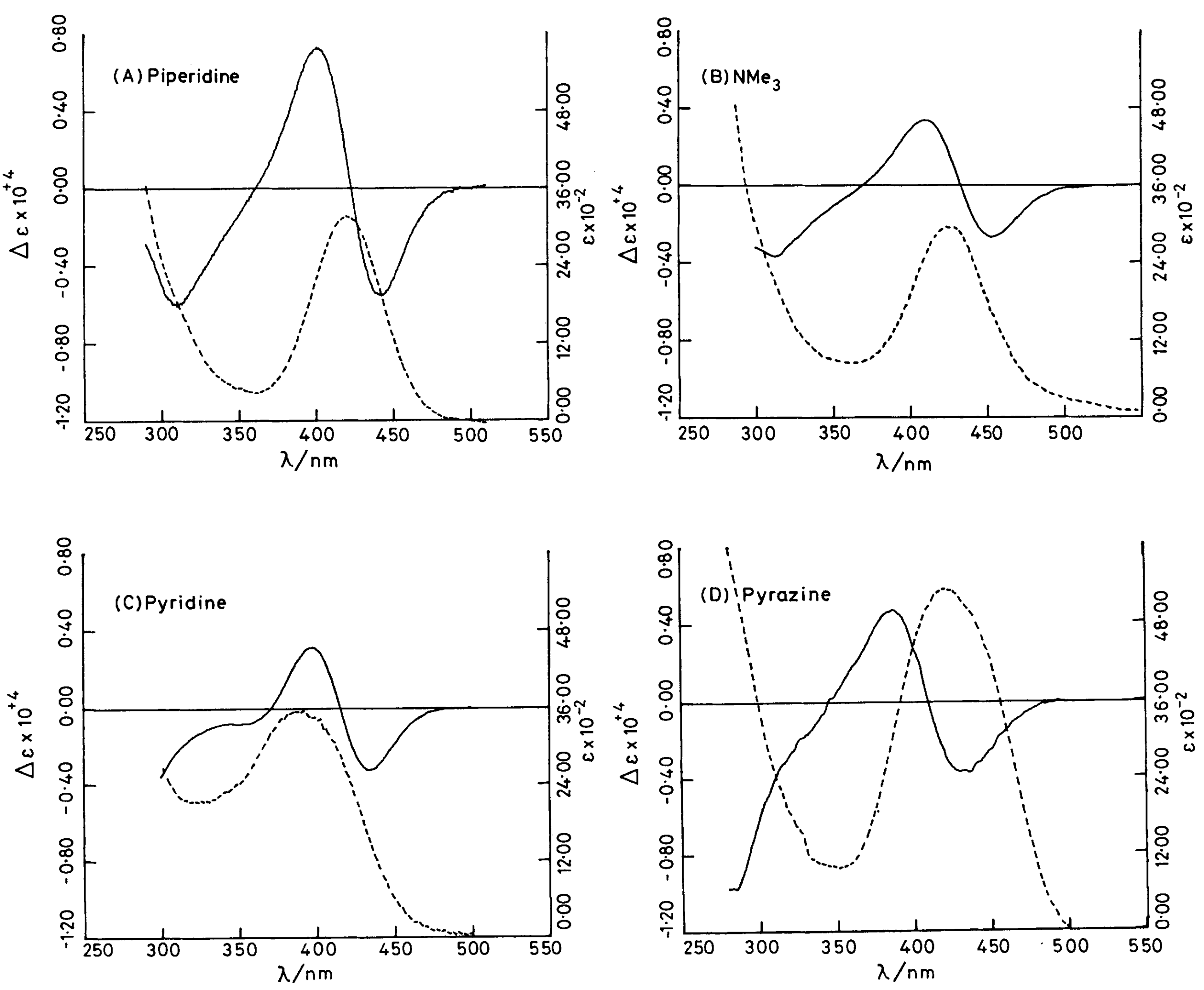

Figure 2. M.c.d. (——) and absorption (- - - - - -) spectra of Cr(CO)$_5$L complexes between 300 and 500 nm in n-hexane at room temperature. (A) L = piperidine, (B) L = NMe$_3$, (C) L = pyridine, (D) L = pyrazine.

By the method of moments a magnetic moment $\mu = 0{\cdot}6\beta$ is deduced from the A-term of $Cr(CO)_5$·piperidine, which is slightly larger than the value $\mu = 0{\cdot}5\beta$ deduced for pure metallic 3*d* orbitals. This higher value is caused by the delocalization of the *d* electrons over the carbonyl groups. In contrast, for L = NMe_3, pyridine, and pyrazine a value μ *ca.* $0{\cdot}3\beta$ is deduced. This lowering of μ with respect to the piperidine complex is most likely due to the lowering of local C_{4v} symmetry, as a result of steric (NMe_3) and electronic (pyridine and pyrazine) interactions. For NMe_3 such steric interaction with coligands is well known[6] and for pyridine and pyrazine π-backbonding from the metal to the ligand will certainly restrict the free rotation of L around the metal–nitrogen bond and reduce the C_{4v} symmetry.

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