

## INTENSITY OF METAL TO LIGAND AND LIGAND TO METAL ELECTRON TRANSFER TRANSITIONS

M. KRÁL

*Department of Chemical Analysis, Institute of Chemical Technology, Prague 6*

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It is shown, how the intensity of electron transfer transitions depends on the symmetry of the cluster formed by  $d$ -electron metal ion and by atoms participating in  $\pi$ -conjugation. Laporte's rule is used as a criterion for transition permission at complexes with centrosymmetrical clusters. The extinction coefficients of Laporte forbidden transitions are of the order  $10^2$ . In case of particles with non-centrosymmetrical clusters the values of extinction coefficients of electron transfer transitions are of the order  $10^3 - 10^4$ .

From the studies of complex compounds it is known, that at many complexes of transition metal ions with organic ligands, in which the donor atom is a part of  $\pi$ -electron system, intensive broad bands appear, that are not present in the spectra of complex-forming components<sup>1,2</sup>. These bands were identified as bands connected with transition of  $d$ -electron from the central field of the metal ion to the  $\pi$ -antibonding ligand orbitals, or with transition of electron from the ligand orbital to the free  $d$ -electron orbital of the metal ion. The intensity of these transitions, as far as the transitions between states of the same spin multiplicity is concerned, is fairly high. The values of the oscillator strength of these transitions may get the order  $10^{-1}$  to  $10^{-3}$  and the values of the molar extinction coefficient have the order from  $10^2$  to  $10^4$ . In this paper we want to show how this intensity depends on the symmetry of the system in which electron transfer transition occur.

From the theoretical study based on the time-dependent perturbation theory, the oscillator strength of an electric dipole transition, for the particle going from the state  $A$  to the state  $B$ , is given by the expression<sup>3-5</sup>

$$f_{A \rightarrow B} = \frac{\hbar}{3\pi m c \sigma_{A \rightarrow B}} |\langle A | \nabla | B \rangle|^2, \quad (1)$$

where  $|A\rangle$  and  $|B\rangle$  are the wave functions of the particle in the state  $A$  or  $B$ , respectively,  $\hbar$  is Dirac's constant,  $m$  is the electronic mass,  $c$  is the speed of light (*in vacuo*) and  $\sigma_{A \rightarrow B}$  is the transition energy in wave numbers. Using group theory it was found<sup>6</sup>, that the expression (1) is not equal to zero if

$$\Gamma_A \otimes \Gamma \cap \Gamma_B \neq 0, \quad (2)$$

where  $\Gamma_A$  and  $\Gamma_B$  are the irreducible representations of the symmetry group  $G$ ,

according to which the wave functions  $|A\rangle$  and  $|B\rangle$  are transformed;  $\Gamma$  is a representation of the same group, according to which the components of the operator  $V$  are transformed. The permission of a transition depends, thus, on the system symmetry. At studied systems an electron goes from the central field of the metal ion to the  $\pi$ -electron ligand system or opposite, and therefore it is necessary to take into account the symmetry of the cluster formed by  $d$ -electron metal ion and by atoms participating in  $\pi$ -conjugation. For simplification we shall call this atoms group  $d$ - $\pi$  chromophore. We can, now, divide the complex compounds in two groups regarding if the  $d$ - $\pi$  chromophore is centrosymmetrical or if it misses the centre of symmetry. At complexes with centrosymmetrical  $d$ - $\pi$  chromophore (Table I) Laporte's rule will be used as a criterion for transition permission, according to which only transitions between states with different parity are permitted. On describing these states we utilize the idea of coupled chromophores<sup>7</sup>. Basing on the idea of this model, the ground state of  $t_{2g}$ - $\pi$  cluster of the symmetry  $C_{2h}$ , e.g. at complexes given in Table I, is the state  $B_g$ . The symmetry of an electron transfer state that arises e.g. by promotion of  $t_{2g}$ -electron from the central field of the metal ion to the antibonding ligand orbitals is  $B_g$ , too. As both states have the same parity, the electron transfer transition should not come into effect in molecule. As it may be seen from Table I, absorption of light at those compounds, however, is different from zero, and the extinction coefficients have values of the order  $10^2$ . Permission of this transition may be explained similarly to permission of  $d$ - $d$  transition<sup>8</sup>, i.e. by lowering the symmetry of  $d$ - $\pi$  chromophore due to vibration motion of ligand.

In case of complex compounds with non-centrosymmetrical  $d$ - $\pi$  chromophore group, the parity of the state is not defined and if an electron transfer bands appear in the spectra of these complexes, they are characterized by fairly high intensity. The examples given in Table II show, that the values of extinction coefficients of these transitions are of the order  $10^3 - 10^4$ .

The change of intensity of electron transfer transition caused by the transition of centrosymmetrical  $d$ - $\pi$  chromophore into non-centrosymmetrical one may be demonstrated on the complex Fe(II) with quinaldic acid. In the molecule of the complex  $FeQ_2 \cdot 2H_2O$  the centrosymmetrical  $d$ - $\pi$  chromophore is present, which appears in the spectrum by two metal to ligand electron transfer bands with wave numbers  $19.6 \cdot 10^3$  and  $22.7 \cdot 10^3 \text{ cm}^{-1}$   $\epsilon = 500 \text{ l cm}^{-1} \text{ mol}^{-1}$  (ref.<sup>9-11</sup>). Due to the reaction with  $CN^-$  ions this complex goes into the  $FeQ(CN)_4^{3-}$  (ref.<sup>10,11</sup>) in which the  $d$ - $\pi$  chromophore is non-centrosymmetrical. This change appears in the spectrum by increasing the value of molar extinction coefficient of electron transfer transition. In this case its value is equal to  $3100 \text{ l cm}^{-1} \text{ mol}^{-1}$  (ref.<sup>12</sup>). Similar difference can be regarded between the complexes  $Fe(\text{oxin})_3^-$  and  $Fe(\text{CH}_3\text{-oxin})_2$  (Tables I, II).

TABLE I

Some Complexes with Centrosymmetrical  $d-\pi$  Chromophore GroupHQ = quinaldic acid, CH<sub>3</sub>-Hoxin = 2-methyl-8-hydroxyquinoline and HpicO = 2-picolinic acid N-oxide.

Complex	Symmetry of $d-\pi$ chromophore	$10^3 \sigma$ $\text{cm}^{-1}$	$\epsilon$ $\text{cm}^{-1} \text{mol}^{-1}$	Ref.
FeQ <sub>2</sub> .2 H <sub>2</sub> O	$C_{2h}$	19.6	$5.00 \cdot 10^2$	9
		22.7	$5.00 \cdot 10^2$	
Fe(CH <sub>3</sub> -oxin) <sub>2</sub>	$C_{2h}$	19.2	$4.00 \cdot 10^2$	13
Mn(picO) <sub>2</sub> .2 H <sub>2</sub> O	$C_{2h}$	24.7	$2.80 \cdot 10^2$	14
Fe(picO) <sub>2</sub> .2 H <sub>2</sub> O	$C_{2h}$	21.05	$2.70 \cdot 10^2$	14
Co(picO) <sub>2</sub> .2 H <sub>2</sub> O	$C_{2h}$	23.8	$1.26 \cdot 10^2$	14

TABLE II

Some Complexes with Non-centrosymmetrical  $d-\pi$  Chromophore Group

Bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline, Hoxin = 8-hydroxyquinoline, Hpic = picolinic acid, bpz = bipyrazinyl, Hacac = acetylacetone.

Complex	Symmetry of $d-\pi$ chromophore	$10^3 \sigma$ $\text{cm}^{-1}$	$\epsilon$ $\text{cm}^{-1} \text{mol}^{-1}$	Ref.
Fe(bipy) <sub>3</sub> <sup>2+</sup>	$D_3$	19.0	$1.00 \cdot 10^4$	15, 16
		20.2	$1.00 \cdot 10^4$	
Fe(phen) <sub>3</sub> <sup>2+</sup>	$D_3$	19.6	$1.00 \cdot 10^4$	15, 16
		21.0	$9.50 \cdot 10^3$	
		22.8	$7.30 \cdot 10^3$	
Fe(oxin) <sub>3</sub> <sup>-</sup>	$C_1$ or $C_3$	17.2	$5.00 \cdot 10^3$	13, 17
		21.7	$6.30 \cdot 10^3$	
Fe(oxin) <sub>3</sub>	$C_1$ or $C_3$	17.2	$4.00 \cdot 10^3$	17, 18
		21.7	$5.00 \cdot 10^3$	
Fe(pic) <sub>3</sub> <sup>-</sup>	$C_1$ or $C_3$	22.4	$1.00 \cdot 10^3$	9
		27.7	$1.00 \cdot 10^3$	
Fe(bpz) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	$D_3$	19.67	$4.27 \cdot 10^3$	19
		21.0	$3.30 \cdot 10^3$	
V(acac) <sub>3</sub> <sup>-</sup>	$D_3$	14.3	$2.70 \cdot 10^3$	20
Ti(acac) <sub>3</sub>	$D_3$	16.9	$1.52 \cdot 10^3$	21, 22
Mo(acac) <sub>3</sub>	$D_3$	27.0	$5.00 \cdot 10^3$	23

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