

IDENTIFICATION OF ELECTRON TRANSFER BANDS IN COMPLEXES $\text{Fe}(\text{OXIN})_3^-$ AND $\text{Fe}(\text{OXIN})_3$

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In the paper the electron transfer bands of Fe(II) and Fe(III) complexes with 8-hydroxyquinoline are studied. The identification of the electron transfer transitions were carried out on the basis of coupled chromophore model. The agreement between measured and calculated values of $\pi \rightarrow \pi^*$ transitions is a criterion of correct attachment of electron transfer transitions.

Our previous paper dealt with the identification of electron transfer transitions observed in the spectra of the complexes Fe(II) with picolinic acid and quinaldic acid¹. In this paper we continue in studying the electron transfer transitions at complexes Fe(II) and Fe(III) with 8-hydroxyquinoline. The spectra of these complexes were studied beforehand^{2,3} and as electron transfer transitions the broad intensive bands present in the visible part of the spectrum were assigned. In the present paper we are going to focus at their identification on the basis of coupled chromophore model.

EXPERIMENTAL

The solutions of $\text{Fe}(\text{oxin})_3^-$ and $\text{Fe}(\text{oxin})_3$ were prepared in 50% dioxane after Tomkinson and Williams². Excess of ligand was used for being ensured, that in the solution there are the complexes with maximum number of ligands 3. All compounds were products of the firm Merck or Lachema, mostly of analytical grade. Solvents were before use purified using methods recommended in the literature⁴. Measurements were carried out on a spectrophotometer SF-4 (USSR) at the temperature $20 \pm 1^\circ\text{C}$. For electron transfer bands studies, cells with thickness 1 cm were used and $d-d$ transitions were measured in 10 cm cells.

RESULTS AND DISCUSSION

The electronic spectra of $\text{Fe}(\text{oxin})_3^-$ and $\text{Fe}(\text{oxin})_3$ were measured within the range $9.0-30.0 \cdot 10^3 \text{ cm}^{-1}$ and the results are given in Table I. At both complexes in the spectra two intensive electron transfer transitions were observed with the wave numbers $17.2 \cdot 10^3$ and $21.7 \cdot 10^3 \text{ cm}^{-1}$. At the complex $\text{Fe}(\text{oxin})_3^-$ one band ($\sigma_{\text{max}} 10.25 \cdot 10^3 \text{ cm}^{-1}$) with low intensity was found in the long wave region of the spectrum. This band was identified as $d-d$ band and as the microsymmetry of the

TABLE I
Spectra of $\text{Fe}(\text{oxin})_3^-$ and $\text{Fe}(\text{oxin})_3$ in 50% Dioxane

Complex	$\sigma, 10^3 \text{ cm}^{-1}$	$\epsilon, \text{l cm}^{-1} \text{ mol}^{-1}$	Note
$\text{Fe}(\text{oxin})_3^-$	10.25	92	$c_{\text{Fe}} = 2 \cdot 10^{-4} \text{ M}$ $c_{\text{oxin}} = 4.16 \cdot 10^{-3} \text{ M}$
	17.2	5 000	
	21.7	6 300	
$\text{Fe}(\text{oxin})_3$	17.2	4 000	$c_{\text{Fe}} = 1.6 \cdot 10^{-4} \text{ M}$ $c_{\text{oxin}} = 4.16 \cdot 10^{-3} \text{ M}$
	21.7	5 000	

system is O_h , it was attached to ${}^5T_{2g} \rightarrow {}^5E_g$ transition. The wave number of this transition is in agreement with values obtained in the number of high-spin complexes $\text{Fe}(\text{II})$ with octahedral microsymmetry⁵. The transitions with the wave numbers higher than $25 \cdot 10^3 \text{ cm}^{-1}$ are identified as the transitions localized on ligands.

The identification of electron transfer transitions will be carried out on the basis of the coupled chromophore model⁶. Similarly as at $\text{Fe}(\text{II})$ complex with picolinic acid, in these complexes, too, come into consideration the transitions $t_{2g} \rightarrow \pi^*$ and $\pi \rightarrow e_g$ only. The symmetry of the complex particle is in both complexes at facial arrangement of ligands C_3 and at meridional arrangement C_1 . The ground state for these symmetrical arrangements is the state A with spin multiplicity 5 at the complex $\text{Fe}(\text{oxin})_3^-$ and 6 at the complex $\text{Fe}(\text{oxin})_3$. At particles with the symmetry C_3 the excited states are the states A and E , at particles with the symmetry C_1 the excited states are the states A . As only spin-allowed transitions are considered, the excited states have the same spin multiplicity as the ground states.

First, we shall pay attention to the complex particle $\text{Fe}(\text{oxin})_3^-$. In this particle iron has the oxidation number +2, *i.e.* an electron is set apart very easily and as the ligand is a π -electron system, this electron may go into its π -antibonding orbital (*i.e.* the transition $t_{2g} \rightarrow \pi^*$). From viewpoint of symmetry this transition is between the states 5A and 5E and the band with the wave number $17.2 \cdot 10^3 \text{ cm}^{-1}$ is attached to it. To the second symmetrically allowed transition (*i.e.* the transition $\pi \rightarrow e_g$) the band with the wave number $21.7 \cdot 10^3 \text{ cm}^{-1}$ is attached and this is the transition ${}^5A \rightarrow {}^5A$. As long as the symmetry of the particle is C_1 , both transitions are between the states ${}^5A \rightarrow {}^5A$. The wave number of $\pi \rightarrow \pi^*$ transition calculated from the wave numbers of electron transfer transitions is $28.65 \cdot 10^3 \text{ cm}^{-1}$ and is in a good agreement with the experimentally gained value, which is for the oxinate ion $28.2 \cdot 10^3 \text{ cm}^{-1}$ (ref.³).

At the complex particle $\text{Fe}(\text{oxin})_3$ the maxima of electron transfer transitions are at the same wave numbers as at the complex $\text{Fe}(\text{oxin})_3^-$. As in this case the accep-

tance of electron by metal is easier than giving a d -electron to a ligand, at the particle with the symmetry C_3 the band with lower wave number is attached to the transition ${}^6A \rightarrow {}^6A$ (i.e. the transition $\pi \rightarrow e_g$) and the band with the wave number $21.7 \cdot 10^3 \text{ cm}^{-1}$ is identified as the transition ${}^6A \rightarrow {}^6A$ (the transition $t_{2g} \rightarrow \pi^*$). If the symmetry of the particle was C_1 , both transitions should be between the states ${}^6A \rightarrow {}^6A$. $\pi \rightarrow \pi^*$ transition has at this complex the wave number $27.0 \cdot 10^3 \text{ cm}^{-1}$. If the parameter Δ is calculated from obtained data, its value is $11.9 \cdot 10^3 \text{ cm}^{-1}$, which is about $2 \cdot 10^3 \text{ cm}^{-1}$ lower than the value observed at the aquocomplex. This is in agreement with experimental results, which showed, that the Δ value is decreased by the effect of ligand to metal transition⁷.

REFERENCES

1. Král M.: This Journal 37, 46 (1972).
2. Tomkinson J. C., Williams R. J. P.: J. Chem. Soc. 1958, 1153.
3. Perkampus H. H., Kortüm K.: Z. Anal. Chem. 190, 111 (1962).
4. Pestemer M.: Angew. Chem. 63, 118 (1951).
5. Lever A. B. P.: *Inorganic Electronic Spectroscopy*, p. 300. Elsevier, Amsterdam 1968.
6. Longuet-Higgins H. C., Murrell J. N.: Proc. Phys. Soc. A 68, 601 (1955).
7. Schläfer H. L., Gliemann G.: *Basic Principles of Ligand Field Theory*, p. 82. Wiley, New York 1969.

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