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The Rotatory Strengths of the Electron-Transfer Transitions of the Tris-(1,10-phenanthroline)ruthenium(II) Ion

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In the present paper the rotatory strengths of the electron-transfer transitions observed in the spectrum of the complex ion (−)-Ru(phen)$_3^{+2}$ (phen = 1,10-phenanthroline) have been calculated theoretically. In the development of the calculation the coupled chromophore model has been used.

Key words: Rotatory strengths of inorganic complexes – Tris-(1,10-phenanthroline)ruthenium(II) ion – Electron-transfer transitions in inorganic chelates

Comparing the CD spectra of (−)-Ru(phen)$_3^{+2}$ with the CD spectra of (−)-Fe(phen)$_3^{+2}$ in the region of electron-transfer transitions [1, 2] it can be seen that the course of the CD curve of Ru(II) complex is opposite to the CD curve of the Fe(II) complex. Hanazaki and Nagakura [3] suppose, in a purely "*ad hoc*" way, that this difference is due to the higher value of the overlap integral between ruthenium and nitrogen. Mason [1, 2] connects, on the other hand, the negative CD band of the (−)-Fe(phen)$_3^{+2}$ with the *d–d* transition. However, in the first case the greater value of the molecular integral cannot change the signs of optical rotatory strengths and in the second case the pertinent *d–d* transition lies at a higher wave number [4, 5] connected with the lower value of the rotatory strength. In this comment we shall try to solve this problem using in the calculation of optical rotatory strengths the same model as in the case of (−)-Fe(phen)$_3^{+2}$ [6].

First of all a spectral identification must be performed. If in the coupled chromophore model we suppose the dipole–dipole interaction between chromophores to be the dominant factor, then the $^1A_1 \rightarrow {}^1A_2$ transition is placed at higher energy and the $^1A_1 \rightarrow {}^1E$ transition placed at lower energy. This level order is observed in the region of $\pi \rightarrow \pi^*$ transitions of all tris(bisbidentate)-complexes

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where the ligands are conjugated π-electron molecules (e.g. 1,10-phenanthroline,2,2'-bipyridyl etc.). In the CD spectra of these complexes having the ligands arranged into the left-handed three-bladed propeller (i.e. $(-)$-M(L)$_3^{+2}$, the negative short wave component is assigned to the $^1A_1 \rightarrow {}^1A_2$ transition, while its positive long wave component is assigned to the transition $^1A_1 \rightarrow {}^1E$ [7]. The same level order is preserved in the region of metal-to-ligand electron-transfer transitions of the complex ions Fe(bipy)$_3^{+2}$ and Fe(phen)$_3^{+2}$. This ordering is, however, not valid in cases where the dipole–dipole interaction is comparable with another interaction. Thus, the reversed level order of electron-transfer transitions is found in complexes of Ru^{+2} and Os^{+2}, where the spin-orbit coupling mechanism is operative [8]. This is in agreement with the results of Crosby and coworkers [9, 10] who studied the luminescence properties of these compounds and found the $^1A_2$ state being lower than the state ^1E. For this reason the positive $^1A_2$ component of the CD curve in the region of metal-to-ligand electron-transfer transitions in the complex ion $(-)$-Ru(phen)$_3^{+2}$ was assigned to the long wavelength transition while the negative ^1E component was assigned to the short wavelength transition. The same assignment holds for the Os^{+2} complexes. In the CD and absorption spectra of these complexes there are therefore the additional bands in the visible part belonging to the $^1A_1 \rightarrow {}^3A_2$ transition.

The optical rotatory strengths were calculated from the formula

$$R_{A\to B} = -\frac{e^2\hbar^2}{4\pi m^2 c^2 \sigma_{A\to B}} \langle A|\vec{V}|B\rangle\langle B|\vec{r}\times\vec{V}|A\rangle$$

where the symbols e, $\hbar$, m and c have their usual meanings and where $\sigma_{A\to B}$ is the energy difference between states A and B measured in cm^{-1}. State A is taken as the ground state and state B as a single-electron excited state.

For the calculation of the matrix elements of the electric dipole and magnetic dipole operators the same procedure was used as in the case of the iron(II)complex [6]. The necessary bond distances were taken from the literature [11] as were the atomic functions for carbon, nitrogen and ruthenium [12, 13]. In addition the SCF molecular orbitals given for 1,10-phenanthroline by Ito *et al.* were used [14].

The rotatory strengths of the transitions $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$ were then calculated and the results are compared with the corresponding experimental values for these transitions in Table 1. The experimental figures were calculated from the data published in the literature [1, 15]. The theoretical and experimental values of the oscillator strengths of these transitions are also given in Table 1.

Table 1. Calculated and experimental results

Transition	R in cgs	R^{exp} in cgs	Oscillator strengths f	f^{exp}
$^1A_1 \rightarrow {}^1A_2$	$+2{\cdot}55.10^{-40}$	$+3{\cdot}39.10^{-39}$	$1{\cdot}6.10^{-2}$	$1{\cdot}8.10^{-1}$
$^1A_1 \rightarrow {}^1E$	$-4{\cdot}28.10^{-40}$	$-2{\cdot}42.10^{-39}$	$1{\cdot}6.10^{-2}$	$1{\cdot}3.10^{-1}$

Comparing the theoretical values of the rotatory strengths with the corresponding experimental data we see that R (theoretical) is lower than R (experimental) by a factor of about ten. To explain this we suppose that the electron-transfer state is not a pure state, but is mixed with mono-excited electron-transfer states arising from the promotion of a d-electron into the first antibonding orbital of the ligands. Such mixings are known [1, 16] to lead to the higher values of electric dipole moments and therefore to higher values of optical rotatory strengths. This assumption is now being tested.

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