Theoret. Chim. Acta (Berl.) 55, 333–336 (1980)

THEORETICA CHIMICA ACTA

The Ligand-Ligand and Spin-Orbit Interactions in $Fe(phen)_3^{+2}$ and $Ru(phen)_3^{+2}$ Ions

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To explain the differences in the spectral properties of the complex ions (−)-$Fe(phen)_3^{+2}$ and (−)-$Ru(phen)_3^{+2}$ the interaction between the ligands and spin-orbit coupling energies have been calculated. It is shown that the spin-orbit coupling energy in case of Ru(II) complex is more important than the ligand-ligand interaction. This leads to a sequence of the lowest excited states $^3A_2 < {}^1A_2 < {}^1E$.

Key words: Electron-transfer transitions in inorganic chelates – Excited states in inorganic chelates – Tris-(1, 10-phenanthroline) ruthenium(II) ion.

1. Introduction

From the spectroscopic investigations of the complex compounds of nd^6-metal ions with π-electron conjugated ligands, like 1,10-phenanthroline and 2,2′-bipyridyl, differences between the spectral properties of the complexes with the metal ions having the main quantum number $n = 3$ and the complexes with n greater than 3 could be seen [1–3]. The main changes were observed in the region of the metal-to-ligand electron-transfer transitions. The studies of CD spectra [1, 4] and luminescence properties were here of especial interest [2, 3, 5–17]. To explain the difference the coupled-chromophore model was used in the description of the electronic states of these complexes. According to this picture, the triply degenerate metal-to-ligand electron-transfer excited states split into the states A_2 and E[18] and their positions depend on the interaction which is operative in the relevant molecule. If the dipole–dipole interaction between the chromophores is the dominant factor, the $^1A_1 \rightarrow {}^1A_2$ transition will be placed at higher energy and the $^1A_1 \rightarrow {}^1E$ transition at correspondingly lower energy. If, however, the spin-orbit interaction should be more important than the dipole-dipole term, the level order could reverse.

In a previous paper [19] we have shown that the spin-orbit mechanism may mix the electron-transfer state $^3A_2$ with the electron-transfer state ^1E. Therefore, this interaction could influence the sequence of the lowest excited states in the pertinent complexes. It is the aim of this paper to calculate the dipole-dipole interaction energy in $\mathrm{Fe(phen)}_3^{+2}$ and $\mathrm{Ru(phen)}_3^{+2}$ and to compare it with the spin-orbit coupling energy in order to interpret the spectral properties of these compounds in the region of metal-to-ligand electron-transfer transitions.

2. Calculation of Interaction Energies

To calculate the dipole-dipole interaction energy, E_{DD}, between the transition dipoles $\mu(1)$ and $\mu(2)$, we started from the expression [20, 21]

$$E_{DD} = \frac{\mu(1)\mu(2)}{R_{12}^3} \tag{1}$$

rewritten into the form

$$E_{DD} = \frac{1}{R_{12}^3}(\mu_{x(1)}\mu_{x(2)} + \mu_{y(1)}\mu_{y(2)} - 2\mu_{z(1)}\mu_{z(2)}, \tag{2}$$

where $\mu_{x(1)}$ is the x-component of the ith transition dipole and R_{12} is the distance between the transition dipoles in cm. The transition moments were calculated from the theoretical expression given by the semiclassical time dependent perturbation theory as [22, 23]

$$\mu_{AB} = \frac{\hbar e}{2\pi m c \sigma_{AB}} \langle A|\nabla|B\rangle. \tag{3}$$

$|A\rangle$ and $|B\rangle$ are the total electronic wave functions for the ground state and the excited state, respectively, and σ_{AB} is the transition energy in wave numbers.

For the calculation of matrix elements of the "del" operator the same procedure was used as in the previous paper [24]. The necessary bond distances were taken from the literature [19, 24] as were the atomic functions for carbon, nitrogen, iron(II) and ruthenium(II) [25–27]. In addition the SCF molecular orbitals given for 1,10-phenanthroline by Ito et al. were used [28]. The distances between the transition dipoles were calculated from the experimental data for the dipole strengths [1]. The results are summarized in Table 1.

Table 1. Interaction energies

Complex	R_{12} cm	E_{DD} cm^{-1}	E_{SO} cm^{-1}
$\mathrm{Fe(phen)}_3^{+2}$	$1.06 \cdot 10^{-8}$	1826	166
$\mathrm{Ru(phen)}_3^{+2}$	$1.17 \cdot 10^{-8}$	110	408

The spin-orbit coupling terms were calculated in Ref. [19]. For comparison the results are also given in Table 1.

Comparing the values of the spin-orbit coupling energies with the dipole-dipole interaction energies it can be seen that in the case of a ruthenium(II) complex the spin-orbit coupling mechanism predominates. Solving for both effects simultaneously, using the spin-orbit coupling term as a perturbation, we get the energies of the metal-to-ligand electron-transfer transition for Ru(phen)_3^{+2}

$^1\mathrm{A}_1 \rightarrow {}^3\mathrm{A}_2$	$19\,030\ \mathrm{cm}^{-1}$
$^1A_1 \rightarrow {}^1A_2$	$23\,500\ \mathrm{cm}^{-1}$
$^1A_1 \rightarrow {}^1E$	$25\,770\ \mathrm{cm}^{-1}$.

3. Discussion

From the theoretical studies of interactions in the tris(bisbidentate) complexes of nd^6 metal ions, where the ligands are conjugated π-electron molecules, it follows that the level sequence of the lowest excited states depends on the interaction which is operative in the relevant molecule. In the complex ion Ru(phen)_3^{+2} where the spin-orbit coupling interaction energy is greater than the interaction energy between the transition dipoles on the ligands the sequence of the low lying metal-to-ligand electron-transfer transitions is $^3A_2 < {}^1A_2 < {}^1E$. On the other hand, in the complex Fe(phen)_3^{+2} where the dominant factor is the dipole-dipole interaction the level order is $^1E < {}^3A_2 < {}^1A_2$. The same conclusions hold for all trigonal dihedral complexes of Fe(II), Ru(II), Os(II) with 2,2'-bipyridyl or 1,10-phenanthroline and related ligands.

These theoretical results are in agreement with the experimental results obtained from studies of luminescence properties and from CD spectra. It can be seen from the CD measurements of (−)-Ru(II) and (−)-Os(II) complexes in the region of electron-transfer transitions [1], that the sign of the CD curves are opposite to that of the CD curves of the (−)-Fe(II) complexes. This is caused by the reversed position of $^1A_2$ and ^1E states [29]. Moreover, the CD spectra of Os(II) complexes exhibit an additional CD band belonging to the $^1A_1 \rightarrow {}^3A_2$ transition.

The luminescence properties of these complexes also confirm the competition of the spin-orbit coupling with the dipole-dipole interaction. Thus, in complexes of Ru(II) and Os(II) with conjugated ligands, a $\pi^* \rightarrow d$ emission has been observed [3] while the Fe(II) chelates do not luminesce. We assume that these properties are associated with the $^3A_2 \rightarrow {}^1A_1$ transition [19]. On the other hand, Crosby and co-workers [3] connect this phenomenon with vibronically allowed $^3A_1 \rightarrow {}^1A_1$ transitions. However, this conclusion is at variance with the results of CD measurements.

Acknowledgement. I am indebted to Professor C. J. Ballhausen for having read the paper in a preliminary form and for his suggestions for improvements.

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Received January 28, 1980