

THE OPTICAL ROTATORY POWER OF THE TRIS-(2,2'-BIPYRIDYL)IRON(II) ION

M. KRÁL

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

Received November 24th, 1971

In the paper the optical rotatory power of electron transfer transitions observed in the complex particle $(-)\text{-Fe}(\text{bipy})_3^{2+}$ is theoretically calculated. Description of electronic states was carried out on the basis of coupled chromophore model. The matrix elements of the electric dipole operator were expressed in the dipole velocity representation and for numerical calculation the auxiliary functions $A_n(p)$ and $B_n(pt)$ were used. The matrix elements of the magnetic dipole operator were expressed as overlap integrals. Calculated values of the optical rotatory power of electron transfer transitions are higher than the experimental values. As the theoretical values of the oscillator strength of these transitions are, on the contrary, lower than the experimental values, we assume that for obtaining better results the configuration interaction between electron transfer states and π -electron states of ligand will necessarily be taken into consideration.

Very interesting optically active compounds for theoretical studies are complex compounds of metal ions with 2,2'-bipyridyl or 1,10-phenanthroline of general formula ML_3^{n+} (for $n = 2$ or 3). From those complex compounds we studied theoretically the optical rotatory power of electron transfer bands of $\text{Fe}(\text{phen})_3^{2+}$ (ref.¹). The aim of this paper is the theoretical study of the optical rotatory power connected with metal-to-ligand electron transfer transitions of $\text{Fe}(\text{bipy})_3^{2+}$ ion. As was experimentally found, the spectrum of this particle is composed from number of bands, most intensive of which are those connected with transitions localized on ligands and a little lower intensity have the bands attached to electron transfer from metal orbitals to the antibonding orbitals of ligands^{2,3}. Optical activity of this compound was studied in the region of electron transfer transitions and in the region of transitions localized on ligands^{2,4}. Both kinds of these transitions are optically active, CD effect, however, is weaker by the first one. To be able to study the optical rotatory power of electron transfer transitions we used for the description of studied system the coupled chromophore model⁵. Hanazaki and Nagakura⁶ studied theoretically optical activity of complex particle $\text{Fe}(\text{bipy})_3^{2+}$, their results, however, are not correct, as they used erroneous function to describe d -electron states.

THEORETICAL

In the theoretical studies of optical rotatory power we start from the relation

$$R_{A \rightarrow B} = - \frac{e^2 \hbar^2}{4\pi m^2 c^2 \sigma_{A \rightarrow B}} \langle A | \nabla | B \rangle \langle B | \mathbf{r} \times \nabla | A \rangle, \quad (1)$$

where $|A\rangle$ and $|B\rangle$ are the wave functions of the particle in the state A or B , respectively, e is the electronic charge, \hbar is the 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. Now, the function describing the state A and the state B must be expressed. In this description the coupled chromophore model⁵ will be used. The state A , which is the ground state, is in this approximation represented by the function

$$|G, \Gamma S\rangle = |M\rangle \prod_{g=1}^n |L(g)\rangle, \quad (2)$$

where the function $|M\rangle$ corresponds to the metal electron state and $|L(g)\rangle$ stands for the electron state of the g th ligand; the symbol Γ indicates the symmetry properties of the function and S is the total spin. In the ground state of the complex $\text{Fe}(\text{bipy})_3^{2+}$ $S = 0$, which followed from the studies of magnetic and spectral properties^{2,3}. The octahedral arrangement of donor atoms being presupposed, the symmetry of this particle is D_3 and the ground state is described by the function

$$|G, A_1 0\rangle = |M\rangle \prod_{g=1}^3 |L(g)\rangle. \quad (3)$$

If the spin-orbital interaction is neglected, *i.e.* when

$$|C_i\rangle = |c_i\rangle |y_i\rangle, \quad (4)$$

where $|c_i\rangle$ is the space part and $|y_i\rangle$ the spin part of the i th spin-orbital, the function $|M\rangle$ is written in the form of Slater determinant

$$|M\rangle = |m_1\alpha \ m_1\beta \ m_2\alpha \ m_2\beta \ m_3\alpha \ m_3\beta|, \quad (5)$$

where to the spin function α corresponds the value $+1/2$ and to the function β the value $-1/2$; m_k are trigonal metal orbitals⁷. Similarly to the function $|M\rangle$ the function $|L(g)\rangle$ is written

$$|L(g)\rangle = |l(g)_1\alpha \ l(g)_1\beta \ \dots \ l(g)_6\alpha \ l(g)_6\beta|, \quad (6)$$

where

$$l(g)_r = \sum_s c_{rs} p_{zs}^{(g)} \quad (7)$$

$p_{zs}^{(g)}$ is the p_z -orbital centered on the s th atom of the g th ligand and c_{rs} are the expansion coefficients. The state B in the equation (1) is one-electron excited state. In our case it belongs to the mono-excited electron-transfer state, which is described by the function

$$|ET, \Gamma_i 0\rangle = \sqrt{\left(\frac{1}{n}\right)} \sum_j \sum_{b=1}^3 D_h^{r_i} \left| \begin{matrix} L(h) \\ M_j \end{matrix} \right\rangle_r \prod_{g=1}^3 |L(g)\rangle, \quad (8)$$

where n is the number of d -electrons, $D_h^{r_i}$ are the group transformation coefficients and $|L(h)_r\rangle$ stands for the singlet determinantal wave function for the state arising from the promotion of a d -electron from the state described by the spin-orbital function $|M_j\rangle$ into the r th antibonding spin-orbital of the h th ligand, described by the spin-orbital function $|L(h)_r\rangle$. By introducing (3) and (8) into (1) and by further adaptation the expression (9) is obtained for the optical rotatory power of electron-transfer transition from the state $(G, A_1 0)$ into the state $(ET, \Gamma_i 0)$ (shortly ${}^1A_1 \rightarrow {}^1\Gamma_i$)

$$R_{1A_1 \rightarrow 1\Gamma_i} = - \frac{e^2 \hbar^2}{4\pi m^2 c^2 \sigma_{1A_1 \rightarrow 1\Gamma_i} n} \frac{2}{n} \sum_k \sum_h (D_h^{r_i})^2 \langle m_k | \nabla | l(h)_r \rangle \langle l(h)_r | \mathbf{r} \times \nabla | m_k \rangle \quad (9)$$

Numerical Calculation

The geometry of complex ion $(-)\text{-Fe}(\text{bipy})_3^{2+}$. The arrangement of ligands around the central ion $\text{Fe}(\text{II})$ is illustrated in Fig. 1. For simplification donor atoms are mentioned only and the ligand molecules are replaced by thick lines. At given arrangement the microsymmetry of complex particle is octahedral and the symmetry of the whole complex ion is D_3 . In Fig. 1 unit vectors are given, that indicate the

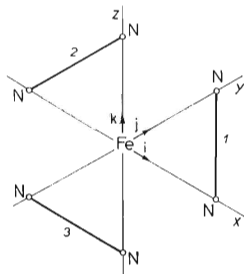


FIG. 1
Geometry of $(-)\text{-Fe}(\text{bipy})_3^{2+}$

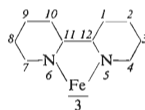


FIG. 2
Numbering of Atoms in the Ligand Molecule

position of ligands. Unit vectors are chosen in such a way, that for ligand 1 these vectors are positive. With regard to this choice the position of ligand 2 and 3 is given as follows

$$\begin{array}{ccc}
 L(1) & L(2) & L(3) \\
 i & k & -j \\
 j & -i & -k \\
 k & -j & i.
 \end{array} \quad (10)$$

The distances of carbon and nitrogen atoms from central ion were not experimentally determined. Therefore the bond distances found for the complex⁸ Fe(phen)₃²⁺ were used for calculation. The pertinent bond distances are given in Table I and the numbering of atoms is in Fig. 2.

The symmetry of excited states and the coefficients $D_h^{r_1}$. With regard to the symmetry of complex particle (D_3) the symmetry of one electron excited states is A_2 and E , i.e. optically active transitions are transitions ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1A_1 \rightarrow {}^1E$. The group transformation coefficients $D_h^{r_1}$, that appear in the expression (9) were obtained by use of projection operators of the symmetry group⁹ D_3 have the following numerical values:

Γ_i^h	1	2	3
A_2	$3^{-1/2}$	$3^{-1/2}$	$3^{-1/2}$
$E(\text{I})$	0	$2^{-1/2}$	$-(2)^{-1/2}$
$E(\text{II})$	$(2/3)^{1/2}$	$-(6)^{-1/2}$	$-(6)^{-1/2}$

TABLE I
Interatomic Distances of Fe(bipy)₃²⁺

M—X	Bond length Å	M—X	Bond length Å
Fe—N ₅	1.97	Fe—C ₂	4.73
Fe—N ₆		Fe—C ₉	
Fe—C ₄	3.12	Fe—C ₁	4.07
Fe—C ₇		Fe—C ₁₀	
Fe—C ₃	4.36	Fe—C ₁₁	2.68
Fe—C ₈		Fe—C ₁₂	

Matrix elements of the operators ∇ and $(\mathbf{r} \times \nabla)$. The matrix elements of the operators ∇ and $(\mathbf{r} \times \nabla)$ appearing in equation (9) were calculated using the relations published beforehand¹⁰. The atomic functions of carbon and nitrogen were in mono- ζ form with the values ζ_C 1.5679 and ζ_N 1.9170 (ref.¹¹). The atomic function for Fe(II) was in form double- ζ (ref.¹²) with c_1 0.5661, c_2 0.5860, ζ_1 5.35 and ζ_2 2.20. Molecular orbitals of ligand were those of Hückel types for δ_N 0.5. In further procedure the electron promotion from metal to the first antibonding ligand orbital is presupposed,

TABLE II
Matrix Elements $\langle \text{Fe(II)}, 3dm^a \xi | \nabla | N, 2p^{(h)} \rangle$

$3dm^a$	Bond length Å	Numerical value, a.u.	
		$\xi_1 = 5.35$	$\xi_2 = 2.2$
$3d_{xz}$	1.97	-0.0011 <i>l</i>	-0.0233 <i>l</i>
$3d_{yz}$	1.97	0.0072 <i>j</i>	0.1019 <i>j</i>
$3d_{z^2}$	1.97	-0.0018 <i>k</i>	-0.0227 <i>k</i>
$3d_{x^2-y^2}$	1.97	-0.0041 <i>k</i>	-0.0626 <i>k</i>

TABLE III
Matrix Elements $\langle \text{Fe(II)}, 3dm^a \xi | \nabla | C, 2p^{(h)} \rangle$

Bond length Å	Numerical value, a.u.			
	$3d_{xz}$		$3d_{yz}$	
	$\xi_1 = 5.35$	$\xi_2 = 2.2$	$\xi_1 = 5.35$	$\xi_2 = 2.2$
3.12	-0.0000 <i>l</i>	-0.0016 <i>l</i>	0.0004 <i>j</i>	0.0121 <i>j</i>
4.36	-0.0000 <i>l</i>	-0.0000 <i>l</i>	0.0000 <i>j</i>	0.0006 <i>j</i>
4.73	-0.0000 <i>l</i>	-0.0000 <i>l</i>	0.0000 <i>j</i>	0.0002 <i>j</i>
4.07	-0.0000 <i>l</i>	-0.0001 <i>l</i>	0.0000 <i>j</i>	0.0012 <i>j</i>
2.68	-0.0002 <i>l</i>	-0.0057 <i>l</i>	0.0014 <i>j</i>	0.0334 <i>j</i>
	$3d_{z^2}$		$3d_{x^2-y^2}$	
	$\xi_1 = 5.35$	$\xi_2 = 2.2$	$\xi_1 = 5.35$	$\xi_2 = 2.2$
3.12	-0.0001 <i>k</i>	-0.0030 <i>k</i>	-0.0002 <i>k</i>	-0.0069 <i>k</i>
4.36	-0.0000 <i>k</i>	-0.0001 <i>k</i>	-0.0000 <i>k</i>	-0.0003 <i>k</i>
4.73	-0.0000 <i>k</i>	-0.0001 <i>k</i>	-0.0000 <i>k</i>	-0.0001 <i>k</i>
4.07	-0.0000 <i>k</i>	-0.0003 <i>k</i>	-0.0000 <i>k</i>	-0.0007 <i>k</i>
2.68	-0.0004 <i>k</i>	-0.0080 <i>k</i>	-0.0008 <i>k</i>	-0.0195 <i>k</i>

which means that the coefficients c_{7s} are used for calculation. The values of c_{7s} are: $c_{7,1} = c_{7,10} = 0.20683$, $c_{7,2} = c_{7,9} = -0.24466$, $c_{7,3} = c_{7,8} = 0.35016$, $c_{7,4} = c_{7,7} = 0.03953$, $c_{7,5} = c_{7,6} = -0.37331$, $c_{7,11} = c_{7,12} = 0.36583$. To gain matrix elements $\langle m_k | \nabla | l(h)_r \rangle$, matrix elements $\langle \text{Fe(II)}, 3dm^a \zeta | \nabla | \text{N}, 2p_{zs}^{(h)} \rangle$ and $\langle \text{Fe(II)}, 3dm^a \zeta | \nabla | \text{C}, 2p_{zs}^{(h)} \rangle$ were calculated first. Numerical values of these integrals are presented in Tables II and III. Matrix elements $\langle m_k | \nabla | l(h)_r \rangle$ are

$$\langle m_1 | \nabla | l(h)_r \rangle = -0.004669 i + 0.01648 k,$$

$$\langle m_2 | \nabla | l(h)_r \rangle = -0.018637 j, \quad \langle m_3 | \nabla | l(h)_r \rangle = 0.006984 k.$$

If those values are presupposed for h 1, for h 2 and 3 the replacement of unit vectors in agreement with (10) must be done. The matrix elements of the operator $(\mathbf{r} \times \nabla)$ were expressed as overlap integrals $\langle X, 2p_{zs}^{(h)} | 3d_{yz}, \text{Fe(II)} \rangle$. The values of these integrals are given in Table IV. For calculation the programme Diatom was used, published by Corbato and Switendick¹³. The matrix elements $\langle l(h)_r | \mathbf{r} \times \nabla | m_k \rangle$ are

$$\langle l(h)_r | \mathbf{r} \times \nabla | m_1 \rangle = -0.42185 i, \quad \langle l(h)_r | \mathbf{r} \times \nabla | m_2 \rangle = -0.42185 j,$$

$$\langle l(h)_r | \mathbf{r} \times \nabla | m_3 \rangle = -0.89488 i.$$

These expressions were attached to the ligand l and using (10) transformed into expressions with h 2 and 3.

After transformation the matrix elements of the operator ∇ from atomic units into the reciprocal centimetres, we introduced these matrix elements together with the matrix elements of the operator $(\mathbf{r} \times \nabla)$ and group transformation coefficients $D_h^{\Gamma'}$ into the equation (9) and calculated the optical rotatory power of the transitions ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1A_1 \rightarrow {}^1E$. Experimental values were calculated using relation¹⁴ (11) with data published in literature².

TABLE IV
Matrix Elements $\langle X, 2p_{zs}^{(h)} | 3d_{yz}, \text{Fe(II)} \rangle$

X	Bond length Å	Numerical value	X	Bond length Å	Numerical value
N	1.97	0.7085	C ₂	4.73	-0.0048
C ₄	3.12	-0.0378	C ₁	4.07	-0.0157
C ₃	4.36	-0.0096	C ₁₂	2.68	0.0180

$$R_{A_1 \rightarrow \Gamma_1}^{\text{exp}} \approx 0.696 \cdot 10^{-42} \sqrt{(\pi)} [\Theta_{A_1 \rightarrow \Gamma_1}^0] \frac{\Delta_{A_1 \rightarrow \Gamma_1}^0}{\lambda_{A_1 \rightarrow \Gamma_1}^0} \quad (11)$$

where
$$[\Theta_{A_1 \rightarrow \Gamma_1}^0] \approx 2.303 \left(\frac{4500}{\pi} \right) (\epsilon_l - \epsilon_r).$$

For calculation $R_{A_1 \rightarrow A_2}^{\text{exp}}$ we took $(\epsilon_l - \epsilon_r) = +20$, $\lambda_{A_1 \rightarrow A_2}^0 = 495$ nm and $\Delta_{A_1 \rightarrow A_2}^0 = 80$ nm. The value $R_{A_1 \rightarrow E}^{\text{exp}}$ was calculated with $(\epsilon_l - \epsilon_r) = -38$, $\lambda_{A_1 \rightarrow E}^0 = 524$ nm and $\Delta_{A_1 \rightarrow E}^0 = 80$ nm. Theoretical and experimental values of the optical rotatory power of pertinent transitions together with theoretical and experimental values of the oscillator strength are as follows:

Transition	R , cgs	R^{exp} , cgs	f	f^{exp}
${}^1A_1 \rightarrow {}^1A_2$	$+5.72 \cdot 10^{-38}$	$+1.31 \cdot 10^{-38}$	$6.77 \cdot 10^{-3}$	0.0717
${}^1A_1 \rightarrow {}^1E$	$-6.82 \cdot 10^{-38}$	$-2.36 \cdot 10^{-38}$	$6.93 \cdot 10^{-3}$	0.0791

For the theoretical calculation of the oscillator strength we used the relation^{15,16}

$$f_{A \rightarrow B} = \frac{\hbar}{2\pi m c \sigma_{A \rightarrow B}} |\langle A | \nabla | B \rangle|^2. \quad (12)$$

Experimental value of the oscillator strength was gained by use of¹⁷

$$f_{A \rightarrow B} = 4.32 \cdot 10^{-9} \epsilon_{\text{max}} (1.0645) h, \quad (13)$$

where h is the band-width in $\epsilon_{\text{max}}/2$, that in our case was 2000 cm^{-1} .

DISCUSSION

At theoretical study of the optical rotatory power of electron transitions we are interested first in the accordance of the sign between the value theoretically calculated and the value obtained from the experimental data and second in the accordance of numerical values. At the complex ion $(-)\text{-Fe}(\text{bipy})_3^{2+}$ it was found, that the value of the optical rotatory power of the transition ${}^1A_1 \rightarrow {}^1A_2$ has the positive sign, while for the transition ${}^1A_1 \rightarrow {}^1E$ this quantity has negative sign. This result is in accordance with experiment. It is, however, necessary to point out, that analogical order of the CD spectrum components is presupposed, as at the transitions localized on ligands and observed at trigonal dihedral complexes of transition metals¹⁸. That

means that the long-wave component of the CD spectrum (σ $18.35 \cdot 10^3 \text{ cm}^{-1}$) is attached to the transition ${}^1A_1 \rightarrow {}^1E$ and the short-wave component (σ $21.00 \cdot 10^3 \text{ cm}^{-1}$) is connected with the transition ${}^1A_1 \rightarrow {}^1A_2$. If the theoretical values of the optical rotatory power are compared with experimental ones, then this attachment is correct, as the value of the optical rotatory power of the transition with lower wave-number is higher than the value for the transition with higher wave-number. The order of levels is, too, in agreement with that, which gives for similar complexes Orgel¹⁹. The study of Faraday effect will prove the correctness of this attachment.

If the value of the optical rotatory power of electron transfer transition is taken into account, we can see, that for both transitions the theoretically obtained value is higher than the experimental value. To explain this difference, it is supposed, that the electron transfer state is not the pure state described by the function (8), but is mixed with mono-excited state localized on ligand. By this the optical rotatory power of both transitions is lowered, because the value of the optical rotatory power of the transitions localized on ligands has opposite sign. By introducing configuration interaction, the theoretical value of the oscillator strength, which is about ten times lower than the experimental value is increasing, too.

From the theoretical study of the CD spectra further follows, that the electron transfer transitions, observed in the spectrum of the complex particle $(-)\text{-Fe}(\text{bipy})_3^{2+}$, are optically active. This result is very important, because it enables to identify the electron transfer transitions with wave-numbers $19.1 \cdot 10^3 \text{ cm}^{-1}$ and $20.2 \cdot 10^3 \text{ cm}^{-1}$ as a transition ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$.

The author thanks professor C. J. Ballhausen, professor A. J. Moscovitz and Dr A. E. Hansen who introduced him into the optical activity study. Thanks are due to Dr R. Zahradnik for the Hückel π -orbital coefficients of the 2,2'-bipyridyl. The matrix elements of the operator ∇ were solved using a program written for the GIER computer (University of Copenhagen). The overlap integrals were calculated on an IBM 7094 Computer (Technical University, Lyngby).

REFERENCES

1. Král M.: Unpublished results.
2. Mason S. F.: *Inorg. Chim. Acta Rev.* 2, 89 (1968).
3. Krumholz P.: *Structure and Bonding* 9, 139 (1971).
4. Hidaka J., Douglas B. E.: *Inorg. Chem.* 3, 1180 (1964).
5. Longuet-Higgins H. C., Murrell J. N.: *Proc. Phys. Soc. A* 68, 601 (1955).
6. Hanazaki I., Nagakura S.: *Inorg. Chem.* 8, 654 (1969).
7. Ballhausen C. J.: *Introduction to the Ligand Field Theory*, p. 68. McGraw-Hill, New York 1962.
8. Templeton D. H., Zalkin A., Ueki T.: *Acta Cryst.* 21, A 154 (1966) (Supplement).
9. Tinkham M.: *Group Theory and Quantum Mechanics*, p. 41. McGraw-Hill, New York 1964.
10. Král M.: *This Journal* 35, 1939 (1970).
11. Clementi E., Raimondi D. L.: *J. Chem. Phys.* 38, 2686 (1963).

12. Richardson J. W., Nieuwpoort W. C., Powell R. R., Edgell W. F.: *J. Chem. Phys.* 36, 1057 (1962).
13. Corbato F. J. in the book: *Methods in Computational Physics* (B. Alder, S. Fernbach, M. Rotenberg, Eds), Vol. 2, p. 155. Academic Press, New York 1963.
14. Moscovitz A. in the book: *Optical Rotatory Dispersion* (C. Djerassi, Ed.), p. 155 and 165. McGraw-Hill, New York 1960.
15. Moscovitz A.: *Thesis*. Harvard University, Cambridge 1957.
16. Moffitt W.: *J. Chem. Phys.* 25, 467 (1956).
17. Sandorfy C.: *Electronic Spectra and Quantum Chemistry*, p. 103. Prentice-Hall, Engelwood Cliffs, New Jersey 1964.
18. McCaffery A. J., Mason S. F., Ballard R. E.: *J. Chem. Soc.* 1965, 2283.
19. Orgel L. E.: *J. Chem. Soc.* 1961, 3683.

Translated by the author.