The π-electron densities calculated for the ground states of the free and coordinated molecules are shown in Table IV. It is clear that the π-electron distributions in the *cis* and *trans* forms of free α,α'-dipyridyl are almost equal to each other whereas the coordinated molecule has an extremely different electron distribution from that of the free molecule. This difference is mainly caused by the electrostatic attraction of metal charge. The total electron number transferred from the metal $3d\pi$ AO's to three ligands through the mixing of the CT configurations is 0.236. The increment of electron density on each $2p\pi$ AO of the ligand is, however, very small because the transferred electron density is distributed on a large number of $2p\pi$ AO's.

Contribution from The Institute of Physical and Chemical Research,
Yamato-Machi, Saitama, Japan, and The Institute for Solid State Physics,
The University of Tokyo, Roppongi, Minato-Ku, Tokyo, Japan

Optical Rotatory Power of the Metal Chelate Compounds Containing Organic Unsaturated Molecules as Ligands

By ICHIRO HANAZAKI and SABURO NAGAKURA

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Rotational strengths due to the π-electron transitions of optically active dihedral metal complexes containing organic unsaturated molecules as ligands were theoretically studied by calculating directly magnetic transition dipole moments. The observed CD bands due to the $\pi-\pi^*$ transitions within the ligand π-electron systems could well be explained by the present theoretical treatment which used the wave functions evaluated by the composite-system method. The absolute configuration of optical isomers could be determined by comparing the theoretical results with the observed CD signs of the ligand $\pi-\pi^*$ transitions. The rotational strengths due to the metal–ligand charge-transfer transitions appearing in certain α,α'-dipyridyl and *o*-phenanthroline complexes were also examined from the theoretical point of view. Two of the three charge-transfer transitions at the 500-mμ region were shown to have large rotational strengths corresponding to the observed two CD bands with opposite signs, though these two transitions gave a small contribution to the electronic absorption spectrum.

Introduction

The basic theory of optical rotatory dispersion (ORD) and circular dichroism (CD) was presented by Condon[1] and was reformulated by Moffitt and Moscowitz.[2] Its application to the observed optical rotatory power due to the d–d transition has been made with successful results at least qualitatively.[3-7]

On the other hand, the CD or ORD due to the strong CT (charge-transfer) or LE (locally excited) transitions observed for the metal chelate compounds containing organic unsaturated molecules as ligands has not been studied so extensively because of the difficulty in their measurements and also because of the lack of reliable wave functions for this type of complexes. To our knowledge, the CD spectra of the strong bands have been measured so far for tris(acetylacetonato)-silicon(IV),[8] for triscatechyl arsenate(V),[9d] and also for some α,α'-dipyridyl and *o*-phenanthroline complexes of transition metal ions.[9-11]

We studied theoretically the electronic structures of some metal complexes by the composite-system treatment.[12-15] In view of the success of the theory in explaining the electronic absorption spectra of the tris-acetylacetonato complexes of the iron-series transition metal ions and also of the tris-dipyridyl, tris-*o*-phenanthroline, and tris-α-diimine complexes of the iron(II) ion, it seems to be interesting to apply our method to the optical rotatory power due to the CT and LE transitions of metal chelate compounds. In actuality, we have undertaken to study theoretically the optical rotatory power of Si(acac)$_3^+$, Fe(dipy)$_3^{2+}$, and Fe-

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$(phen)_3^{2+}$.[16] The main purposes of the present study are to understand the nature of the observed CD bands in detail and to determine the absolute configuration of the optical isomer.

Theory

The intensities of CD and ORD are determined by the optical rotatory power defined by the imaginary part of the scalar product of the electric and magnetic transition dipole moments.[1,2]

By keeping the fact in mind that we use always the real wave function, it can be written as

$$R(V) = -(e^2\hbar/2mc)\langle G|\mathbf{Q}|V\rangle\cdot\langle V|\boldsymbol{\Lambda}|G\rangle \qquad (1)$$

where

$$\begin{aligned}\mathbf{Q} &= \sum_j \mathbf{q}_j\\ \boldsymbol{\Lambda} &= \sum_j \boldsymbol{\lambda}_j\\ \boldsymbol{\lambda}_j &= \mathbf{q}_j \times \nabla_j\end{aligned} \qquad (2)$$

Here, e, m, c, $\hbar$, and i are the electronic charge, mass of electron, light velocity, Planck's constant divided by 2π, and imaginary unit, respectively. The quantity $\mathbf{q}_j$ is the position vector of the jth electron. The electric transition moment $\langle G|\mathbf{Q}|V\rangle$ accompanied by the transition G → V was calculated in our previous papers.[12-14] In the following, we focus our attention on estimating $\langle V|\boldsymbol{\Lambda}|G\rangle$ for the LE transition within the ligand π-electron system and for the metal to ligand CT transition.

$Si(acac)_3^+$.—The assumed geometrical configuration and the coordinate system are illustrated in Figure 1. The LE wave functions corresponding to the nth transition in the ligand π-electron system are written as[12]

$$\begin{aligned}LE_n(A_2) &= (3)^{-1/2}[LE_n^a + LE_n^b + LE_n^c]\\ LE_n(E) &= (2)^{-1/2}[LE_n^a - LE_n^b]\\ LE_n(E') &= (6)^{-1/2}[2LE_n^c - LE_n^a - LE_n^b]\end{aligned} \qquad (3)$$

for the x-polarized transition. If the nth transition is y polarized, the first part of eq 3 belongs to the irreducible representation A_1. We use the CI (configuration interaction) result in ligand μ (= a, b, or c) for the wave function LE_n^μ [12,13]

$$LE_n^\mu = \sum_{i,k} U_{i\to k}^n \cdot LE_{i\to k}^\mu \qquad (4)$$

Hence

$$\langle LE_n^\mu|\boldsymbol{\Lambda}|G\rangle = \Lambda_n \cdot \boldsymbol{\sigma}_\mu \qquad (5)$$

where $\boldsymbol{\sigma}_\mu$ is the unit vector perpendicular to the molecular plane of ligand μ[17] and

$$\Lambda_n = (2)^{1/2}\sum_{i,k} U_{i\to k}^n \cdot \lambda(i, k) \qquad (6)$$

The quantity $\lambda(i, k)$ is defined as

$$\langle \varphi_k^\mu|\boldsymbol{\lambda}|\varphi_i^\mu\rangle = \lambda(i, k)\cdot\boldsymbol{\sigma}_\mu \qquad (7)$$

where φ_i^a and φ_k^a are π MO's in ligand a.[17] Hence, for an x-polarized transition

$$\begin{aligned}\langle LE_n(A_2)|\boldsymbol{\Lambda}|G\rangle &= \Lambda_n\cdot\boldsymbol{\sigma}(A_2)\\ \langle LE_n(E)|\boldsymbol{\Lambda}|G\rangle &= -\Lambda_n\cdot\boldsymbol{\sigma}(E)\\ \langle LE_n(E')|\boldsymbol{\Lambda}|G\rangle &= \Lambda_n\cdot\boldsymbol{\sigma}(E')\end{aligned} \qquad (8)$$

where unit vectors are defined as

$$\begin{aligned}\boldsymbol{\sigma}(A_2) &= (3)^{-1/2}(\mathbf{i} + \mathbf{j} + \mathbf{k})\\ \boldsymbol{\sigma}(E) &= (2)^{-1/2}(\mathbf{j} - \mathbf{k})\\ \boldsymbol{\sigma}(E') &= (6)^{-1/2}(2\mathbf{i} - \mathbf{j} - \mathbf{k})\end{aligned}$$

For a y-polarized transition, Λ_n vanishes as is easily deduced from the symmetry consideration. Hence there is no contribution to the rotatory power from the y-polarized transition.

Similarly, the electric transition dipoles for the x-polarized transition are expressed as

$$\begin{aligned}\langle LE(A_2)|\mathbf{Q}|G\rangle &= -(2)^{1/2}Q_n\cdot\boldsymbol{\sigma}(A_2)\\ \langle LE(E)|\mathbf{Q}|G\rangle &= -(2)^{-1/2}Q_n\cdot\boldsymbol{\sigma}(E)\\ \langle LE(E')|\mathbf{Q}|G\rangle &= (2)^{-1/2}Q_n\cdot\boldsymbol{\sigma}(E')\end{aligned} \qquad (9)$$

where

$$Q_n = (2)^{1/2}\sum_{i,k} U_{i\to k}^n q(i, k)$$

and the quantity $q(i, k)$ is the magnitude of $\langle \varphi_k^\mu|\mathbf{q}|\varphi_i^\mu\rangle$ in the x direction of ligand μ. By use of the above-mentioned results

$$\begin{aligned}R(LE_n(A_2)) &= -2R(LE_n(E))\\ &= -2R(LE_n(E'))\\ &= -(2)^{1/2}(e^2\hbar/2mc)Q_n\Lambda_n\end{aligned} \qquad (10)$$

The quantity $\lambda(i, k)$ can be reduced into the integrals

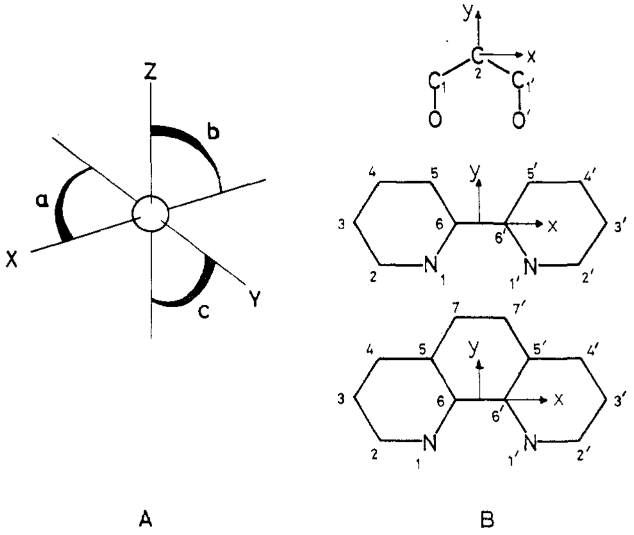

Figure 1.—(A) The geometrical configuration and coordinate system of the right-handed optically active complex. (B) Numbering of ligand 2pπ AO's: acetylacetonate, upper; α,α'-dipyridyl, middle; o-phenanthroline, lower.

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[16] Tris(acetylacetonato)silicon(IV), tris(dipyridyl)iron(II), and tris(o-phenanthroline)iron(II) are hereafter abbreviated to $Si(acac)_3^+$, $Fe(dipy)_3^{2+}$, and $Fe(phen)_3^{2+}$, respectively.

[17] σ_μ = $\mathbf{k}$, $\mathbf{j}$, and $\mathbf{i}$ for μ = a, b, and c, respectively.

over AO's as

$$\lambda(i, k) = \sum_{\mathrm{p}} \sum_{\mathrm{q}} C_{i\mathrm{p}} C_{k\mathrm{p}} \lambda(\mathrm{p}, \mathrm{q}) \qquad (11)$$

where $\lambda(\mathrm{p}, \mathrm{q})$ is defined by the relation[18]

$$\langle \chi_{\mathrm{q}}{}^{\mu} | \lambda | \chi_{\mathrm{p}}{}^{\mu} \rangle = \lambda(\mathrm{p}, \mathrm{q}) \cdot \delta_{\mu} \qquad (12)$$

The one-center integral $\lambda(\mathrm{p}, \mathrm{p})$ is easily shown to vanish. In order to calculate the two-center integral $\lambda(\mathrm{p}, \mathrm{q})$, we transform the coordinate system from (X, Y, Z) shown in Figure 1 to $(\xi_{\mathrm{p}}, \eta_{\mathrm{p}}, \zeta_{\mathrm{p}})$. The latter is obtained by transferring the origin from the metal to atom p in ligand a and by rotating the system so as to put atom q on the ξ_{p} axis. If we denote the position of atom p as $(X_{\mathrm{p}}, Y_{\mathrm{p}}, Z_{\mathrm{p}})$ and the angle of rotation of the coordinate system as θ_{pq}

$$\lambda(\mathrm{p}, \mathrm{q}) = (X_{\mathrm{p}} \sin \theta_{\mathrm{pq}} - Y_{\mathrm{p}} \cos \theta_{\mathrm{pq}}) \tau(\mathrm{p}, \mathrm{q}) \qquad (13)$$

where

$$\tau(\mathrm{p}, \mathrm{q}) = \left\langle \chi_{\mathrm{q}} \left| \frac{\partial}{\partial \xi_{\mathrm{p}}} \right| \chi_{\mathrm{p}} \right\rangle \qquad (14)$$

The following relations can easily be proved (see the Appendix)

$$\lambda(\mathrm{q}, \mathrm{p}) = -\lambda(\mathrm{p}, \mathrm{q}) \qquad (15a)$$

$$\tau(\mathrm{q}, \mathrm{p}) = \tau(\mathrm{p}, \mathrm{q}) \qquad (15b)$$

Finally, the quantity $\tau(\mathrm{p}, \mathrm{q})$ is approximated as

$$\tau(\mathrm{p}, \mathrm{q}) = -1.16(\bar{\alpha}/2) S_{\mathrm{pq}} \qquad (16)$$

where S_{pq} is the overlap integral between AO's χ_{p} and χ_{q}. The parameter $\bar{\alpha}$ is defined as

$$\bar{\alpha} = (\alpha_{\mathrm{p}} + \alpha_{\mathrm{q}})/2 \qquad (17)$$

where α_{p} and α_{q} are the orbital exponents of $2\mathrm{p}\pi$ AO's χ_{p} and χ_{q}, respectively. The approximation in eq 16 is discussed in the Appendix.

Generally speaking, the inner product in eq 1 is not invariant with regard to coordinate transformation unless the wave functions are exact. It is invariant, however, for the present case because the wave functions employed are the bases of irreducible representation of D_3 symmetry. The proof is given in the Appendix.

$\mathrm{Fe(dipy)_3}^{2+}$ and $\mathrm{Fe(phen)_3}^{2+}$.—These species exhibit the CT absorption bands due to the electron transfer from the metal $3\mathrm{d}\pi$ AO to the ligand π-electron system.[13,14] The CT configuration is expressed by the configurational wave function of the type[12,13]

$$\begin{aligned} \mathrm{CT}(\mathrm{d}_1 \rightarrow \varphi_k{}^{\mathrm{a}}) = (2)^{-1/2}[\,|(1\bar{1}2\bar{2}\ldots)^{\mathrm{a}}(1\bar{1}2\bar{2}\ldots)^{\mathrm{b}} \times \\ (1\bar{1}2\bar{2}\ldots)^{\mathrm{c}}\mathrm{d}_1\bar{\varphi}_k\mathrm{d}_2\bar{\mathrm{d}}_2\mathrm{d}_3\bar{\mathrm{d}}_3| + |(1\bar{1}2\bar{2}\ldots)^{\mathrm{a}} \times \\ (1\bar{1}2\bar{2}\ldots)^{\mathrm{b}}(1\bar{1}2\bar{2}\ldots)^{\mathrm{c}}\varphi_k{}^{\mathrm{a}}\bar{\mathrm{d}}_1\mathrm{d}_2\bar{\mathrm{d}}_2\mathrm{d}_3\bar{\mathrm{d}}_3|\,] \qquad (18) \end{aligned}$$

where d_1, d_2, and d_3 denote $3\mathrm{d}_{XY}$, $3\mathrm{d}_{YZ}$, and $3\mathrm{d}_{ZX}$, respectively.

In these complexes, the CT configuration interacts with the ground and LE configurations and also with the other CT configurations. Therefore, in order to calculate $\langle \mathrm{V} | \Lambda | \mathrm{G} \rangle$ between the ground state G and excited state V, we need the matrix elements of Λ between all of these configurations. They can be summarized in the form

$$\langle \mathrm{CT}(\mathrm{d}_t \rightarrow \varphi_k{}^{\mu}) | \Lambda | \mathrm{CT}(\mathrm{d}_s \rightarrow \varphi_k{}^{\mu}) \rangle = -\langle \mathrm{d}_s | \lambda | \mathrm{d}_t \rangle \qquad (19a)$$

$$\langle \mathrm{CT}(\mathrm{d}_t \rightarrow \varphi_k{}^{\mu}) | \Lambda | \mathrm{CT}(\mathrm{d}_t \rightarrow \varphi_l{}^{\nu}) \rangle = \delta_{\mu\nu} \langle \varphi_k{}^{\mu} | \lambda | \varphi_l{}^{\mu} \rangle \qquad (19b)$$

$$\begin{aligned} \langle \mathrm{CT}(\mathrm{d}_t \rightarrow \varphi_l{}^{\mu}) | \Lambda | \mathrm{Le}_n{}^{\nu} \rangle = \\ -\delta_{\mu\nu} \sum_{i,k} U_{i\rightarrow k}{}^{n} \delta_{kl} \langle \varphi_i{}^{\nu} | \lambda | \mathrm{d}_t \rangle \qquad (19c) \end{aligned}$$

$$\begin{aligned} \langle \mathrm{LE}_n{}^{\mu} | \Lambda | \mathrm{LE}_m{}^{\nu} \rangle = \delta_{\mu\nu} \sum_{i,k} \sum_{j,l} U_{i\rightarrow k}{}^{n} U_{j\rightarrow l}{}^{m} \times \\ [\delta_{ij} \langle \varphi_k{}^{\mu} | \lambda | \varphi_1{}^{\nu} \rangle - \delta_{kl} \langle \varphi_j{}^{\nu} | \lambda | \varphi_i{}^{\mu} \rangle] \qquad (19d) \end{aligned}$$

$$\langle \mathrm{G} | \Lambda | \mathrm{CT}(\mathrm{d}_t \rightarrow \varphi_k{}^{\mu}) \rangle = (2)^{1/2} \langle \mathrm{d}_t | \lambda | \varphi_k{}^{\mu} \rangle \qquad (19e)$$

The right-hand side of eq 19b vanishes when $\varphi_k{}^{\mu} \times \varphi_l{}^{\mu}$ is symmetric with respect to the symmetry plane of the ligand molecule.

Of the integrals appearing in eq 19, $\langle \varphi_k{}^{\mu} | \lambda | \varphi_l{}^{\mu} \rangle$ can be estimated in a similar way as before. The integral $\langle \mathrm{d}_s | \lambda | \mathrm{d}_t \rangle$ is of the same type as those appearing in the calculation of the optical rotatory power of the d–d transition. We simply give the results in Table I. The integral $\langle \varphi_i{}^{\mu} | \lambda | \mathrm{d}_t \rangle$ can be reduced to

$$\langle \varphi_i{}^{\mu} | \lambda | \mathrm{d}_t \rangle = C_{i\mathrm{N}}{}^{\mu} \langle \chi_{\mathrm{N}}{}^{\mu} | \lambda | \mathrm{d}_t \rangle + C_{i\mathrm{N}}{}^{\mu} \langle \chi_{\mathrm{N}'}{}^{\mu} | \lambda | \mathrm{d}_t \rangle \qquad (20)$$

where $\chi_{\mathrm{N}}{}^{\mu}$ and $\chi_{\mathrm{N}'}{}^{\mu}$ are the $2\mathrm{p}\pi$ AO's of nitrogen atoms N and N′, respectively, in ligand μ. The integrals appearing on the right-hand side of eq 20 can be reduced to the overlap integrals between the metal $3\mathrm{d}\pi$ and nitrogen $2\mathrm{p}\pi$ AO's. Hence it is convenient to express them in terms of σ_i defined as

$$\sigma_i = S_{\mathrm{dN}} C_{i\mathrm{N}} \qquad (21)$$

where S_{dN} is the overlap integral between d_3 and $\chi_{\mathrm{N}}{}^{\mathrm{a}}$ and $C_{i\mathrm{N}}$ is the coefficient of $\chi_{\mathrm{N}}{}^{\mathrm{a}}$ in MO $\varphi_i{}^{\mathrm{a}}$. The result is summarized in Table II.

TABLE I[a]

VALUES OF $\langle \mathrm{d}_s | \lambda | \mathrm{d}_t \rangle$

	d_s		
d_t	d_{XY}	d_{YZ}	d_{ZX}
d_{XY}	0	**j**	−**i**
d_{YZ}	−**j**	0	**k**
d_{ZX}	**i**	−**k**	0

[a] The unit vectors in the X, Y, and Z directions are denoted as **i**, **j**, and **k**, respectively.

The Experimental Value of $R(\mathrm{V})$.—The experimental value of $R(\mathrm{V})$ can be obtained from the observed CD curve by use of the relation[2,19]

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(18) The value of $\lambda(\mathrm{p}, \mathrm{q})$ is the same for the corresponding sets of χ_{p} and χ_{q} of all three ligands. Hence, hereafter, we consider ligand a without specification.

(19) Moffitt and Moscowitz gave an expression for $R(\mathrm{V})$ in terms of vibrational and librational states.[2] Since no fine structure exists in our cases, we take the sum over all vibrational and librational states corresponding to each electronic excited state and replace the sum with the integral. See also Th. Bürer, *Helv. Chim. Acta*, **46**, 242 (1963).

$$R(\mathrm{V}) = (\ln 10)10^3(3\hbar c)/(16\pi^2 N_{\mathrm{av}}) \int (3/(n_{\mathrm{s}}^2 + 2)) \times (\Delta\epsilon/\nu)\mathrm{d}\nu$$
$$= 7.9185 \times 10^{-5} \int (\Delta\epsilon/\nu)\mathrm{d}\nu \quad (\text{Å}^2) \qquad (22)$$

where N_{av} and ν are Avogadro's number and the wave number, respectively. The quantity n_{s} is the refractive index of the solvent and is taken to be 1.33, the refractive index of water at 20°,[20] because the solvent is always water in our cases. $\Delta\epsilon$ is defined as

$$\Delta\epsilon = \epsilon_{\mathrm{l}} - \epsilon_{\mathrm{r}} \qquad (23)$$

where ϵ_{l} and ϵ_{r} are the molar extinction coefficients for left and right circularly polarized light, respectively.

TABLE II[a]

VALUES OF $\langle \varphi_i^{\mu} | \lambda | \mathrm{d}_t \rangle$

	d_t		
μ	d_{XY}	d_{YZ}	d_{ZX}
a	$-\sigma_i\cdot(\mathbf{i} \pm \mathbf{j})$	$\sigma_i\cdot\mathbf{k}$	$\pm\sigma_i\cdot\mathbf{k}$
b	$\sigma_i\cdot\mathbf{j}$	$\pm\sigma_i\cdot\mathbf{j}$	$-\sigma_i\cdot(\mathbf{k} \pm \mathbf{i})$
c	$\pm\sigma_i\cdot\mathbf{i}$	$-\sigma_i\cdot(\mathbf{j} \pm \mathbf{k})$	$\sigma_i\cdot\mathbf{i}$

[a] The results are given in terms of the unit vectors **i**, **j**, and **k** in the *X*, *Y*, and *Z* directions, respectively. The quantity σ_i is defined by eq 21. The upper and lower signs correspond to the cases in which MO φ_i^{μ} is symmetric and antisymmetric, respectively, with respect to the symmetry plane of the ligand molecule.

Results and Discussion

$\mathrm{Si(acac)_3}^+$.—This complex ion shows an absorption peak at 34,700 cm^{-1} and a shoulder at 33,500 cm^{-1}. The observed absorption bands can safely be assigned to the lowest transition in the ligand π-electron system which splits into A_2 and E components of the D_3 symmetry. Since no metal–ligand CT absorption band appears, the theoretical results for $\mathrm{Al(acac)_3}$ and $\mathrm{Sc(acac)_3}$ seem to be applicable to this complex ion.[12] The theoretical consideration shows that the interaction D between the transition dipoles in two ligands is responsible for the splitting, lowering the E component by D and lifting the A_2 component by $2D$ (D is always positive in the D_3 symmetry). The transition energies and oscillator strengths calculated for the A_2 and E transitions are shown in the upper part of Figure 2 in comparison with the observed absorption spectrum. For *l*-$\mathrm{Si(acac)_3}^+$, the two CD bands conceivably corresponding to the above-mentioned absorption bands appear at 33,200 and 36,300 cm^{-1} with negative and positive signs, respectively.[8]

In order to calculate the matrix elements of $\mathbf{\Lambda}$ between the ground state and the above-mentioned two excited states, let us first estimate $\tau(\mathrm{p, q})$ by use of eq 16. Assuming the Slater AO's for the $2p\pi$ AO's of carbon and oxygen atoms, eq 16 gives the following values: $\tau(\mathrm{O, C_1}) = \tau(\mathrm{O', C_1'}) = -0.243$ au and $\tau(\mathrm{C_1, C_2}) = \tau(\mathrm{C_1', C_2}) = -0.222$ au. By use of them and eq 13, $\lambda(\mathrm{p, q})$'s are calculated as follows: $\lambda(\mathrm{O, C_1}) = -\lambda(\mathrm{O', C_1'}) = 0.675$ and $\lambda(\mathrm{C_1, C_2}) = -\lambda(\mathrm{C_1', C_2}) = 1.218$. By use of eq 6 and 11 and of the SCF–MO's and CI coefficients for $Q^{\mathrm{metal}} = +1$,[12] Λ_n is commonly calculated for the two transitions to be 2.308. The corresponding Q_n for the electric transition dipole moment is calculated as -1.113 Å.[12] Thus, by use of eq 1, the optical rotatory powers for A_2 and E components are obtained as[21]

$$R(A_2) = R(\mathrm{E}) = 6.20 \times 10^{-3}\ \text{Å}^2$$

The experimental values of rotatory power can be obtained from the CD curve[8] by use of eq 22 as follows

$$R(A_2) = 1.1 \times 10^{-4}\ \text{Å}^2$$
$$R(\mathrm{E}) = -1.2 \times 10^{-4}\ \text{Å}^2$$

Thus, the theoretical values are about 50 times larger than the observation. The occurrence of such a large discrepancy seems to be improbable in view of the adequacy of the approximations involved in the calculation. This is also supported by the fact that, as described later, the discrepancy in the rotatory power between the theoretical and observed values is not large for the LE bands in $\mathrm{Fe(dipy)_3}^{2+}$ and $\mathrm{Fe(phen)_3}^{2+}$. One of reasons for the great discrepancy in the case of $\mathrm{Si(acac)_3}^+$ is the cancellation of the two CD curves with opposite signs.[8] The occurrence of a great cancellation seems to be supported by the fact that the splittings of the A_2 and E components are considerably greater for the CD curve (3100 cm^{-1}) than for the absorption curve (1200 cm^{-1}). Another reason for the great discrepancy is the decrease in the observed rotatory power due to the partial racemization of the optical isomer during the purification and other treatments. In fact, the crude product before recrystallization gives a higher CD value than that reported by Larsen, *et al.*[22] The theoretical results are schematically illustrated in Figure 2 in comparison with the observed CD and absorption spectra.

The absolute configuration of the complex ion can be determined from the comparison of the theoretical CD sign with the experimental one. There is no question about the assignment of A_2 and E transitions in the absorption spectrum. Hence it is clear that the right-handed optical isomer shown in Figure 1, for which the present calculation is made, corresponds to the *l*-$\mathrm{Si(acac)_3}^+$ isomer the CD measurement of which was made by Larsen, *et al.* Our conclusion agrees, at least qualitatively, with the previous one[8] which is based on the simple SCF–MO calculation.

$\mathrm{Fe(dipy)_3}^{2+}$.—The wave functions of ground and excited states were obtained by the composite type of CI calculation among the ground, LE, and CT configurations. The calculated transition energies and oscillator strengths could well explain the observed electronic absorption spectrum.[13] By use of these wave functions and assuming the molecular configura-

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(20) The average value measured at 4341, 4861, 5893, and 6563 Å.

(21) Equation 1 gives half of this value for the transition to each of the degenerate components of the E state. We take here the sum of them which seems to correspond to the observation.

(22) T. Ito, private communication.

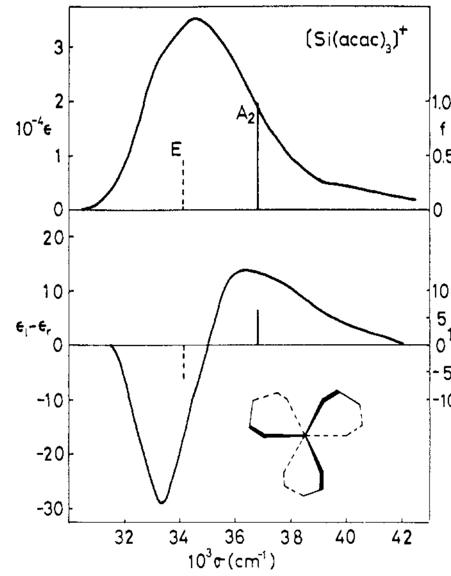

Figure 2.—The electronic absorption (upper) and circular dichroism (lower) spectra of l-$Si(acac)_3^+$. The theoretical results for the right-handed optical isomer are indicated by vertical lines.

tion shown in Figure 1, the matrix elements of Λ are calculated as follows.

Assuming the Slater AO's again for the ligand 2pπ AO's

$\tau(C, N) = -0.201$ au
$\tau(C, C) = -0.238$ au (for the neighboring carbon atoms of the pyridine ring)
$\tau(C, C) = -0.195$ au (for C_6 and C_6' atoms)

From these, λ(p,q)'s are calculated

$\lambda(N, C_2) = -0.549$ $\lambda(C_2, C_3) = 0.779$
$\lambda(C_3, C_4) = 1.970$ $\lambda(C_4, C_5) = 1.733$
$\lambda(C_5, C_6) = 0.304$ $\lambda(C_6, N) = -0.750$
$\lambda(C_6, C_6') = 0.976$

The integral values for the primed atoms can be obtained by changing the signs of the corresponding integrals between unprimed atoms. By the aid of the above λ(p, q) values, the matrix elements of Λ given in eq 5, 19b, and 19d can be evaluated.

Another necessary quantity is σ_i defined in eq 21. If we assume the double-ζ AO[23] for the metal 3dπ AO and the Slater AO for the nitrogen 2pπ AO, the overlap integral S_{dN} is determined to be 0.0784 from the table of Jaffé.[24] By use of C_{iN}'s obtained previously by the SCF calculation for $Q^{metal} = 0$,[13] σ_i's are determined

$\sigma_1 = 0.0331$ $\sigma_2 = -0.0361$
$\sigma_3 = -0.0330$ $\sigma_4 = 0.0244$
$\sigma_5 = 0.0229$ $\sigma_6 = 0.0065$
$\sigma_7 = -0.0268$ $\sigma_8 = 0.0222$
$\sigma_9 = -0.0075$ $\sigma_{10} = -0.0030$

These results, together with those given in Table I, allow us to calculate the matrix elements of Λ between

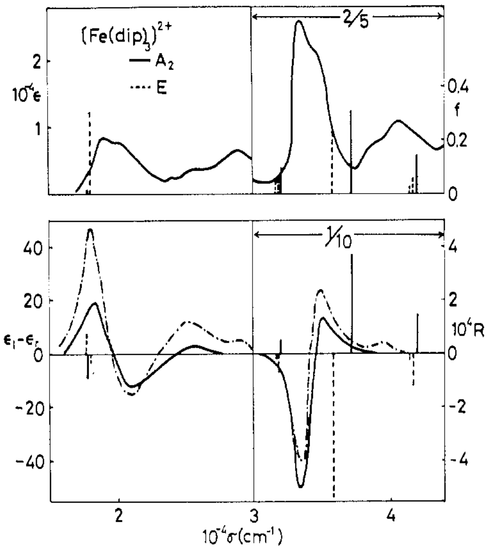

Figure 3.—The electronic absorption (upper) and circular dichroism spectra of (+)-$Fe(dipy)_3^{2+}$. The circular dichroism spectra measured by Hidaka and Douglas and by McCaffery, *et al.*, are shown by solid and dotted curves, respectively. The theortical results for the right-handed optical isomer are indicated by vertical lines.

several electron configurations. Furthermore, the matrix elements between the ground and lower excited states are obtained from the above-mentioned matrix elements and from the coefficients of the configurations determined by the composite-system calculation.[13] The matrix elements of Q were calculated in the previous paper.[13] Therefore, the optical rotatory powers due to the lower transitions are easily calculated by use of eq 1. The results are summarized in Table III and illustrated in Figure 3.

The LE transitions to $V_7(E)$ and $V_8(A_2)$ are predicted to show large optical rotatory powers with negative and positive signs, respectively. This result is in good agreement with the observation for the (+) isomer in its signs and order of magnitude. As was discussed in the previous paper,[13] the order of energies for the $V_7(E)$ and $V_8(A_2)$ transitions seems not to depend on what approximation is employed in the calculation. Hence, we can safely conclude that (+)-$Fe(dipy)_3^{2+}$ observed by McCaffery, *et al.*,[9b] and by Hidaka and Douglas[11] is the right-handed optical isomer shown in Figure 1 for which the present calculation is made. The theoretical R(V) values for the LE transitions are larger also for $Fe(dipy)_3^{2+}$ than the observations, though the discrepancy is far less than that for $Si(acac)_3^+$. A reason for the disagreement is, again, the cancellation of the two CD bands with opposite signs. This effect, however, seems to be smaller for $Fe(dipy)_3^{2+}$ than for $Si(acac)_3^+$, as may be revealed from the fact that the splittings into the E and A_2 bands for the absorption and CD bands are not much different from each other (1000 and 1800 cm^{-1}, respectively). The rapid racemization of the complex ion in solution may be another reason for the

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[23] J. W. Richardson, W. C. Nieuwpoort, R. R. Powel, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
[24] H. H. Jaffé, *ibid.*, **21**, 258 (1953).

TABLE III

THEORETICAL AND EXPERIMENTAL OPTICAL ROTATORY POWERS DUE TO THE LOWER ELECTRONIC TRANSITIONS IN $Fe(dipy)_3^{2+}$

	Calcd						Obsd[a]			
							I		II	
State	E^b	f^c	Assignment[d]	$\langle G\|\mathbf{Q}\|V_n\rangle^{e,h}$	$\langle V_n\|\mathbf{A}\|G\rangle^h$	$R(V_n)^{f,i}$	E^g	$R(V_n)^f$	E^g	$R(V_n)^f$
$V_1(E)$	18.82	0.005	CT(7)	0.109	−0.184	0.078	18.0	0.36	18.4	0.15
$V_2(A_2)$	18.82	0.013		−0.254	−0.177	−0.087	21.0	−0.12	21.0	−0.12
$V_3(E)$	19.04	0.306		0.863	0.007	−0.025				
$V_4(E)$	31.78	0.131	CT(8)	0.437	0.033	−0.056				
$V_5(E)$	31.83	0.142		0.455	0.422	−0.741	25.3	0.12	26.0	0.01
$V_6(A_2)$	31.86	0.242		−0.839	0.324	0.525	29	0.02	...	...
$V_7(E)$	35.77	0.589	LE_1	0.873	1.557	−5.251	33.2	−1.27	33.3	−1.48
$V_8(A_2)$	37.20	0.778		−1.392	1.461	3.925	35.0	1.14	35.2	0.42
$V_9(E)$	41.44	0.069	CT(9)	0.277	0.182	−0.195				
$V_{10}(E)$	41.62	0.148		0.406	0.740	−1.161	39	0.12	...	...
$V_{11}(A_2)$	41.85	0.351		−0.881	0.877	1.491				

[a] For (+)-$Fe(dipy)_3^{2+}$; I and II are the data taken from ref 9a and 11, respectively. [b] Calculated transition energy in 10^3 cm^{-1}. [c] Calculated oscillator strength. [d] The main component of the excited state is shown. [e] In Å. [f] In 10^{-3} Å^2. [g] The peak position in the CD curve in 10^3 cm^{-1}. [h] The magnitudes in the $\mathbf{d}(A_2)$ and $\mathbf{d}(E)$ directions for the A_2 and E transitions, respectively, are shown. [i] The sum over degenerate components is shown for the E transition.

disagreement between the theoretical and observed $R(V)$ values.

The most noticeable result on the rotatory powers due to the CT transitions at ~20,000 cm^{-1} is that the transition to $V_3(E)$, which has extremely high intensity in the absorption, shows only a minor contribution to the optical rotatory power. On the other hand, the other two transitions, to $V_1(E)$ and $V_2(A_2)$, which have almost no contribution to the absorption, exhibit relatively high optical rotatory powers. In view of this, the observed two CD peaks at 18,000 and 21,000 cm^{-1} are safely assigned to the transitions to $V_1(E)$ and $V_2(A_2)$, respectively. The 19,050-cm^{-1} peak and 20,400-cm^{-1} shoulder observed in the electronic absorption spectrum were assigned, as described in detail in the preceding paper, to the vibrational structure of the transition to $V_3(E)$.[13] Thus the present result shows that the correspondence between the absorption and CD bands should not be derived simply from the apparent similarity in their peak positions.

It is difficult to compare quantitatively the theoretical and observed CD strengths of the CD band due to the CT transition at 18,000 cm^{-1} because of the large discrepancy between the two measurements.[10,11] However, the CD band due to the CT transition at 21,000 cm^{-1}, to which the two measurements give a coincident result, exhibits a rotatory power close to the theoretical value. Generally speaking, the calculated magnitude of $R(V)$ for the CT transition is less reliable than that of the LE transition, because the $R(V)$ value for the CT transition is obtained as the result of the cancellation between the small contributions of the LE configurations of high rotatory powers and the CT configuration of relatively low rotatory power. The low value of $R(V)$ for the transition to $V_3(E)$ is due to the fact that the CT configuration which is the main component of the $V_3(E)$ state has no contribution to $\langle V_3(E)|\mathbf{A}|G\rangle$ and the mixings of the upper LE configurations are very small in comparison with the other two CT states.

We give here no detailed discussion on the CD bands appearing near 30,000 cm^{-1} due to the second CT transition because no reliable CD strength can be obtained experimentally owing to the large disagreement between the two measurements. A comparison with the theoretical result indicates, however, that three CD bands due to this CT transition strongly cancel each other.

$Fe(phen)_3^{2+}$.—The calculation procedure is the same as that for $Fe(dipy)_3^{2+}$. Assuming the common bond distance, 1.39 Å, for all of the adjacent atoms, $\tau(p, q)$'s are estimated as $\tau(N, C) = -0.201$ au and $\tau(C, C) = -0.238$ au for all of the nearest neighbor carbon atoms. From these and the SCF–MO's calculated for $Q^{metal} = 0$,[15] $\lambda(p, q)$'s are calculated

$\lambda(N, C_2) = -0.528$
$\lambda(C_2, C_3) = 0.770$
$\lambda(C_3, C_4) = 1.937$
$\lambda(C_4, C_5) = 1.708$
$\lambda(C_5, C_6) = 0.313$
$\lambda(C_6, N) = -0.721$
$\lambda(C_5, C_7) = 1.395$
$\lambda(C_6, C_6') = 1.167$
$\lambda(C_7, C_7') = 2.249$

The quantity σ_i is also calculated from the SCF–MO's and from the S_{dN} which is determined to be 0.0901 by use of the double-ζ and Slater AO's for the 3dπ and nitrogen 2pπ AO's, respectively

$\sigma_3 = -0.0340$
$\sigma_4 = 0.0118$
$\sigma_5 = 0.0377$
$\sigma_6 = -0.0193$
$\sigma_7 = -0.0242$
$\sigma_8 = 0.0334$
$\sigma_9 = 0.0217$
$\sigma_{10} = 0.0112$
$\sigma_{11} = -0.0173$
$\sigma_{12} = -0.0111$

The calculated optical rotatory powers of the lower transitions of right-handed $Fe(phen)_3^{2+}$ are summarized in Table IV together with the observed values for the (+) isomer. They are also illustrated in Figure 4.

In this complex ion, a number of transitions are predicted theoretically in the near-ultraviolet region and therefore it seems to be rather difficult to relate them to the observation. However, by comparing the calculated oscillator strength with the observed absorption curve and comparing the calculated $R(V)$ values with the observed ones, it can be concluded that the observed absorption peak at 37,800 cm^{-1} and

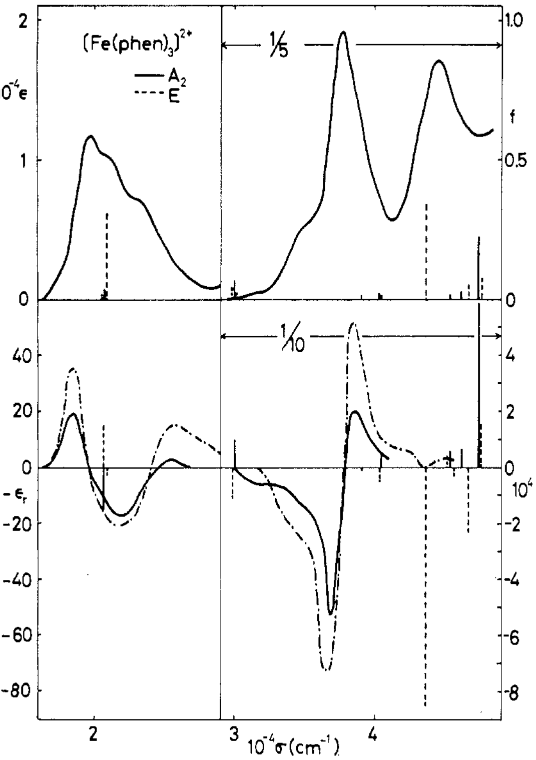

Figure 4.—The electronic absorption (upper) and circular dichroism (lower) spectra of (+)-Fe(phen)$_3{}^{2+}$. The circular dichroism spectra measured by Hidaka and Douglas and by McCaffery, *et al.*, are shown by solid and dotted curves, respectively. The theoretical results for the right-handed optical isomer are indicated by vertical lines.

shoulder at 35,000 cm^{-1} which correspond, respectively, to the CD peaks at 38,300 and 36,400 cm^{-1} are principally due to the transitions to $V_{10}(E)$ and $V_{17}(A_2)$, respectively. Besides them, there are several transitions predicted to appear in this region with moderate CD strengths. Although they cannot be recognized distinctly, they seem to be responsible for the several shoulders appearing in the CD curve.

The nature of the visible CT transition bands for Fe(phen)$_3{}^{2+}$ is similar to that for Fe(dipy)$_3{}^{2+}$. The transition to $V_3(E)$, which is intense in the absorption, gives a minor contribution to CD, whereas the other two transitions to $V_1(E)$ and $V_2(A_2)$, which have almost no contribution to the absorption, seem to be responsible for the CD peaks at 18,500 and 22,000 cm^{-1}, respectively.

There were two different opinions about the absolute configuration of this complex ion. McCaffery, *et al.*,[9a] proposed, on the basis of "solubility criterion," that (−)-Fe(phen)$_3{}^{2+}$ is the same type of optical isomer as (+)-Fe(dipy)$_3{}^{2+}$. Hidaka and Douglas[11] stated, however, that (+)-Fe(phen)$_3{}^{2+}$ corresponds to (+)-Fe(dipy)$_3{}^{2+}$ on the basis of similarity of the CD spectra. Comparing the present theoretical result with the observation, it is reasonable to assign (+)-Fe(phen)$_3{}^{2+}$, as well as (+)-Fe(dipy)$_3{}^{2+}$, to the right-handed isomers illustrated in Figure 1. This result is well coincident with that derived by the aid of an X-ray crystal analysis technique.[25]

McCaffery and Mason[9b] measured the CD spectrum of (−)-Ru(phen)$_3{}^{2+}$. The CD bands due to the LE transitions appearing in the near-ultraviolet region are very similar to those of (+)-Fe(phen)$_3{}^{2+}$ in their shapes and signs. Hence we conclude that the (−) isomer of the Ru complex has the same absolute configuration (right-handed type) as the (+) isomer of the Fe complex.

Concerning the electronic absorption spectrum, the Ru complex exhibits the CT absorption band in the 20,000-cm^{-1} region which is very similar in its shape to the Fe complex. The intensity of the band of the Ru complex is, however, considerably higher than that of the Fe complex. This indicates that the Ru complex has a higher S_{dN} value and, hence, a higher metal–ligand resonance integral value than the Fe complex. The fact that the two complex ions exhibit opposite CD signs in the visible region may be understood as due to the difference in S_{dN} and, therefore, in the metal–ligand resonance integral.[26] The former contributes to the matrix elements of Λ between the ground and CT configurations and the latter determines the degree of the mixings of the LE configurations with the CT configuration. This seems to mean that these two quantities give a great effect to the CD strength of the CT bands in the visible region.

The Coupled-Oscillator Model and Determination of Absolute Configuration.—It seems to be interesting to examine the relation of the present treatment to the coupled-oscillator approximation. The latter is expected to be applicable to the LE transition when there is a weak, if any, interaction with the CT transition. Let us consider the integral $\langle LE^a|\Lambda|G\rangle$ as an example. If the operator Λ is expressed in terms of the xyz coordinate system (Figure 1)

$$\langle LE^a|\Lambda|G\rangle = \left[\langle LE^a|\Lambda_z|G\rangle - d\left\langle LE^a\left|\frac{\partial}{\partial x}\right|G\right\rangle\right]\cdot\mathbf{k} \quad (24)$$

According to the coupled-oscillator model, the first term is dropped out and the second term is replaced as

$$\left\langle LE^a\left|\frac{\partial}{\partial x}\right|G\right\rangle = -(m/\hbar^2)\cdot E\cdot\langle LE^a|x|G\rangle = -(m/\hbar^2)\cdot E\cdot Q \quad (25)$$

where E is the transition energy, d is the distance from the metal to the origin of the xyz system, and Q is defined in eq 9. Hence

$$\langle LE^a|\Lambda|G\rangle \simeq (m/\hbar^2)\cdot d\cdot E\cdot Q\cdot\mathbf{k} \quad (26)$$

The calculation of the two terms in eq 24 without invoking eq 25 shows that the neglect of the first term brings about a 15% error into $\langle LE^a|\Lambda|G\rangle$. The

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[25] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst.*, **21A**, 154 (1966), show that (−)-Fe(phen)$_3{}^{2+}$ is the left-handed isomer.

[26] On the other hand, since the CD strength of the LE band in the near-ultraviolet region should be insensitive to S_{dN}, the optical isomers of the same absolute configuration should exhibit the CD bands of the same sign and of similar shapes in this region.

TABLE IV

THEORETICAL AND EXPERIMENTAL OPTICAL ROTATORY POWERS DUE TO THE LOWER ELECTRONIC TRANSISIONS IN $Fe(phen)_3^{2+}$

	Calcd						Obsd			
							I[a]		II[b]	
State	E^c	f^d	Assignment[e]	$\langle G\|\mathbf{Q}\|V_n\rangle^{f,g}$	$\langle V_n\|\mathbf{A}\|G\rangle^f$	$R(V_n)^{h,i}$	E^j	$R(V^n)^h$	E^j	$R(V_n)^h$
$V_1(E)$	20.75	0.013	CT(8)	−0.167	0.229	0.148	18.5	0.22	18.5	0.12
$V_2(A_2)$	20.75	0.030	CT(8)	0.364	0.222	0.156	22.0	−0.22	22.2	−0.16
$V_3(E)$	20.89	0.306	CT(8)	−0.823	−0.007	−0.023				
$V_4(E)$	29.91	0.231	CT(9)	0.598	0.479	−1.107	26.0	0.16	25.0	0.00
$V_5(A_2)$	30.01	0.321	CT(9)	−0.995	0.512	0.983				
$V_6(E)$	30.09	0.113	CT(9)	0.418	−0.025	0.041				
$V_7(E)$	39.04	0.064	LE_1	0.276	0.129	−0.138				
$V_8(E)$	40.39	0.080	LE_2	0.303	0.859	−1.004				
$V_9(A_2)$	40.44	0.059	LE_2	−0.367	0.686	0.485				
$V_{10}(E)$	43.66	1.706	$LE_3 + LE_4$	1.345	1.633	−8.479	36.4	−3.69	36.8	−2.29
$V_{11}(E)$	45.18	0.007	$LE_3 + LE_4$	0.084	−1.100	0.356				
$V_{12}(A_2)$	45.38	0.085	$CT(11) + LE_3 + CT(10)$	−0.416	0.773	0.621				
$V_{13}(E)$	45.65	0.018	CT(11)	0.136	0.598	−0.313				
$V_{14}(A_2)$	46.17	0.129	$CT(11) + LE_3 + CT(10)$	−0.509	0.663	0.651				
$V_{15}(E)$	46.39	0.005	CT(11)	−0.068	−0.002	−0.001				
$V_{16}(E)$	46.72	0.265	CT(10)	−0.513	−1.154	−2.284				
$V_{17}(A_2)$	47.41	1.074	$CT(10) + LE_3$	1.448	−2.109	5.898	38.3	2.16	38.4	0.71
$V_{18}(E)$	47.63	0.378	CT(10)	0.606	−0.656	1.536				
$V_{19}(E)$	52.23	0.162	LE_6	0.378	0.002	0.003				
$V_{20}(A_2)$	53.09	0.098	LE_5	0.414	−1.413	1.131				

[a] Taken from ref 9a, where the CD curve for $(-)$-$Fe(phen)_3^{2+}$ is shown. We show here the *R*(V) values for the (+) isomer for the convenience of comparison. [b] For (+)-$Fe(phen)_3^{2+}$, taken from ref 11. [c] Calculated transition energy in 10^3 cm^{-1}. [d] Calculated oscillator strength. [e] Main components of the transition are indicated. [f] The magnitudes in the $\boldsymbol{\sigma}(A_2)$ and $\boldsymbol{\sigma}(E)$ directions for the A_2 and E transitions, respectively, are shown. [g] In Å. [h] In 10^{-3} Å^2. [i] The sum over degenerate components is shown for the E transition. [j] The peak position in the CD curve in 10^3 cm^{-1}.

calculation by use of eq 26 gives $\langle LE^a|\mathbf{A}|G\rangle = 2.022$ in comparison with the present value, 2.038. Thus the coupled-oscillator model is a fairly good approximation for the LE band of $Si(acac)_3^+$. The error brought about by the coupled-oscillator approximation may become larger for the dipyridyl and phenanthroline complexes since the size of the ligand molecule becomes larger in comparison with *d*.

As was already made clear, the absolute configuration of the optical isomer can be determined by examining the CD signs of the LE transitions. If the observed LE band is due to the *y*-polarized ligand $\pi-\pi^*$ transition, it exhibits a single absorption band due to the E transition and it does not contribute to the rotatory power at least in the zeroth-order approximation. Although it gains the optical rotatory power through the mixing with CT configurations, its power is usually far less than the LE band due to the *x*-polarized $\pi-\pi^*$ transition. The latter usually exhibits extremely high optical rotatory power and is split into the E and A_2 components in the absorption spectrum. Furthermore, the A_2 component is always in the higher energy and twice as intense as the E component.[27] The coupled-oscillator model gives the following expression for the A_2 transition

$$\langle\Psi(A_2)|\mathbf{A}|G\rangle \simeq (m/\hbar^2)dEQ\cdot\boldsymbol{\sigma}(A_2)$$

From this and eq 9, we obtain

$$R(A_2) = -R(E) = (2)^{-1/2}(e^2/\hbar c)dEQ^2$$

which is always positive. Therefore, if the interaction with the CT configuration is weak and if the coupled-oscillator model gives at least a correct sign for the magnetic moment, the determination of the absolute configuration is straightforward without any detailed calculation by examining the signs of the observed CD band due to the LE transition with the character of the *x*-polarized $\pi-\pi^*$ transition. If the mixing of the CT transition is very strong, as is the case for $Fe(phen)_3^{2+}$, the theoretical calculation may be necessary in order to determine the absolute configuration.

Appendix

Proofs for Eq 15 and 16.—We first prove eq 15b. By the definition of eq 14

$$\tau(q, p) = \int \chi_p \frac{\partial}{\partial \xi_q} \chi_q d\xi_q d\eta_q d\zeta_q$$

By the partial integration and by use of the relations

$$\xi_q = -\xi_p + R_{pq}$$

$$d\xi_q d\eta_q d\zeta_q = d\xi_p d\eta_p d\zeta_p$$

where R_{pq} is the distance between atoms p and q

$$\tau(q, p) = -\int \chi_q \frac{\partial}{\partial \xi_q} \chi_p d\xi_q d\eta_q d\zeta_q$$

$$= \int \chi_q \frac{\partial}{\partial \xi_p} \chi_p d\xi_p d\eta_p d\zeta_p$$

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(27) In contrast to MacCaffery and Mason's assignment which is based on the Orgel's theory (L. E. Orgel, *J. Chem. Soc.*, 3683 (1961)), our theoretical treatment shows that the principal factor to determine the splitting is the interligand transition dipole interaction. The latter always lowered the energy of the E component with respect to the A_2 component in the D_3 symmetry.

$$\tau(\mathrm{q},\, \mathrm{p}) = \tau(\mathrm{p},\, \mathrm{q})$$

Equation 15a is easily proved by use of

$$\theta_{\mathrm{qp}} = \pi + \theta_{\mathrm{pq}}$$

$$X_{\mathrm{q}} = X_{\mathrm{p}} - R_{\mathrm{pq}} \cos \theta_{\mathrm{pq}}$$

$$Y_{\mathrm{q}} = Y_{\mathrm{p}} - R_{\mathrm{pq}} \sin \theta_{\mathrm{qp}}$$

as

$$\begin{aligned} \lambda(\mathrm{q},\, \mathrm{p}) &= (X_{\mathrm{q}} \sin \theta_{\mathrm{qp}} - Y_{\mathrm{q}} \cos \theta_{\mathrm{qp}}) \cdot \tau(\mathrm{q},\, \mathrm{p}) \\ &= -(X_{\mathrm{p}} \sin \theta_{\mathrm{pq}} - Y_{\mathrm{p}} \cos \theta_{\mathrm{pq}}) \cdot \tau(\mathrm{p},\, \mathrm{q}) \\ &= -\lambda(\mathrm{p},\, \mathrm{q}) \end{aligned}$$

We next give the derivation of eq 16. Assuming the Slater AO's for χ_{p} and χ_{q}, $\tau(\mathrm{p},\, \mathrm{q})$ can be reduced as

$$\tau(\mathrm{p},\, \mathrm{q}) = -\alpha_{\mathrm{p}} \langle \chi_{\mathrm{q}} | \xi_{\mathrm{p}}/R_{\mathrm{p}} | \chi_{\mathrm{p}} \rangle$$

where R_{p} is the distance from atom p. By use of the Mulliken-type approximation

$$\begin{aligned} \tau(\mathrm{p},\, \mathrm{q}) &\simeq (-\alpha_{\mathrm{p}} S_{\mathrm{qp}}/2) [\langle \chi_{\mathrm{q}} | \xi_{\mathrm{p}}/R_{\mathrm{p}} | \chi_{\mathrm{q}} \rangle + \langle \chi_{\mathrm{p}} | \xi_{\mathrm{p}}/R_{\mathrm{p}} | \chi_{\mathrm{p}} \rangle] \\ &= (-\alpha_{\mathrm{p}} S_{\mathrm{qp}}/2) \langle \chi_{\mathrm{q}} | \xi_{\mathrm{p}}/R_{\mathrm{p}} | \chi_{\mathrm{q}} \rangle \end{aligned}$$

since $\langle \chi_{\mathrm{p}} | \xi_{\mathrm{p}}/R_{\mathrm{p}} | \chi_{\mathrm{p}} \rangle = 0$. If we calculate the integral in the last equation and take up to the second power of $(\alpha_{\mathrm{q}} R_{\mathrm{pq}})^{-1}$

$$\tau(\mathrm{p},\, \mathrm{q}) \simeq -(\alpha_{\mathrm{p}} S_{\mathrm{qp}}/2) [1 - 3(\alpha_{\mathrm{q}} R_{\mathrm{pq}})^{-2}]$$

In order to retain the Hermitian character, we take the average of $\tau(\mathrm{q},\, \mathrm{p})$ and $\tau(\mathrm{p},\, \mathrm{q})$. Then

$$\begin{aligned} \tau(\mathrm{q},\, \mathrm{p}) &= \tau(\mathrm{p},\, \mathrm{q}) \\ &\simeq -(\bar{\alpha} S_{\mathrm{pq}}/2) [1 - 3(1 + t^2) p^{-2}] \end{aligned}$$

where the parameters p and t are defined in the usual manner as

$$p = (\alpha_{\mathrm{p}} + \alpha_{\mathrm{q}}) R_{\mathrm{pq}}/2$$

$$t = (\alpha_{\mathrm{p}} - \alpha_{\mathrm{q}})/(\alpha_{\mathrm{p}} + \alpha_{\mathrm{q}})$$

For the $2\mathrm{p}\pi$ AO's of hydrocarbons including nitrogen or oxygen as a heteroatom, p and t fall in the ranges: $4 \leq p \leq 6$ and $|t| \leq 0.2$. Therefore we can omit the second term to obtain

$$\begin{aligned} \tau(\mathrm{q},\, \mathrm{p}) &= \tau(\mathrm{p},\, \mathrm{q}) \\ &\simeq -\bar{\alpha} S_{\mathrm{pq}}/2 \end{aligned}$$

On the other hand, $\tau(\mathrm{q},\, \mathrm{p})$ can be calculated exactly as

$$\begin{aligned} \tau(\mathrm{q},\, \mathrm{p}) = -(2R_{\mathrm{pq}})^{-1} p^{-3} (3 + 3p + p^2) e^{-p} (1 - t^2)^{7/2} \times \\ t^{-5} [(3 - 3pt + p^2 t^2) e^{pt} - (3 + 3pt + p^2 t^2) e^{-pt}] \end{aligned}$$

Comparing the exact value calculated from this formula with the approximate value, the latter is found to be not so good because of the error brought about by the Mulliken approximation. Therefore we put a constant on the approximate formula and determine it to give the best fit to the exact values in the above-mentioned ranges of p and t. The constant was determined to be 1.16 to give eq 16. This approximation gives the value within the error of a few per cent in the above-mentioned ranges of p and t.

The Invariance of R with Respect to Coordinate Transformation.—Suppose the coordinate transformation between the systems $(x,\, y,\, z)$ and $(x',\, y',\, z')$ is defined as

$$\mathbf{q} = A\mathbf{q}' + \mathbf{q}_0'$$

where $\mathbf{q}$ and $\mathbf{q}'$ are vectors in $(x,\, y,\, z)$ and $(x',\, y',\, z')$ spaces, respectively, $\mathbf{q}_0'$ is the vector representing the translation of origin, and A is a unitary matrix. Then, the inner product $\langle \mathrm{G} | \mathbf{q} | V \rangle \cdot \langle V | \mathbf{q} \times \boldsymbol{\nabla} | \mathrm{G} \rangle$, which determines the rotating power, is transformed as

$$\begin{aligned} \langle \mathrm{G} | A\mathbf{q}' | \mathrm{V} \rangle \cdot \langle \mathrm{V} | (A\mathbf{q}') \times (A\boldsymbol{\nabla}') | \mathrm{G} \rangle + \\ \langle \mathrm{G} | A\mathbf{q}' | \mathrm{V} \rangle \cdot [\mathbf{q}_0' \times \langle \mathrm{V} | A\boldsymbol{\nabla}' | \mathrm{G} \rangle] \end{aligned}$$

By use of the relation $(A\mathbf{q}') \times (A\boldsymbol{\nabla}') = A(\mathbf{q}' \times \boldsymbol{\nabla}')$ and of the orthogonality of wave functions, the first and second terms of the above equation are, respectively, written as

$$\langle \mathrm{G} | \mathbf{q}' | \mathrm{V} \rangle \cdot \langle \mathrm{V} | \mathbf{q}' \times \boldsymbol{\nabla}' | \mathrm{G} \rangle$$

and

$$\langle \mathrm{G} | \mathbf{q}' | \mathrm{V} \rangle \cdot [\mathbf{q}_0 \times \langle \mathrm{V} | \boldsymbol{\nabla}' | \mathrm{G} \rangle]$$

where $\mathbf{q}_0 = \tilde{A}\mathbf{q}_0'$, $\tilde{A}$ being the transposed matrix of A.

Hence, if the second term vanishes for any value of $\mathbf{q}_0$, the inner product is invariant under any coordinate transformation. As was pointed out by Moffitt,[28] the second term cannot generally be said to vanish for approximate wave functions as those employed here, because eq 25 does not hold. However, in our case, in which molecules have the D_3 symmetry, it can be proved to vanish by symmetry consideration.

If the excited state V belongs to the irreducible representation A_2, both of the vectors $\langle \mathrm{G} | \mathbf{q}' | \mathrm{V} \rangle$ and $\langle \mathrm{V} | \Delta' | \mathrm{G} \rangle$ are parallel to the C_3 rotation axis, and, therefore, the second term vanishes. For the excited state belonging to the representation E, we can choose any orthogonal set for the degenerate pair of wave functions. However, if we choose any one set, $\psi_{\mathrm{V}}(\mathrm{E})$ and $\psi_{\mathrm{V}}(\mathrm{E})'$, the vectors $\langle \mathrm{G} | \mathbf{q}' | \mathrm{V} \rangle$ and $\langle \mathrm{G} | \mathbf{q}' | \mathrm{V}' \rangle$ are uniquely determined in the plane perpendicular to the C_3 axis and $\langle \mathrm{V} | \boldsymbol{\nabla}' | \mathrm{G} \rangle$ and $\langle \mathrm{V}' | \boldsymbol{\nabla}' | \mathrm{G} \rangle$ are also parallel to $\langle \mathrm{G} | \mathbf{q}' | \mathrm{V} \rangle$ and $\langle \mathrm{G} | \mathbf{q}' | \mathrm{V}' \rangle$, respectively. Hence the second term vanishes again for any $\mathbf{q}_0$ and the inner product can be said to be invariant under any coordinate transformation if the wave functions are the bases of irreducible representations.

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(28) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).