compared with available parameters for terminal group exchange in other group IIIb metal β-diketonates. Based on the frequency factor observed for isomerization of *cis*-Co(tfac)$_3$, Fay and Piper[7] estimated the activation energy for exchange of trifluoromethyl groups in Ga(tfac)$_3$ in deuteriochloroform solution to be 20.8 ± 1.6 kcal/mol; the activation energy was estimated to be somewhat higher for Al(tfac)$_3$, 23.5 ± 1.8 kcal/mol, and appreciably lower for In(tfac)$_3$, $<$13.5 ± 1.1 kcal/mol. Fortman and Sievers[8] used the simplified Gutowsky–Holm equation to obtain first-order rate constants for terminal group exchange in Al(acac)$_2$(hfac), Al(thd)$_2$(acac), and Al(thd)$_2$(hfac), where thd = dipivaloylmethanate, in chlorobenzene solution. The reported activation energies and the activation entropies which we calculate from the reported values of log A are, respectively: 2.7 kcal/mol and -46 eu for Al(acac)$_2$(hfac); 6.4 kcal/mol and -39 eu for Al(thd)$_2$(acac); 7.0 kcal/mol and -30 eu for Al(thd)$_2$(hfac). Despite the different nature of the metal ion and solvent, the latter activation parameters, especially those for Al(acac)$_2$(hfac), are in serious disagreement with the parameters reported here. The disagreement is attributed to temperature-dependent solvation effects which were not considered in obtaining values of $\delta\nu$ for the aluminum(III) complexes. If we take the largest observed frequency separation for Ga(acac)$_2$(bzbz) in benzene, 12.15 Hz at 15°, to be equal to $\delta\nu$ and attribute the temperature dependence of $\delta\nu_e$ above 15° to exchange effects (*cf.* Figure 4), which would be equivalent to the procedure used by Fortman and Sievers, then we also obtain a low activation energy, 4.6 ± 0.8 kcal/mol, and an unreasonably large, negative activation entropy, -42 ± 2 eu.

Based on the reported frequency separations for Al(thd)$_2$(acac), values of $\delta\nu_e$ and corrected values of $\delta\nu$ at four temperatures in the region of exchange give $E_a \simeq 19$ kcal/mol and $\Delta S^* \simeq -6$ eu. Insufficient data are reported for Al(acac)$_2$(hfac) and Al(thd)$_2$(hfac) in the region of exchange, but the frequency separations for Al(acac)$_2$(hfac) clearly indicate an appreciable temperature dependence for $\delta\nu$. Thus the desirability of correcting $\delta\nu$ for temperature-dependent solvation effects is to be emphasized.

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The Electronic Structure of the Tris(α,α′-dipyridyl)iron(II) Ion

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The π-electron structure of the tris(α,α′-dipyridyl)iron(II) ion was theoretically studied by the method of composite system, with the results successful in explaining the observed peak positions and intensities of the electronic absorption spectrum. According to the results, the bands at ~20,000 and 33,600 cm^{-1} were assigned, respectively, to the charge-transfer transition from the metal to the lowest vacant MO of the ligand and to the π–π* transition within the ligand π-electron system. The other two bands at ~29,000 and ~40,000 cm^{-1} with several shoulders were assigned to the charge-transfer transition to the second lowest vacant MO and to the third charge-transfer transition mixing with the second π–π* transition in the ligand, respectively. The ground state was calculated to be stabilized by 0.86 eV by the charge-transfer interaction of π electrons between the metal ion and the ligand. This can explain the remarkable stability of the complex ion. The nature of the excited states was also discussed in detail, with the result that the transferred electron is delocalized on the whole ligand π-electron system, in contrast with the current view that the character of the charge-transfer transition is predominantly determined by the α-diimine skeleton.

Introduction

In previous papers,[1] we developed a theoretical method to treat the π-electron structures of metal complexes containing organic unsaturated molecules as ligands. The method was shown to be successfully applied to the tris-acetylacetonato complexes of the iron-series transition metal ions.

In the present paper, the theory is applied to a well-known complex ion, tris(α,α′-dipyridyl)iron(II).[2] This complex ion has long been an interesting research subject in view of its great stability, of the extremely strong charge-transfer absorption band appearing in the visible region, and also of the application to analytical chemistry. Several authors have extensively

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(1) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, in press.

(2) Hereafter abbreviated to Fe(dipy)$_3^{2+}$.

studied its physicochemical properties such as the electronic absorption spectra,[3-10] the polarized crystal spectra,[11] the infrared spectrum,[10,12,13] the nuclear magnetic resonance spectrum,[14] the circular dichroism,[15,16] and the Mössbauer effect.[17] Some thermodynamic and electrical properties[18,19] were also reported.

Judging from the fact that the strong metal–ligand charge-transfer band appears in the visible region, the complex ion may be expected to have a great contribution of the charge-transfer configuration in the ground state and, therefore, to be greatly stabilized through the metal–ligand π bonding.

In view of this, the present work has been performed in order to clarify the nature of the metal–ligand π bonding in $Fe(dipy)_3^{2+}$ and also to understand the characteristics of its electronic absorption spectra on the basis of the π-electron structure. Since the simple Hückel calculation already made with this complex ion is unsuitable to the above purposes, we adopt in the present study the theoretical treatment which considers explicitly the interelectronic interaction.

Theory

In the present study, the π-electron structure of the complex ion is treated by the composite-system method[1,20] in which the π-electron structure of the complex is calculated by the configuration interaction between several electron configurations constructed by putting π electrons in the metal 3d AO's and ligand π MO's.

Therefore, first of all, we must calculate the π-electron structure of α,α'-dipyridyl in the complex ion which is strongly affected by the electrostatic potential field caused by the central metal ion and the other two ligands. We made the Pariser–Parr–Pople SCF–CI calculation[21] on the π-electron system of the ligand taking into account the influence of the electrostatic field. Details of this treatment were described in previous papers.[1] The interatomic distances in the ring are all taken to be equal to the benzene value, 1.39 Å. The distance between the α- and α'-carbon atoms is taken to be 1.50 Å. They are assumed on the basis of the X-ray crystal analysis data for the free α,α'-dipyridyl.[22,23] The resonance integrals between the two adjacent carbon $2p\pi$ AO's in the ring are all taken to be equal to the benzene value, -2.39 eV.[21] Those between the carbon and nitrogen AO's and between the carbon atoms at α and α' positions were estimated to be -1.79 and -1.98 eV, respectively, on the basis of their proportionality to the overlap integrals. The calculated transition energies and oscillator strengths are shown in Table I. In this table the results for the free molecule in both *trans* and *cis* forms are also shown for the purpose of comparison.[24]

TABLE I

CALCULATED LOWER EXCITED STATES OF α,α'-DIPYRIDYL

	Free *cis*		Free *trans*		In complex[a]	
Symmetry[b]	Transition energy, 10^3 cm^{-1}	Oscillator strength	Transition energy, 10^3 cm^{-1}	Oscillator strength	Transition energy, 10^3 cm^{-1}	Oscillator strength
A	34.14	0.313	33.35	0.360	29.54	0.550
S	35.39	0.011	35.87	0.000	37.35	0.103
A	39.32	0.015	39.47	0.007	38.80	0.000
S	41.76	0.013	41.59	0.000	40.72	0.073
A	46.98	1.407	47.35	1.377	48.30	0.213
S	49.84	0.037	48.92	0.000	48.31	0.303
S	53.09	0.652	54.60	0.000	50.42	0.726
A	55.50	0.646	54.60	1.506	54.67	0.688

[a] The SCF–CI result calculated by taking into account the electrostatic effect caused by the metal and the other two ligands. [b] S and A denote that the excited state is symmetric and antisymmetric, respectively, with respect to the symmetry plane of the α,α'-dipyridyl molecule which is perpendicular to the molecular plane.

With the aid of the ligand MO's obtained by the above-mentioned SCF calculation under the effect of electrostatic field and the metal 3d AO's, we can construct various electron configurations which are classified into three types: the ground, LE (locally excited), and CT (charge-transfer) configurations.

Although the molecular structure of $Fe(dip)_3^{2+}$ has not been known, it seems to be reasonable to assume the structure shown in Figure 1. This is because the X-ray crystal structure analysis data on some other dipyridyl complexes have confirmed similar molecular structures.[25,26] The spin state of the complex ion has been found to be singlet.[27] This indicates that the six 3d electrons of the Fe^{2+} ion occupy the three $3d\pi$ ($3d_{xy}$, $3d_{yz}$, and $3d_{zx}$) AO's with paired spins.

The wave function for the ground configuration can be expressed as

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(23) In the actual molecule, there are small deviations from the value, 1.39 Å, for the interatomic distances in the ring. However, we neglect these deviations for the sake of simplicity.

(24) The X-ray crystal analysis technique shows that the molecule is in the *trans* form with the two pyridine rings coplanar.[22] The molecular structure in solution is uncertain but the dipole moment measurement indicates that the two pyridine rings are not coplanar. Since there are some ambiguities in the free α,α'-dipyridyl molecule, we calculated its π-electron structure for both the *trans* and the *cis* forms assuming the coplanar structure.

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$$G = |(1\bar{1}\ldots 6\bar{6})^{a}(1\bar{1}\ldots 6\bar{6})^{b}(1\bar{1}\ldots 6\bar{6})^{c}d_1d_1d_2\bar{d}_2d_3\bar{d}_3| \quad (1)$$

where numbers $i = 1\text{–}6$ in the parentheses denote the occupied π-MO's φ_i's of the ligands, superscripts a, b, and c denote three ligands as indicated in Figure 1, and d_1, d_2, and d_3 represent the $3d\pi$ AO's d_{xy}, d_{yz}, and d_{zx}, respectively.

The spin-singlet basis functions for the LE configurations can be constructed from eq 1 by removing an electron in occupied MO φ_i to vacant MO φ_k

$$\begin{aligned} LE^{a}(i \rightarrow k) = (2)^{-1/2}[&|(1\bar{1}\ldots i\bar{k}\ldots 6\bar{6})^{a}(1\bar{1}\ldots 6\bar{6})^{b} \times \\ &(1\bar{1}\ldots 6\bar{6})^{c}d_1\bar{d}_1d_2\bar{d}_2d_3\bar{d}_3| + |(1\bar{1}\ldots k\bar{i}\ldots 6\bar{6})^{a} \times \\ &(1\bar{1}\ldots 6\bar{6})^{b}(1\bar{1}\ldots 6\bar{6})^{c}\, d_1\bar{d}_1d_2\bar{d}_2d_3\bar{d}_3|\,] \end{aligned} \quad (2)$$

In actuality the wave function Ψ_m for the mth excited state in the ligand was evaluated by the SCF–CI calculation taking into account the electrostatic field of the metal and the other two ligands

$$\Psi_m = \sum_{i,k} \lambda_{ik}{}^{m}\Psi(i \rightarrow k) \quad (3)$$

Here $\lambda_{ik}{}^{m}$'s are coefficients determined by CI calculation and $\Psi(i \rightarrow k)$'s are the configuration wave functions corresponding to the $i \rightarrow k$ excitation within one of the ligands. Therefore, it is convenient to take the LE wave function in the following form instead of eq 2

$$LE_m{}^{a} = \sum_{i,k} \lambda_{ik}{}^{m}LE^{a}(i \rightarrow k) \quad (4)$$

The similar wave functions $LE_m{}^{b}$ and $LE_m{}^{c}$ can be obtained for the excitation in ligands b and c, respectively. The functions $LE_m{}^{a}$, $LE_m{}^{b}$, and $LE_m{}^{c}$ are combined together to make the bases of the irreducible representation of the D_3 symmetry of the complex ion

$$\begin{aligned} LE_m(A_1 \text{ or } A_2) &= (3)^{-1/2}[LE_m{}^{a} + LE_m{}^{b} + LE_m{}^{c}] \\ LE_m(E) &= (2)^{-1/2}[LE_m{}^{a} - LE_m{}^{b}] \\ LE_m{}'(E) &= (6)^{-1/2}[2LE_m{}^{c} - LE_m{}^{a} - LE_m{}^{b}] \end{aligned} \quad (5)$$

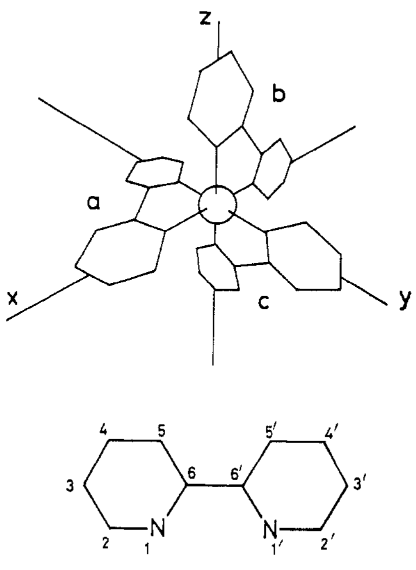

Figure 1.—Geometrical structure of Fe(dipy)$_3{}^{2+}$ (upper) and the numbering of ligand atoms (lower).

The first one of eq 5 belongs to A_1 if $\varphi_i \times \varphi_k$ is symmetric with respect to the symmetry plane of the ligand molecule; otherwise it belongs to A_2.

The CT wave function is constructed by removing an electron from one (for example d_1) of the $3d\pi$ AO's to a vacant MO φ_k of one (for example a) of three ligands. The basic function is, for example

$$\begin{aligned} CT_1{}^{a}(k) = (2)^{-1/2}[&|(1\bar{1}\ldots 6\bar{6})^{a}(1\bar{1}\ldots 6\bar{6})^{b} \times \\ &(1\bar{1}\ldots 6\bar{6})^{c}\varphi_k{}^{a}\bar{d}_1d_2\bar{d}_2d_3\bar{d}_3| + |(1\bar{1}\ldots 6\bar{6})^{a}(1\bar{1}\ldots 66)^{b} \times \\ &(1\bar{1}\ldots 6\bar{6})^{c}d_1\bar{\varphi}_k{}^{a}d_2\bar{d}_2d_3\bar{d}_3|\,] \end{aligned} \quad (6)$$

There are nine wave functions of this type corresponding to the electron transfer from the three $3d\pi$ AO's to the three π-MO's $\varphi_k{}^{a}$, $\varphi_k{}^{b}$, and $\varphi_k{}^{c}$. The linear combination of these wave functions brings about the CT wave functions CT(k)'s which are the bases of the D_3 group.

The matrix elements between the LE configurations are[28]

$$\begin{aligned} A_1 \text{ or } A_2:\quad & \langle LE_m|H|LE_m\rangle = E_m + 2D_{mm} \\ & \langle LE_m|H|LE_n\rangle = 2D_{mn} \\ E:\quad & \langle LE_m|H|LE_m\rangle = E_m - D_{mm} \\ & \langle LE_m|H|LE_n\rangle = -D_{mn} \\ & \langle LE_m|H|LE_n{}'\rangle = -(3)^{1/2}D_{mn} \end{aligned} \quad (7)$$

where E_m is the excitation energy of the mth transition obtained from the above-mentioned SCF–CI calculation of the ligand π-electron system. D_{mn} is the interaction energy of the transition dipoles accompanied with the mth transition in ligand a and nth transition in ligand b. It is calculated by use of the dipole approximation.

The diagonal elements of the CT configurations corresponding to the electron transfer to the ligand vacant MO φ_k are all equal to $E_{CT}(k)$ defined as

$$E_{CT}(k) = I(3d\pi) - A(k) - J(3d\pi, \varphi_k) \quad (8)$$

where $I(3d\pi)$ is the valence-state ionization potential for removing a $3d\pi$ electron under the potential field caused by three ligands, $A(k)$ is the electron affinity to put an electron into the vacant MO φ_k, and $J(3d\pi, \varphi_k)$ represents the Coulomb repulsion integral between the electrons in the $3d\pi$ AO and in MO φ_k of any one of three ligands. The valence-state ionization potential of the metal is obtained from the analysis of atomic spectroscopic data.[29] $A(k)$ is estimated as[30]

$$A(k) \simeq -(\epsilon_k + 1.7)\ \text{eV} \quad (9)$$

where ϵ_k is the calculated orbital energy of the vacant MO φ_k.

The off-diagonal element between CT(k) and CT(l) is nonvanishing for the case of a nonzero value of the integral $(3d\pi, 3d\pi|\varphi_k, \varphi_l)$ which is calculated by use of the point-charge approximation.

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(28) Note that the right-hand side of the fourth equation in eq 7 vanishes if the mth and nth transitions belong to the different symmetry. Similarly, the right-hand side of the last equation vanishes if they belong to the same symmetry.

(29) I. Hanazaki and S. Nagakura, to be submitted for publication.

(30) The details of this equation were described in ref 1.

The off-diagonal matrix elements between the CT and ground configurations and between the CT and LE configurations are reduced to the form $c \times \beta_{MN}$, where c is a unique constant for each off-diagonal element. The resonance integral β_{MN} between the metal 3dπ AO and the 2pπ AO of nitrogen is determined by use of the relation

$$\beta_{MN} = -S_{MN}(I_M + I_N)/2 \qquad (10)$$

The quantity S_{MN} is the overlap integral between the metal 3dπ and nitrogen 2pπ AO's and is calculated assuming the double-ζ AO[31] and Slater AO for the metal 3dπ and nitrogen 2pπ AO's, respectively.[32] The metal–nitrogen distance is determined to be 2.04 Å on the assumption that the ligand is coordinated to the metal retaining its molecular geometry (Figure 1) unaltered.[33] I_M and I_N are the ionization potentials of the metal 3dπ and nitrogen 2pπ AO's, respectively.

Results and Discussion

The π-Electron Structure of α,α'-Dipyridyl.—First of all, we discuss the π-electron structure of the free molecule, comparing the calculated transition energies and oscillator strengths given in Table I with the observed absorption bands. The α,α'-dipyridyl molecule shows absorption bands at 35,600 and 42,600 cm^{-1} with a shoulder at 40,800 cm^{-1} in methanol solution. The oscillator strengths of these two bands are 0.26 and 0.23, respectively. The observed lowest transition band at 35,600 cm^{-1} is in good agreement with the calculated values for the lowest transition in its energy and intensity. The observed band at 42,600 cm^{-1} and the shoulder at 40,800 cm^{-1} are not in good agreement with the theoretical predictions of their intensities. This disagreement may be removed if we assume that the two pyridine rings are not coplanar in solution but rotate toward each other forming a dihedral angle.[19] If so, the calculated transitions in the 35,000–45,000-cm^{-1} region may borrow intensities through further mixings with the high-intensity transitions in the higher energy region.

The main features of the calculated lower transitions differ little from each other in the *cis* and *trans* forms. Therefore, it is difficult to determine from the comparison of the theoretical results with the observed absorption spectrum whether the free molecule takes the *trans* or *cis* form.

Now let us examine the effect of the electrostatic field caused by the metal ion and the other ligands. The potential field working on the ligand under consideration depends on the σ-electron distribution in the metal 3dσ, 4s, 4p, and nitrogen lone pair AO's. Hence, we calculate three cases: $Q^{\text{metal}} = 2$, 1, and 0. Except for $Q^{\text{metal}} = 2$, the plus charge is distributed on the ligands, in particular on the σ AO's which make the dative bond with the metal. The charge on each of these σ AO's turns out $+^1/_6$ and $+^1/_3$ for $Q^{\text{metal}} = 1$ and 0, respectively, on the assumption that it is completely localized on the σ AO's under consideration within each ligand. Such positive holes in the ligand σ AO's also produce the electrostatic potential field upon the ligand π-electron system. The result is summarized in Table I only for the case $Q^{\text{metal}} = 0$, because it seems to be a farily good approximation to the actual charge distribution.

It should be noticed that the first strong absorption band shifts to lower energy and is intensified remarkably in comparison with the corresponding band of the free molecule. This is just the electrostatic effect of the coordination on the ligand π–π^* transition and is important to explain the observed electronic absorption spectrum of the complex ion.

The Electronic Structure and Assignment of the Electronic Absorption Spectrum of Fe(dipy)$_3^{2+}$.—The π-electron structure of the complex ion was calculated with the aid of eq 1–10. In addition to the ground configuration, 27 LE and 36 CT configurations are taken into account. The LE configurations are due to the lower nine π–π^* transitions in ligands a, b, and c. The CT configurations are due to the electron transfers from the three 3dπ AO's to the lower four vacant MO's in the three ligands.

The values of $E_{CT}(7)$, the CT energy for the electron transfer to the lowest vacant MO φ_7, were calculated by use of eq 8. The results are shown in Figure 2 as the function of Q^{metal} and ρ_{4s}, the electron density on the 4s AO. If the observed 19,050-cm^{-1} band is assigned to this CT transition, it is clear from the figures in Figure 2 that the combination of $Q^{\text{metal}} \simeq 0$ with a small ρ_{4s} is adequate. We adopt $E_{CT}(7) = 1.6$ eV in the present calculation so as to obtain the best fit between the calculated and observed transition energies and intensities. The energies of the higher CT transitions ($E_{CT}(8) = 3.177$, $E_{CT}(9) = 4.377$, and $E_{CT}(10) = 5.158$ eV) were estimated by the relation

$$E_{CT}(k) = E_{CT}(7) + E_{CT}(k)^{\text{theoret}} - E_{CT}(7)^{\text{theoret}}$$

where $E_{CT}(k)^{\text{theoret}}$ is the CT energy calculated by use of eq 8, assuming $Q^{\text{metal}} = 0$ and $\rho_{4s} = 0$. On the same assumption for the charge distribution, β_{MN} is estimated to be -1.0 eV by use of eq 10.

The calculated results are summarized in Table II, together with the observed peak positions and intensities for Fe(dipy)$_3^{2+}$. They are also illustrated in Figure 3.

In view of the present theoretical result, the observed 19,050-cm^{-1} band can safely be assigned to the CT transition from the metal 3dπ AO to the ligand lowest

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(31) J. W. Richardson, W. C. Niewpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(32) H. H. Jaffé, *ibid.*, **21**, 258 (1953).

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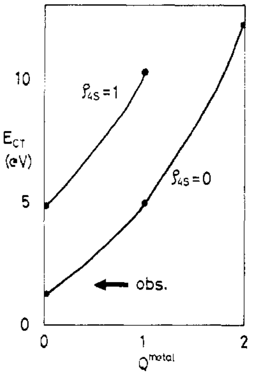


Figure 2.—CT configuration energy for the electron transfer to the lowest vacant MO φ_7.

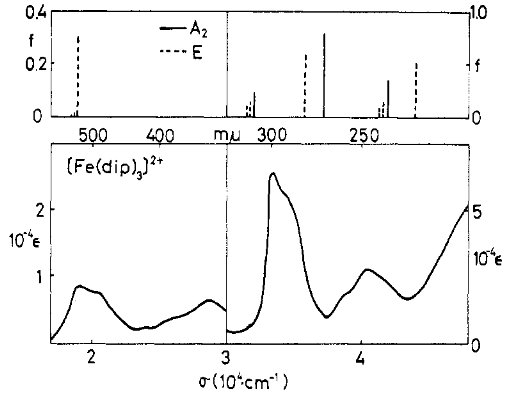


Figure 3.—The electronic absorption spectrum of $[Fe(dipy)_3]Cl_2$ in aqueous solution (lower) and the theoretical result (upper).

TABLE II

THEORETICAL AND EXPERIMENTAL ELECTRONIC TRANSMISSIONS OF $Fe(dipy)_3^{2+}$

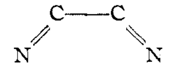
	Calcd				Obsd[a]		
State	Transition energy, 10^3 cm^{-1}	Oscillator strength	Symmetry	Character[b]	Transition energy, 10^3 cm^{-1}	ϵ[c]	Oscillator strength
V_1	18.82	0.005	E	CT(7)			
V_2	18.82	0.013	A_2	CT(7)	19.05	8,600	0.148
V_3	19.04	0.306	E	CT(7)	20.4	(7,700)	
V_4	31.78	0.131	E	CT(8)	24.2	(2,400)	
V_5	31.83	0.142	E	CT(8)	25.6	(3,500)	0.135
V_6	31.86	0.242	A_2	CT(8)	28.74	6,400	
V_7	35.77	0.589	E	LE_1	33.56	64,000	0.832
V_8	37.20	0.778	A_2	LE_1	34.5	(55,000)	
V_9	41.44	0.069	E	CT(9)	38.8	(18,000)	0.459
V_{10}	41.62	0.148	E	CT(9)	40.49	27,500	
V_{11}	41.85	0.351	A_2	CT(9)	41.5	(24,000)	
V_{12}	44.14	0.509	E	LE_2 + CT(9)			
V_{13}	46.63	0.002	E	LE_3			
V_{14}	46.63	0.004	A_2	LE_3			
V_{15}	47.95	0.132	E	LE_4 + CT(10)	48	(50,000)	
V_{16}	48.34	0.000	E	CT(10)			
V_{17}	48.40	0.013	A_2	CT(10)			
V_{18}	48.64	0.002	E	CT(10) + LE_4			
V_{19}	54.28	0.866	E	LE_5			

[a] $[Fe(dipy)_3]Cl_2 \cdot 7H_2O$ in aqueous solution. [b] Main components of the excited states are indicated. CT(*k*) is the CT to the vacant MO φ_k and LE_m is the LE configuration due to the *m*th π–π^* transition in the ligand. [c] Molar extinction coefficient. Shoulder bands are shown in parentheses.

vacant MO φ_7. The theoretically predicted transitions in this region consist of three allowed CT transitions to φ_7, two of which belong to E and the other to A_2 of the D_3 symmetry. The strongest transition to $V_3(E)$ gains its intensity through the mixing with the ground configuration whereas the other two, to $V_1(E)$ and to $V_2(A_2)$, borrow their intensities from the lowest LE transitions to $V_7(E)$ and $V_8(A_2)$, respectively.

The polarized crystal spectrum measurement[11] shows that two bands appearing at 18,690 and 20,280 cm^{-1}, respectively, belong to the E symmetry. They seem to correspond to the 19,050- and 20,400-cm^{-1} bands of the solution. The measurement at liquid nitrogen temperature shows that these two bands have the same order of intensity. On the other hand, our calculation shows that the transition to $V_1(E)$ is much weaker than that to $V_3(E)$. In view of this, we assign these two bands and the shoulder at ~21,600 cm^{-1} in the crystal spectrum to the vibrational structure of the strong transition to $V_3(E)$. The separation is ~1600 cm^{-1}, which corresponds to the C–N stretching frequency of the ligand.[10,12,13] The transitions to $V_1(E)$ and $V_2(A_2)$ are probably hidden by the strong E band.[34]

The tris-iron(II) complexes containing α-diimine[35] and *o*-phenanthroline[36] as ligands exhibit visible absorption bands similar to those of the dipyridyl complex in their energies and shapes. At first glance, this seems to support the Krumholz view[4] that the visible band is essentially due to the transition from the metal to the α-diimine skeleton



The present theoretical result, however, shows that the MO φ_7 of α,α'-dipyridyl, to which an electron is transferred, is not localized on the α-diimine skeleton. The case for the *o*-phenanthroline complex is similar. The shapes of the lowest vacant MO's of ligand π-electron systems are schematically shown in Figure 4 for the three complexes. Thus the Krumholz view is hardly acceptable from the theoretical point of view.[37]

In order to explain the similarity of the visible bands of the complexes containing the α-diimine skeleton, we evaluated theoretically the CT energies for the α-diimine, α,α'-dipyridyl, and *o*-phenanthroline complexes with the results given in Table III. This table clearly shows that the E_{CT} values for the electron transfers

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(34) This assignment seems, at a first glance, to contradict the circular dichroism measurement[15,16] which exhibits two CD bands in this region with opposite signs. However, the theoretical study on the optical rotatory power of the present complex ion (I. Hanazaki and S. Nagakura, to be submitted for publication) has revealed that the transitions having strong rotatory powers are those to $V_1(E)$ and $V_2(A_2)$. The transition to $V_3(E)$, which is intense in the absorption spectrum, has a minor contribution to the rotatory power. This also supports the present assignment.

(35) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Japan*, **41**, 365 (1968).

(36) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, to be submitted for publication.

(37) There is a possibility that the transferred electron is localized on the skeleton through the CI effect. However, the present composite-system calculation shows clearly that this effect is very small.

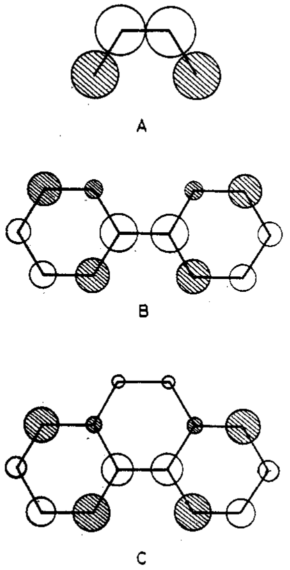

Figure 4.—The lowest vacant MO's: A, α-diimine; B, α,α'-dipyridyl; C, *o*-phenanthroline. The diameters of the circles are proportional to the coefficients of atomic orbitals. The shaded circle indicates that the coefficient is negative.

TABLE III

THE LOWEST CT ENERGIES FOR α-DIIMINE, α,α'-DIPYRIDYL, AND *o*-PHENANTHROLINE COMPLEXES[a,b]

	α-Diimine	α,α'-Dipyridyl	*o*-Phenanthroline
ϵ_k[c]	−12.25	−8.62	−8.40
$J(3d\pi, \varphi_k)$[d]	6.10	4.82	4.93
γ[e]	−1.23	−3.00	−2.99
$I(3d\pi)$[d,f]	18.30	12.97	13.01
$A(k)$[d,g]	10.55	6.92	6.70
$E_{CT}(k)$[h]	1.65	1.22	1.38

[a] All values are shown in eV. [b] Calculated assuming $Q^{\text{metal}} = 0$ and $\rho_{4s} = 0$. [c] Orbital energy of the lowest vacant MO φ_k including the electrostatic effect caused by the coordination. [d] Defined in eq 8. [e] The interaction of a 3d electron with the ligand-charge distribution; $\gamma = -\Sigma_p J(3d\pi, \chi_p)q_p$. Here $J(3d\pi, \chi_p)$ is the Coulomb repulsion between a 3dπ AO and a ligand 2pπ AO χ_p. The quantity q_p is the formal charge on AO χ_p. The sum is taken over all 2pπ AO's in a ligand. [f] $I(3d\pi) = I^0(3d\pi) + 3\gamma + \gamma'$, where $I^0(3d\pi)$ is the valence-state ionization potential of iron with $Q^{\text{metal}} = 0$ and $\rho_{4s} = 0$. The quantity γ' is the Coulomb interaction between a 3dπ electron and the positive holes in the ligand σ AO's, which is estimated to be −16.91 eV. [g] $A(k) = -\epsilon_k - 1.7$ eV. [h] The lowest CT energy theoretically estimated by use of eq 8.

TABLE IV

THE ELECTRON DENSITIES IN α,α'-DIPYRIDYL

	Free		Coordinated	
Atom[a]	*trans*	*cis*	Electrostatic field alone	Actual complex
1	1.253	1.234	1.512	1.520
2	0.868	0.867	0.786	0.792
3	1.038	1.038	1.005	1.008
4	0.943	0.944	0.825	0.834
5	1.020	1.038	0.976	0.978
6	0.878	0.879	0.897	0.907
3dπ[b]	...	...	6.000	5.764

[a] The numbering is shown in Figure 1. [b] The total electron density on three 3dπ AO's.

to the lowest vacant MO's of three complexes are close to one another, though the orbital energies differ remarkably from one another. This is because of the cancellation among the ionization potential ($I_{3d\pi}$), the electron affinity (A_k), and the Coulomb energy ($J(3d\pi, \varphi_k)$), as is clearly seen from Table III. On the basis of the above-mentioned cancellation, the constancy of E_{CT} can be explained without the assumption that the transferred electron is localized on the α-diimine skeleton.

A strong band appearing at 33,560 cm^{-1} and a shoulder at 34,500 cm^{-1} can be assigned to the lowest LE transitions. If the CT configuration does not mix with the LE configurations, the three excited states due to the antisymmetric transitions in ligands a, b, and c split into A_2 and E components (V_7(E) and $V_8(A_2)$) according to eq 7. The splitting is determined by $3D_{11}$, where D_{11} is the interaction energy of the transition dipoles accompanied with the lowest π–π^* transitions in two ligands, say, a and b. D_{11} is always positive so that the E component appears in lower energy. Furthermore, our theoretical calculation given in Table I shows that the V_7(E) transition has lower intensity than the $V_8(A_2)$ transition.

The corresponding band of $Zn(dipy)_3^{2+}$, which is composed of a main peak and a shoulder on the lower energy side,[5] seems to be in good agreement with the theoretical prediction. On the other hand, the band observed with $Fe(dipy)_3^{2+}$ has a shoulder on the shorter wavelength side of the peak in contrast to the theoretical prediction. A possible interpretation for this is to assign the shoulder to the vibrational structure of the main peak.[38] In this assignment, the E component is considered to be unrecognizable because of the overlapping.

The observed peak and shoulder at 28,740 and 25,600 cm^{-1}, respectively, are assigned to three overlapping transitions (V_4(E), V_5(E), and $V_6(A_2)$) to the second CT configuration in which an electron is transferred to the next lowest vacant MO φ_8. The observed peak at 40,490 cm^{-1} and two shoulders on both of its sides are assigned to the theoretically predicted transitions to V_9(E), V_{10}(E), $V_{11}(A_2)$, and V_{12}(E), in view of their energies and intensities. These transitions are composed of the third CT to φ_9 and the LE transition due to the second π–π^* transition in the ligand.

The Electron Delocalization and Stabilization of the Ground State.—The energy of the ground configuration is lowered by 0.860 eV through the π-electron interaction between the metal and ligands which is caused mainly by the mixing of the CT(7) and CT(8) configurations with the ground configuration. This great stabilization of the ground state is apparently responsible for the remarkable stability of the complex ion.

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(38) The theoretical consideration shows that the interaction with the CT configuration can never reverse the order of transition energies of the two components and also that it can never make the intensity of the E component higher than that of the A_2 component.

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 3dπ AO's to three ligands through the mixing of the CT configurations is 0.236. The increment of electron density on each 2pπ AO of the ligand is, however, very small because the transferred electron density is distributed on a large number of 2pπ AO's.

CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL AND CHEMICAL RESEARCH,
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Optical Rotatory Power of the Metal Chelate Compounds Containing Organic Unsaturated Molecules as Ligands

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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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