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Electronic Structure of Tris(1,10-phenanthroline)iron(II) Complex

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The SCF MO's for the π-electron system of 1,10-phenanthroline have been determined by following the Pariser-Parr-Pople's treatment. For the description of the lower excited states, the configuration interaction among nineteen singly-excited configurations with lower energy has been taken into account. The electronic spectrum of 1,10-phenanthroline has been interpreted on the basis of the results of the theoretical calculation. The SCF MO's for the π-electron system of a coordinated 1,10-phenanthroline in the tris-iron(II) complex have been determined to be self-consistent under the electrostatic potential field of the central metal ion and the other ligand molecules. On the basis of the results for coordinated ligand, the π-electronic structure of tris-(1,10-phenanthroline)iron(II) ion has been investigated from the theoretical point of view. It has been shown that two kinds of the charge-transfer transitions are responsible for an intense absorption band in the visible region, namely electron transfers from the $3d\pi$ orbital of iron to the lowest and the second lowest vacant π MO's of the ligand 1,10-phenanthroline. The discussions have been given on the change of the π-π^* states of 1,10-phenanthroline by the coordination.

The nature of the intensely colored complexes which iron(II) ions form with heterocyclic diamines, such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen), has received much attention and has been extensively studied. The π-bond formation between the central metal atom and the ligand molecules seems to play an important role on the nature of these complexes.1)

The π electronic structures of such a type of metal complexes were theoretically treated with success at first on acetylacetonato complexes of metal ions of the first transition series2) and then on tris-(2,2'-bipyridine)-3) and tris(α-diimine)iron(II)4) complexes.

The purpose of the present work is to extend this theoretical treatment to tris(1,10-phenanthroline)-iron(II) ion, $[Fe(phen)_3]^{2+}$. The outline of the calculation will be given, because the method of theoretical treatment was previously described.2,4) The integral values characteristic for the present system, however, will be discussed in detail.

Experimental

Materials. Commercial 1,10-phenanthroline monohydrate (Yoneyama Chemical Industries Co., Ltd). was used without further purification. $[Fe(phen)_3]Cl_2\cdot 7H_2O$5) and tris(2,2'-bipyridine)iron(II) perchlorate, $[Fe(bipy)_3](ClO_4)_2$,6) were prepared by the standard methods and identified by the chemical analysis.

Measurements. Electronic absorption spectra were measured by a Hitachi recording spectrophotometer Model EPS-3.

SCF MO and Lower Excited States of 1,10-Phenanthroline

The structures of 1,10-phenanthroline and $[Fe(phen)_3]^{2+}$ are shown in Fig. 1 together with the coordinate system used. Also shown are the numbering of the atom and the name of the ligand.

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1) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

2) I. Hanazaki, F. Hanazaki and S. Nagakura, *J. Chem. Phys.*, to be published.

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6) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.

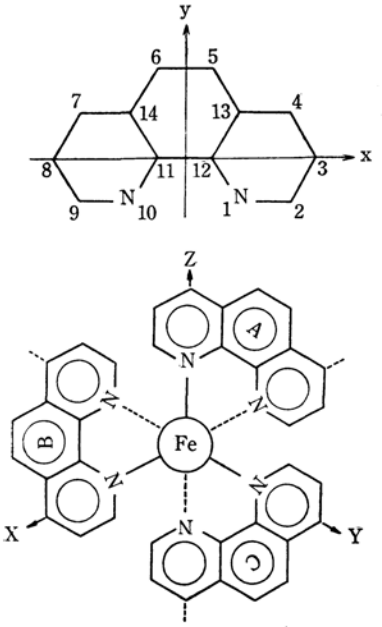

Fig. 1. The geometrical structures of 1,10-phenanthroline and $[Fe(phen)_3]^{2+}$ ion.

Since no experimental work on their geometrical structures has been reported, the bond lengths of all C–C and C–N bonds in the ring were assumed to be 1.39 Å and that of the Fe–N bond was assumed to be 1.97 Å.[*3]

Free Molecule. The π-electron system of 1,10-phenanthroline, containing 14 π-electrons, was studied by following the Pariser-Parr-Pople's treatment.[8,9]

The valence state ionization potential (I) and the electron affinity (A) were obtained from the table given by Pilcher and Skinner[10] as follows:

$I = 11.22$ eV and $A = 0.62$ eV for carbon
$I = 14.51$ eV and $A = 1.20$ eV for nitrogen

The core resonance integrals between the nearest neighbor AO's (atomic orbitals), β_{ij}, were calculated by the equation,

$$\beta_{ij} = \frac{S_{ij}}{S_0}\beta_0$$

where S_0 (0.248) and β_0 (-2.39 eV) are the overlap integral and the core resonance integral for benzene molecule, respectively. Evaluating the overlap integral, S_{ij}, from the table of Mulliken *et al.*,[11] the core resonance integrals were determined to be

$$\beta_{CN} = -1.879 \text{ eV} \quad \text{and} \quad \beta_{CC} = -2.39 \text{ eV}$$

Table 1 gives the SCF MO's (self-consistent field molecular orbitals) and their orbital energies for 1,10-phenanthroline. The electron densities are given in Table 2. The energies and the wave functions of the lower excited states of 1,10-phenanthroline were obtained by the configuration interaction calculation taking into account nineteen singly-excited configurations with lower energy.

TABLE 1. SCF MO's AND THEIR ORBITAL ENERGIES OF 1,10-PHENANTHROLINE

MO	Symmetry	Orbital energy (eV)	Coefficient*						
			$(\chi_1 \pm \chi_{10})$	$(\chi_2 \pm \chi_9)$	$(\chi_3 \pm \chi_8)$	$(\chi_4 \pm \chi_7)$	$(\chi_5 \pm \chi_6)$	$(\chi_{11} \pm \chi_{12})$	$(\chi_{13} \pm \chi_{14})$
1	b_2	−15.744	0.23463	0.15449	0.17086	0.23452	0.27488	0.35862	0.36431
2	a_2	−14.557	−0.26309	−0.27704	−0.33108	−0.33416	−0.09869	0.17092	−0.30628
3	b_2	−13.305	−0.32703	−0.31232	−0.21055	−0.00639	0.44584	−0.09854	0.20652
4	b_2	−12.452	0.22680	−0.14729	−0.41424	−0.33665	−0.05650	0.37247	0.00336
5	a_2	−12.114	−0.42524	−0.32317	−0.02784	0.27493	0.13640	0.00404	0.34604
6	a_2	−10.890	0.29924	−0.13870	−0.40573	−0.18198	0.14415	−0.29097	0.29672
7	b_2	−10.334	−0.26381	−0.28249	0.00227	0.28025	−0.42221	0.23898	0.19154
8	a_2	− 1.843	−0.24793	0.34863	0.05702	−0.37173	0.36978	0.09243	0.17399
9	b_2	− 1.735	0.38374	−0.11925	−0.30513	0.32295	−0.07944	−0.34154	0.13477
10	b_2	− 0.165	0.19452	−0.42681	0.21735	0.16280	0.16410	0.13016	−0.40297
11	a_2	0.580	0.18580	0.07776	−0.28634	0.27995	0.29351	0.45676	−0.06554
12	a_2	1.102	0.18728	−0.39127	0.34251	−0.12503	0.39047	0.00757	−0.16237
13	b_2	2.047	−0.17852	0.28410	−0.33843	0.34970	0.10474	0.17958	−0.32768
14	a_2	3.817	−0.17129	0.13744	−0.14982	0.21782	0.27483	−0.41094	−0.37078

*) + for b_2, − for a_2

[*3] During the development of the present work, the Fe–N bond length was determined to be 1.97 Å by X-ray analysis.[7] Any other detailed description on the bond length and the bond angle was not given.

7) D. H. Templeton, A. Zalkin and T. Ueki, *Acta Cryst.*, **21**, A154 (Supplement) (1966).

8) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

9) J. A. Pople, *Proc. Phys. Soc.* (*London*), **A68**, 81 (1955).

10) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

11) R. S. Mulliken, C. A. Ricke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

TABLE 2. ELECTRON DENSITY OF 1,10-PHENANTHROLINE

Atom	Electron density
1	1.2453
2	0.8467
3	1.0403
4	0.9346
5	1.0098
12	0.8961
13	1.0273

TABLE 3. CALCULATED AND OBSERVED TRANSITION ENERGY (E) AND OSCILLATOR STRENGTH (f) FOR THE ABSORPTION SPECTRUM OF 1,10-PHENANTHROLINE

Calculated			Observed		
Symmetry	E, eV	f	E, eV	ε[*1]	f[*2]
A_1	3.83	0.0008	3.85	500	
B_1	4.04	0.10	4.34(sh)[*3]	~8000	
B_1	4.61	0.73	4.69	27000	0.526
A_1	5.05	0.15			
B_1	5.33	0.30	5.43	40700	0.686
A_1	5.57	0.36			
B_1	5.86	0.90			
A_1	6.19	0.11			

[*1] molar extinction coefficient
[*2] reported by Favini and Paglia.[12]
[*3] shoulder band

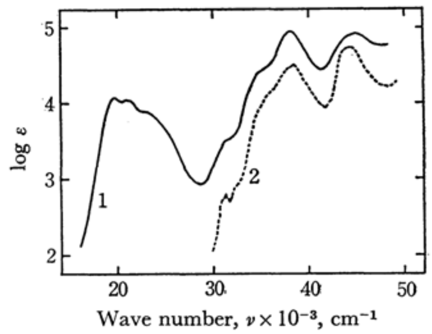

Fig. 2. The absorption spectra of (1) $[Fe(phen)_3]Cl_2 \cdot 7H_2O$ in aqueous solution and (2) 1,10-phenanthroline in ethanol solution.

In Table 3, the predicted π–π^* transition energies and oscillator strengths are presented in comparison with the experimental results. The electronic absorptin spectra of 1,10-phenanthroline and $[Fe(phen)_3]^{2+}$ are shown in Fig. 2. As is seen in Table 3, an agreement between the calculated and the observed results looks satisfactory.

Badger and Walker[13] found no evidence for n–π^* transition in the absorption spectrum of 1,10-phenanthroline. Their conclusion was based on the absence of solvent effect with variation of solvent polarity. Perkampus and Köhler[14] studied the absorption spectra in methanol and acid methanol solution in detail. They reported that the general structure of the absorption spectrum of phenanthrene was maintained even in 1,10-phenanthroline. Noticeable difference is only the loss of the vibrational structure in the 1,10-phenanthroline spectrum. Consequently, the π–π^* excited states are considered to be similar to these two molecules. Nishimoto and Forster[15] and Skancke[16] gave the assignments for phenanthrene molecule on the basis of the theoretical calculation. Their assignments are similar to the present one for 1,10-phenanthroline. These seem to provide a further support for the present theoretical result.

Coordinated Ligand. The SCF MO's of chelated 1,10-phenanthroline in $[Fe(phen)_3]^{2+}$ were determined, considering not only the field of the 1,10-phenanthroline itself but also the electrostatic potential field due to the central metal atom and the distribution of the π-electrons in the other ligands.[*4] Such calculations were carried out for three cases in which the number of the formal charge of iron was assumed to be 0, +1 and +2, since the degree of σ-donation caused by the coordination was not certain. Table 4 shows the result for the case when the formal charge of iron is zero. This was used in the calculation given in this paper. The reason for this is as follows:

TABLE 4. CALCULATED TRANSITION ENERGY (E) AND OSCILLATOR STRENGTH (f) FOR COORDINATED 1,10-PHENANTHROLINE IN IRON COMPLEX*

E, eV	Symmetry	f
3.67	A_1	0.009
3.82	B_1	0.004
4.42	B_1	0.853
4.71	A_1	0.327
5.28	B_1	0.109
5.31	A_1	0.109
5.97	B_1	0.153
6.02	A_1	0.186

* Obtained for the case when the formal charge of iron is zero.

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12) G. Favini and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 158 (1958).

13) G. M. Badger and I. S. Walker, *J. Chem. Soc.*, **1956**, 122.

14) H. H. Perkampus and H. Köhler, *Z. Electrochem.*, **64**, 365 (1964).

15) K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta*, **3**, 407 (1965).

16) P. N. Skancke, *Acta Chem. Scand.*, **19**, 401 (1965).

[*4] The details of the SCF procedure are referred to Ref. 2.

The energy of an electron transfer from the 3*d* AO of iron to the vacant ligand π-MO depends strongly on the formal charge of iron, in other word, the σ-electron distribution in the metal complex.[17] The parametrization of this energy to the observed value suggested that the formal charge of iron was close to zero.[17] As is seen in Table 4, the spectral feature of a coordinated ligand is not greatly different from that of the free ligand molecule, although the π-electrons of the ligand in the metal complex are conceivably subjected to the strong electrostatic potential field by the central metal atom and the other ligand molecules.

Electronic Structure of Tris(1,10-phenanthroline)iron(II) Complex

The so-called π-electron approximation was adopted in the present study.[*5] As component orbitals, π-type 3*d* AO of iron and π-MO's of ligands were taken into account. By placing π-electrons in the appropriate orbitals, the following three types of electronic configurations are obtained: (1) the ground configuration (G), (2) the locally excited configuration (LE) and (3) charge transfer configuration (CT). The π-electronic structure of $[Fe(phen)_3]^{2+}$ was studied by the configuration interaction calculation among these configurations.

Symmetries of Electronic Configurations. The electronic spin of $[Fe(phen)_3]^{2+}$ is singlet in the ground state.[18] Therefore, six *d*-electrons of iron(II) may be in the π-type 3*d* AO, d_{xy}, d_{yz} and d_{zx} with antiparallel spins. The π-electron system of this complex can be divided into four components, namely a π-electron system of iron AO and those of three ligands. The wave function for the ground configuration (G) can be represented as follows:

$$G=|(1\bar{1}2\bar{2}3\bar{3}4\bar{4}5\bar{5}6\bar{6}7\bar{7})^{\mathrm{A}}(\ )^{\mathrm{B}}(\ )^{\mathrm{C}}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}|^{*6}$$

where the superscripts A, B and C denote the three coordinated 1,10-phenanthroline molecules shown in Fig. 1. In addition to the ground configuration, thirty six charge transfer (CT) configurations and thirty locally excited (LE) configurations were taken into account, which are given in Table 5. In a way similar to the ground configuration, the wave function for the CT configuration in which an electron is transferred from d_{xy} to φ_8^{A} is expressed as,

$$CT(d_{xy}\rightarrow\varphi_8^{\mathrm{A}})=\frac{1}{\sqrt{2}}\left\{\begin{array}{l}|(\ )^{\mathrm{A}}(\ )^{\mathrm{B}}(\ )^{\mathrm{C}}\,8^{\mathrm{A}}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}| \\ +|(\,)^{\mathrm{A}}(\,)^{\mathrm{B}}(\,)^{\mathrm{C}}d_{xy}\overline{8^{\mathrm{A}}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}|\end{array}\right\}$$

TABLE 5. SINGLY-EXCITED CONFIGURATIONS TAKEN INTO ACCOUNT FOR THE CONFIGURATION INTERACTION CALCULATION

Configuration	Character	Total number
CT	from $\left\{\begin{array}{l}d_{xy}\\ d_{yz}\\ d_{zx}\end{array}\right\}$ to $\{\varphi_8, \varphi_9, \varphi_{10}, \varphi_{11}\}$ in each ligand A, B, C	36
LE	lower ten excited states in each ligand A, B, C	30

The wave function for the LE configuration in which only the ligand A is in the μth excited state is expressed as,

$$LE(\Phi_\mu^{\mathrm{A}})=\sum a_{ij}\frac{1}{\sqrt{2}}\left\{\begin{array}{l}|(\ldots i\bar{j}..)^{\mathrm{A}}(\,)^{\mathrm{B}}(\,)^{\mathrm{C}}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}| \\ +|(\ldots j\bar{i}..)^{\mathrm{A}}(\,)^{\mathrm{B}}(\,)^{\mathrm{C}}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}})\end{array}\right\}$$

where i and j mean the number of the occupied and the vacant MO of the ground configuration, respectively and a_{ij} means the coefficient of the $(\varphi_i-\varphi_j)$ excited configuration for the μth excited state. The value of a_{ij} was determined in the configuration interaction calculation for coordinated 1,10-phenanthroline. Other CT and LE configurations are expressed in a similar way. The ground, the CT and the LE configurations are classified into the irreducible representations of D_3 symmetry by taking the linear combination, which are given in Table 6.

Configuration Interaction. The matrix elements of the total electronic Hamiltonian between the configurations were calculated in a way similar to the case previously reported.[2,4] The accurate evaluation of the diagonal element of the CT configuration, E_{CT}, is extremely difficult. The difficulty mainly comes from the fact that the value of E_{CT} is very sensitive to the σ-electron distribution, which is uncertain.[2,4] It is also difficult to obtain any reliable value of the π-electron affinity of the coordinated ligand. Therefore, in the present calculation, the diagonal element of the CT configuration with the lowest energy was treated as a parameter. The values of the other CT diagonal elements were determined, considering the difference of the MO's to which an electron is transferred. The diagonal elements of LE configurations are expressed as the sum of the excitation energy in the coordinated 1,10-phenanthroline and the additional term, the latter of which originates from the inter-ligand interaction of the transition dipoles. The interaction energies of the transition dipoles on different ligands, $K'_{\mu\nu}$, were calculated in the same way as previously used.[3] ($K'_{\mu\nu}$ is the interaction energy of the transition dipoles accompanied by the μth transition in ligand A and the νth transition in ligand B). The off-diagonal

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17) See Ref. 4.

[*5] The applicability of this approximation was already discussed in Ref. 2.

18) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.

[*6] The abbreviated notation ($)^\mu$ means $(1\bar{1}2\bar{2}3\bar{3}4\bar{4}5\bar{5}6\bar{6}7\bar{7})^\mu$.

TABLE 6. WAVE FUNCTIONS FOR G, CT AND LE CONFIGURATIONS BELONGING TO EACH IRREDUCIBLE REPRESENTATION OF D_3 GROUP*

A$_1$:

$$G=G$$

$$\begin{aligned}CT_1^{A_1}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_8^A)-CT(d_{yz}\rightarrow\varphi_8^A)+CT(d_{yz}\rightarrow\varphi_8^B)\\&-CT(d_{zx}\rightarrow\varphi_8^B)+CT(d_{zx}\rightarrow\varphi_8^C)-CT(d_{xy}\rightarrow\varphi_8^C)\}\end{aligned}$$

$$\begin{aligned}CT_2^{A_1}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_9^A)+CT(d_{yz}\rightarrow\varphi_9^A)+CT(d_{yz}\rightarrow\varphi_9^B)\\&+CT(d_{zx}\rightarrow\varphi_9^B)+CT(d_{zx}\rightarrow\varphi_9^C)+CT(d_{xy}\rightarrow\varphi_9^C)\}\end{aligned}$$

$$CT_3^{A_1}=\frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_9^A)+CT(d_{yy}\rightarrow\varphi_9^B)+CT(d_{yz}\rightarrow\varphi_9^C)\}$$

$$\begin{aligned}CT_4^{A_1}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_{10}^A)-CT(d_{yz}\rightarrow\varphi_{10}^A)+CT(d_{yz}\rightarrow\varphi_{10}^B)\\&-CT(d_{zx}\rightarrow\varphi_{10}^B)+CT(d_{zx}\rightarrow\varphi_{10}^C)-CT(d_{xy}\rightarrow\varphi_{10}^C\}\end{aligned}$$

$$\begin{aligned}CT_5^{A_1}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_{11}^A)+CT(d_{yz}\rightarrow\varphi_{11}^A)+CT(d_{yz}\rightarrow\varphi_{11}^B)\\&+CT(d_{zx}\rightarrow\varphi_{11}^B)+CT(d_{zx}\rightarrow\varphi_{11}^C)+CT(d_{xy}\rightarrow\varphi_{11}^C)\}\end{aligned}$$

$$CT_6^{A_1}=\frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_{11}^A)+CT(d_{xy}\rightarrow\varphi_{11}^B)+CT(d_{yz}\rightarrow\varphi_{11}^C)\}$$

$$LE_1^{A_1}=\frac{1}{\sqrt{3}}\{LE(\Phi_1^A)+LE(\Phi_1^B)+LE(\Phi_1^C)\}$$

$$LE_4^{A_1}=\frac{1}{\sqrt{3}}\{LE(\Phi_4^A)+LE(\Phi_4^B)+LE(\Phi_4^C)\}$$

$$LE_6^{A_1}=\frac{1}{\sqrt{3}}\{LE(\Phi_6^A)+LE(\Phi_6^B)+LE(\Phi_6^C)\}$$

$$LE_8^{A_1}=\frac{1}{\sqrt{3}}\{LE(\Phi_8^A)+LE(\Phi_8^B)+LE(\Phi_8^C)\}.$$

$$LE_{10}^{A_1}=\frac{1}{\sqrt{3}}\{LE(\Phi_{10}^A)+LE(\Phi_{10}^B)+LE(\Phi_{10}^C)\}$$

A$_2$:

$$\begin{aligned}CT_1^{A_2}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_8^A)+CT(d_{yz}\rightarrow\varphi_8^A)+CT(d_{yz}\rightarrow\varphi_8^B)\\&+CT(d_{zx}\rightarrow\varphi_8^B)+CT(d_{zx}\rightarrow\varphi_8^C)+CT(d_{xy}\rightarrow\varphi_8^C)\}\end{aligned}$$

$$CT_2^{A_2}=\frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_8^A)+CT(d_{xy}\rightarrow\varphi_8^B)+CT(d_{yz}\rightarrow\varphi_8^C)\}$$

$$\begin{aligned}CT_3^{A_2}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_9^A)-CT(d_{yz}\rightarrow\varphi_9^A)+CT(d_{yz}\rightarrow\varphi_9^B)\\&-CT(d_{zx}\rightarrow\varphi_9^B)+CT(d_{zx}\rightarrow\varphi_9^C)-CT(d_{xy}\rightarrow\varphi_9^C)\}\end{aligned}$$

$$\begin{aligned}CT_4^{A_2}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_{10}^A)+CT(d_{yz}\rightarrow\varphi_{10}^A)+CT(d_{yz}\rightarrow\varphi_{10}^B)\\&+CT(d_{zx}\rightarrow\varphi_{10}^B)+CT(d_{zx}\rightarrow\varphi_{10}^C)+CT(d_{xy}\rightarrow\varphi_{10}^C)\}\end{aligned}$$

$$CT_5^{A_2}=\frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_{10}^A)+CT(d_{xy}\rightarrow\varphi_{10}^B)+CT(d_{yz}\rightarrow\varphi_{10}^C)\}$$

$$\begin{aligned}CT_6^{A_2}=\frac{1}{\sqrt{6}}\{&CT(d_{xy}\rightarrow\varphi_{11}^A)-CT(d_{yz}\rightarrow\varphi_{11}^A)+CT(d_{yz}\rightarrow\varphi_{11}^B)\\&-CT(d_{zx}\rightarrow\varphi_{11}^B)+CT(d_{zx}\rightarrow\varphi_{11}^C)-CT(d_{xy}\rightarrow\varphi_{11}^C)\}\end{aligned}$$

$$LE_2^{A_2}=\frac{1}{\sqrt{3}}\{LE(\Phi_2^A)+LE(\Phi_2^B)+LE(\Phi_2^C)\}$$

$$LE_3^{A_2}=\frac{1}{\sqrt{3}}\{LE(\Phi_3^A)+LE(\Phi_3^B)+LE(\Phi_3^C)\}$$

$$LE_5^{A_2}=\frac{1}{\sqrt{3}}\{LE(\Phi_5^A)+LE(\Phi_5^B)+LE(\Phi_5^C)\}$$

$$LE_7^{A_2}=\frac{1}{\sqrt{3}}\{LE(\Phi_7^A)+LE(\Phi_7^B)+LE(\Phi_7^C)\}$$

$$LE_9^{A_2}=\frac{1}{\sqrt{3}}\{LE(\Phi_9^A)+LE(\Phi_9^B)+LE(\Phi_9^C)\}$$

E:

$$CT_1^{E}=\frac{1}{\sqrt{2}}\{CT(d_{xy}\rightarrow\varphi_8^B)-CT(d_{yz}\rightarrow\varphi_8^C)\}$$

$$\begin{aligned}CT_2^{E}=\frac{1}{2}\{&CT(d_{yz}\rightarrow\varphi_8^B)-CT(d_{zx}\rightarrow\varphi_8^C)+CT(d_{zx}\rightarrow\varphi_8^B)\}\\&-CT(d_{xy}\rightarrow\varphi_8^C)\}\end{aligned}$$

$$\begin{aligned}CT_3^{E}=\frac{1}{\sqrt{12}}\{&2CT(d_{xy}\rightarrow\varphi_8^A)-CT(d_{yz}\rightarrow\varphi_8^B)-CT(d_{zx}\rightarrow\varphi_8^C)\\&-2CT(d_{yz}\rightarrow\varphi_8^A)+CT(d_{zx}\rightarrow\varphi_8^B)+CT(d_{xy}\rightarrow\varphi_8^C)\}\end{aligned}$$

$$CT_4^{E}=\frac{1}{\sqrt{6}}\{2CT(d_{zx}\rightarrow\varphi_9^A)-CT(d_{xy}\rightarrow\varphi_9^B)-CT(d_{yz}\rightarrow\varphi_9^C)\}$$

$$\begin{aligned}CT_5^{E}=\frac{1}{\sqrt{12}}\{&2CT(d_{xy}\rightarrow\varphi_9^A)-CT(d_{yz}\rightarrow\varphi_9^B)-CT(d_{zx}\rightarrow\varphi_9^C)\\&+2CT(d_{yz}\rightarrow\varphi_9^A)-CT(d_{zx}\rightarrow\varphi_9^B)-CT(d_{xy}\rightarrow\varphi_9^C)\}\end{aligned}$$

$$\begin{aligned}CT_6^{E}=\frac{1}{2}\{&CT(d_{yz}\rightarrow\varphi_9^B)-CT(d_{zx}\rightarrow\varphi_9^C)-CT(d_{zx}\rightarrow\varphi_9^B)\\&+CT(d_{xy}\rightarrow\varphi_9^C)\}\end{aligned}$$

$$CT_7^{E}=\frac{1}{\sqrt{2}}\{CT(d_{xy}\rightarrow\varphi_{10}^B)-CT(d_{yz}\rightarrow\varphi_{10}^C)\}$$

$$\begin{aligned}CT_8^{E}=\frac{1}{2}\{&CT(d_{yz}\rightarrow\varphi_{10}^B)-CT(d_{zx}\rightarrow\varphi_{10}^C)+CT(d_{zx}\rightarrow\varphi_{10}^B)\\&-CT(d_{xy}\rightarrow\varphi_{10}^C)\}\end{aligned}$$

$$\begin{aligned}CT_9^{E}=\frac{1}{\sqrt{12}}\{&2CT(d_{xy}\rightarrow\varphi_{10}^A)-CT(d_{yz}\rightarrow\varphi_{10}^B)-CT(d_{zx}\rightarrow\varphi_{10}^C)\\&-2CT(d_{yz}\rightarrow\varphi_{10}^A)+CT(d_{zx}\rightarrow\varphi_{10}^B)+CT(d_{xy}\rightarrow\varphi_{10}^C)\}\end{aligned}$$

$$CT_{10}^{E}=\frac{1}{\sqrt{6}}\{2CT(d_{zx}\rightarrow\varphi_{11}^A)-CT(d_{xy}\rightarrow\varphi_{11}^B)-CT(d_{yz}\rightarrow\varphi_{11}^C)\}$$

$$\begin{aligned}CT_{11}^{E}=\frac{1}{\sqrt{12}}\{&2CT(d_{xy}\rightarrow\varphi_{11}^A)-CT(d_{yz}\rightarrow\varphi_{11}^B)-CT(d_{zx}\rightarrow\varphi_{11}^C)\\&+2CT(d_{yz}\rightarrow\varphi_{11}^A)-CT(d_{zx}\rightarrow\varphi_{11}^B)-CT(d_{xy}\rightarrow\varphi_{11}^C)\}\end{aligned}$$

$$\begin{aligned}CT_{12}^{E}=\frac{1}{2}\{&CT(d_{yz}\rightarrow\varphi_{11}^B)-CT(d_{zx}\rightarrow\varphi_{11}^C)-CT(d_{zx}\rightarrow\varphi_{11}^B)\\&+CT(d_{xy}\rightarrow\varphi_{11}^C)\}\end{aligned}$$

$$LE_1^{E}=\frac{1}{\sqrt{6}}\{2LE(\Phi_1^A)-LE(\Phi_1^B)-LE(\Phi_1^C)\}$$

$$LE_2^{E}=\frac{1}{\sqrt{2}}\{LE(\Phi_2^B)-LE(\Phi_2^C)\}$$

$$LE_3^{E}=\frac{1}{\sqrt{2}}\{LE(\Phi_3^B)-LE(\Phi_3^C)\}$$

$$LE_4^{E}=\frac{1}{\sqrt{6}}\{2LE(\Phi_4^A)-LE(\Phi_4^B)-LE(\Phi_4^C)\}$$

$$LE_5^{E}=\frac{1}{\sqrt{2}}\{LE(\Phi_5^B)-LE(\Phi_5^C)\}$$

$$LE_6^{E}=\frac{1}{\sqrt{6}}\{2LE(\Phi_6^A)-LE(\Phi_6^B)-LE(\Phi_6^C)\}$$

$$LE_7^{E}=\frac{1}{\sqrt{2}}\{LE(\Phi_7^B)-LE(\Phi_7^C)\}$$

$$LE_8^{E}=\frac{1}{\sqrt{6}}\{2LE(\Phi_8^A)-LE(\Phi_8^B)-LE(\Phi_8^C)\}$$

$$LE_9^{E}=\frac{1}{\sqrt{2}}\{LE(\Phi_9^B)-LE(\Phi_9^C)\}$$

$$LE_{10}^{E}=\frac{1}{\sqrt{6}}\{2LE(\Phi_{10}^A)-LE(\Phi_{10}^B)-LE(\Phi_{10}^C)\}$$

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* The subscript(μ) of LE_μ^s means that LE_μ^s corresponds to the μth excited state of the ligand 1,10-phenanthroline.

matrix elements between G and CT and between CT and LE were accounted for by β, the core resonance integral between the appropriate $3d\pi$ AO of iron and $2p\pi$ AO of nitrogen. It was evaluated with the usual relation,

$$\beta = -S\frac{I_{Fe} + I_N}{2}$$

where S is the overlap integral, and I_{Fe} and I_N are the valence state ionization potentials of iron and nitrogen, respectively. The overlap integral was estimated with the aid of the Slater AO of nitrogen and the double zeta expanded $3d$ AO of iron determined by Richardson *et al.*[19] It was calculated to be 0.090, using the table given by Jaffé.[20] I_{Fe} and I_N are 5.08 eV and 18.68 eV respectively and β amounts to -1.07 eV. In the off-diagonal elements between the CT configurations, only the two-center repulsion integrals of the type $(d_i d_i | \varphi_k^{\mu} \varphi_l^{\mu})$ are taken into account with the point charge approximation. The off-diagonal matrix elements between the LE configurations are expressed in terms of $K'_{\mu\nu}$.

TABLE 7. WAVE FUNCTIONS AND ENERGIES OF THE LOWER ELECTRONIC STATES OF TRIS(1,10-PHENANTHROLINE)IRON(II)ION

	E, eV*1)	Sym.	Wave function*2
W_0	-1.144	A_1	$0.849G-0.449CT_1^{A_1}+0.212CT_2^{A_1}$
W_1	1.429	E	$0.974CT_2^{E}$
W_2	1.429	A_2	$0.974CT_1^{A_2}$
W_3	1.445	E	$0.974CT_3^{E}$
W_4	2.564	E	$0.929CT_6^{E}$
W_5	2.576	A_2	$0.937CT_3^{A_2}$
W_6	2.586	E	$0.941CT_5^{E}$
W_7	3.696	E	$0.970LE_1^{E}$
W_8	3.863	E	$0.960LE_2^{E}$
W_9	3.869	A_2	$0.963LE_2^{A_2}$
W_{10}	4.269	E	$0.695LE_3^{E}+0.603LE_4^{E}$
W_{11}	4.458	E	$-0.609LE_3^{E}+0.529LE_4^{E}-0.283CT_8^{E}$ $-0.319CT_9^{E}$
W_{12}	4.481	A_2	$0.421CT_4^{A_2}-0.611CT_6^{A_2}$ $+0.543LE_3^{A_2}$
W_{13}	4.515	E	$0.834CT_{12}^{E}+0.223CT_9^{E}$ $-0.242LE_4^{E}-0.212LE_5^{E}$
W_{14}	4.580	A_2	$0.462CT_4^{A_2}+0.703CT_6^{A_2}$ $+0.490LE_3^{A_2}$
W_{15}	4.607	E	$-0.815CT_{11}^{E}-0.468CT_9^{E}$
W_{16}	4.648	E	$0.856CT_8^{E}+0.223CT_{11}^{E}$ $+0.304CT_{12}^{E}$
W_{17}	4.733	A_2	$0.726CT_4^{A_2}-0.656LE_3^{A_2}$
W_{18}	4.760	E	$0.204CT_8^{E}+0.674CT_9^{E}$ $-0.394CT_{11}^{E}+0.408LE_4^{E}$
W_{19}	5.331	E	$0.932LE_6^{E}-0.212CT_9^{E}$ $-0.229LE_4^{E}$
W_{20}	5.429	E	$0.946LE_5^{E}$
W_{21}	5.438	A_2	$0.952LE_5^{A_2}$
W_{22}	5.948	E	$0.895LE_8^{E}+0.226LE_7^{E}$
W_{23}	6.044	E	$0.942LE_7^{E}-0.246LE_8^{E}$

*1 The energy of the ground configuration is taken to be zero.

*2 Only main configurations are written.

TABLE 8. CALCULATED AND OBSERVED RESULTS ON THE ELECTRONIC SPECTRUM OF TRIS (1,10-PHENANTHROLINE)IRON(II) ION

	Calculated		Observed*1	
From W_0 to	E, eV*2	f	E, eV*2	log ε
W_1	2.57	0.013		
W_2	2.57	0.030	2.43	4.05
W_3	2.59	0.306		
W_4	3.71	0.231	~2.6*3	~4.0
W_5	3.72	0.321	2.85	3.85
W_6	3.73	0.113		
W_7	4.84	0.064	3.87	3.55
W_8	5.01	0.080		
W_9	5.01	0.059	~4.28*3	~4.4
W_{10}	5.41	1.706		
W_{11}	5.60	0.007		
W_{12}	5.63	0.085		
W_{13}	5.66	0.018	4.66	4.95
W_{14}	5.72	0.129		
W_{15}	5.75	0.005		
W_{16}	5.79	0.265		
W_{17}	5.88	1.074		
W_{18}	5.90	0.378		
W_{19}	6.48	0.162		
W_{20}	6.57	0.036	5.50	4.91
W_{21}	6.58	0.098		
W_{22}	7.09	0.699		
W_{23}	7.19	0.040		

*1 Observed value for tris(1,10-phenanthroline)iron(II) chloride heptahydrate in aqueous solution.

*3 Transitionn energy.

*3 Shoulder band.

The results obtained by the configuration interaction are shown in Table 7 and the calculated transition energies and the oscillator strengths are given in Table 8 together with the observed ones.

Interpretation of the Electronic Spectrum. From the results given in Tables 7 and 8 it can be concluded that the intense band at the visible region is reasonably assigned to the almost pure CT absorption due to the π-electron migration from the $3d\pi$ AO of iron to the lowest vacant MO, φ_8, of the ligand. The observed absorption bands are too broad and poorly resolved to indicate the components. However, the broad tail appearing

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[19] J. W. Richardson, W. C. Nieuwport, R. R. Powell and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

[20] H. H. Jaffé, *ibid.*, **21**, 258 (1953).

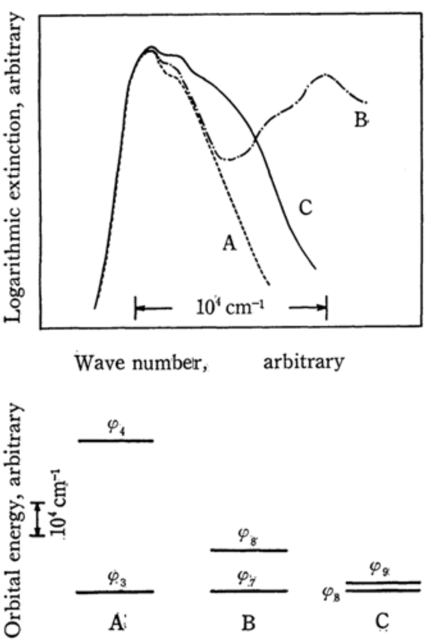

Fig. 3. The CT band shapes and the energies of the two lowest vacant ligand MO's for (A) tris(biacetyl-bis-*N*-methylimine), (B) tris(bipyridine) and (C) tris(phenanthroline) complexes of iron(II).
The spectra are drawn at the appropriate position and on the appropriate intensity scale as the longer wavelength part of the spectrum overlap each other. In the energy level diagram the energy of the lowest vacant orbital is taken equal in order to make easier the comparison of the energy separations between the lowest and the nesxt lowest vacant orbital.

at the shorter wavelength side of this band may be assigned to the overlapping of the second CT band ($3d\pi \rightarrow \varphi_9$). Figure 3 shows the CT band shapes of tris(biacetyl-bis-*N*-methylimine) iron (II), $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions. Also shown are the lowest two vacant MO's for these ligand molecules, to which an electron is transferred. These complexes are considered to have similar electronic structures. As is shown in the previous paper,[4] the CT band of tris(biacetyl-bis-*N*-methylimine)-iron(II) is composed of one kind of CT, namely $3d\pi \rightarrow \varphi_3$. The orbital energy level of the next lowest vacant MO, φ_4, is far from that of φ_3. On the other hand, the lowest two levels are very close to each other for 1,10-phenanthroline and moderately separated for 2,2′-bipyridine. It can be seen in Fig. 3 that the CT band in the visible region is composed of one kind of CT transition for the biacetyl-bis-*N*-methylimine complex, whereas it is composed of two kinds of very closely located CT transitions for the 1,10-phenanthroline complex. It is also clear that such CT bands for the 2,2′-bipyridine complex are resolved into two components.

From great similarities between the absorption curve of 1,10-phenanthroline and $[Fe(phen)_3]^{2+}$, the bands of the complex above 30000 cm^{-1} have been ascribed to the ligand transition beyond reasonable doubt. (See Fig. 2). This was confirmed by the present study. However, it was also shown that the π–π^* transition in the ligand becomes complicated when the ligand is coordinated to form the tris-complex.

One reason for the complication of the absorption bands is that the higher CT bands ($3d\pi \rightarrow \varphi_{10}$ and φ_{11}) appear in the ultraviolet region. They appear in overlap with the LE bands. This situation may be seen clearly in the circular dichroism (CD) spectrum.[*7]

Since 1,10-phenanthroline has C_{2v} symmetry, the π–π^* transitions should be either y-polarized along the two-fold axis, or x-polarized along the long axis of the ligand molecule (Fig. 1). As has been discussed,[4,21] the x-polarized transition of three ligands in metal complex with D_3 symmetry gives rise to the $A_1 \rightarrow A_2$ and the $A_1 \rightarrow E$ transition while the y-polarized transition gives rise to the $A_1 \rightarrow A_1$ and the $A_1 \rightarrow E$ one, the $A_1 \rightarrow A_1$ transition being symmetrically forbidden. Consequently, if the transition is y-polarized, the resultant electronic absorption spectrum of metal complex consists of single band, which is three times as intense as that of a free 1,10-phenanthroline. On the other hand, if the μth transition is x-polarized, the intensity ratio of the $A_1 \rightarrow E$ to the $A_1 \rightarrow A_2$ transition must be 1 : 2. The transition energy for the $A_1 \rightarrow E$ is smaller by $3K'_{\mu\mu}$ than that for the $A_1 \rightarrow A_2$.[*8] Such changes by the coordination take place on each π–π^* level of 1,10-phenanthroline, although the situation becomes more complicated because of the mixing of several LE configurations through the configuration interaction.

The correspondence of the third LE transition theoretically predicted to the observed peak at 37600 cm^{-1} is obvious. The theoretical result shows that this band is intense and x-polarized, which splits into two components in the tris-complex. This splitting is undoubtedly responsible for the observation that an optically active $[Fe(phen)_3]^{2+}$ shows two intense CD peaks with the opposed sign in regard to this absorption band.[22–24]

[*7] Two of the present authors (I. H. and S. N.) studied theoretically the CD spectrum of $[Fe(phen)_3]^{2+}$, on the basis of the present results. The details will be reported elsewhere.

21) E. Larsen, S. F. Mason and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

[*8] $K'_{\mu\mu}$ is the interaction energy of the transition dipoles accompanying the μth transition in ligand A and the same kind of transition in ligand B.

22) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, **1963**, 211.

23) A. J. McCaffery, S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, **1964**, 259.

24) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964).

The overall agreement of the theoretical transition energy with the observed one is rather poor compared with the case studied previously.[2–4] The calculated transition energies are somewhat high. This discrepancy may probably be attributed to the neglect of the doubly excited LE configurations. In fact, some doubly excited configurations usually appear in a considerably lower energy region, which will possibly bring about a strong effect on the lower singly-excited LE transitions.

The energies of some of the LE transitions are very close to each other in molecules which have the extensive π-electron system such as 1,10-phenanthroline. The transition dipole interaction between the different excited configurations in such a case has an important influence on the electronic states of metal complex through the configuration interaction. The calculated third π–π^* level is close to the fourth one. In metal complex, therefore, the E component of the third level mixes strongly with the fourth one to acquire a larger intensity than what is expected when the configuration interaction is neglected. This fact may partly account for the observation that the lower energy component of the corresponding CD peaks is usually more intense than the higher energy one.*9

Stabilization by the Charge-Delocalization. According to the present theoretical study, $[\mathrm{Fe(phen)_3}]^{2+}$ is stabilized by 1.14 eV (26.3 kcal/mol). This stabilization is caused by the mixing of CT configurations into the ground state. In other words, the π-bonding is formed between the iron atom and the ligand molecules. This large stabilization is undoubtedly responsible for the high stability of this complex.

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The numerical calculation was carried out by means of an OKITAC 5090H electronic computer at the Institute of Physical and Chemical Research, a NEAC 2230 at Tohoku University and a HITAC 5020 at the University of Tokyo.

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*9 The zero-order rotational strength (R) of these two states is related by the equation, $R(\mathrm{A_2}) = -R(\mathrm{E})$.