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Electronic Structure of Tris(α-diimine)iron(II) Complexes

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The electronic structures of tris(α-diimine)iron(II) complexes have been investigated. The theoretical consideration has revealed that a considerable π-back donation takes place in the ground state and as a result unusually stable complexes of iron(II) are formed. The intense band which appears in the visible region has been proved to be due to the charge transfer transition from 3dπ AO (atomic orbital) of iron to the lowest vacant π MO (molecular orbital) of the ligand α-diimine. It was found both theoretically and experimentally that the $\pi\rightarrow\pi^*$ transition with the lowest energy in α-diimine is polarized parallel to the nitrogen-nitrogen direction of the molecule, and that transition dipoles in the three ligands of tris(α-diimine)iron(II) ion interact to give resultant $A_1\rightarrow A_2$ and $A_1\rightarrow E$ transitions in the metal complex with D_3 symmetry. Details of the electronic structures, including the splitting energy and the intensity of the local excitation in α-diimine molecule and the nature of the charge transfer band, have been discussed.

It is well known that α-diimine, 2, 2′-bipyridine and 1, 10-phenanthroline form intensely colored stable complexes with iron(II) ions. The chromophoric nature and the unusual stability of such complexes have received a considerable attention and a number of experimental studies have been carried out.[1,2] Some researchers emphasized the importance of the π-bond formation between the ligands and the central metal ion.[3,4]

The aim of the present work is to extend the theoretical treatment previously developed for the acetylacetonato complexes[5] to tris(α-diimine)iron(II) ions and to study the electronic structures of the latter complexes as quantitatively as possible.[*1] The absorption spectra, not only visible but also ultraviolet, of three kinds of tris(α-diimine)iron(II) complexes, namely tris(glyoxal-bis-*N*-methylimine)-, tris(biacetyl-bis-*N*-methylimine)- and tris(biacetyl-bis-*N*-butylimine)iron(II) ions, were measured to obtain the information on the electronic energy levels of the complexes.

Experimental

Materials. Tris(glyoxal-bis-*N*-methylimine)iron(II) iodide,[1] tris(biacetyl-bis-*N*-methylimine)iron(II) iodide[1] and tris(biacetyl-bis-*N*-butylimine)iron(II) tetrafluoroborate[6] were prepared by the methods described in the literatures. For the measurements of ultraviolet absorption spectra, the above iodides were converted to tetrafluoroborates. Among these three ligands, only biacetyl-bis-*N*-butylimine was able to be isolated by the method of Barany *et al.*[7]

Measurements. A Hitachi recording spectrophotometer Model EPS-3 was used for the measurements of the visible and the ultraviolet absorption spectra. The measurements in the vacuum ultarviolet region were made down to 182 mμ in aqueous solutions with 0.1 mm quartz cells using a vacuum ultraviolet spectrophotometer[8] at the Institute for Solid State Physics, the University of Tokyo.

Experimental Results

The absorption spectra of three kinds of tris(α-diimine)iron(II) complex were measured in aqueous solutions. As may be seen in Fig. 1, very similar spectra were obtained not only in the visible but also in the ultraviolet region, though a slight frequency shift was observed. A band

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[1] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[2] E. Bayer, *Angew. Chem.*, **76**, 76 (1964).

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

[4] K. Nakamoto, "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner, Macmillan, New York (1961), p. 437.

[5] I. Hanazaki, F. Hanazaki and S. Nagakura, *J. Chem. Phys.*, to be published.

[*1] Similar studies on the electronic structure of 2, 2′-bipyridine and 1, 10-phenanthroline complexes of iron(II) ion will be described elsewhere.

[6] S. Otsuka, T. Yoshida and A. Nakamura, *Inorg. Chem. (Washington)*, **6**, 20 (1967).

[7] H. C. Barany, E. A. Braude and M. Pianka, *J. Chem. Soc.*, **1949**, 1898.

[8] H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964).

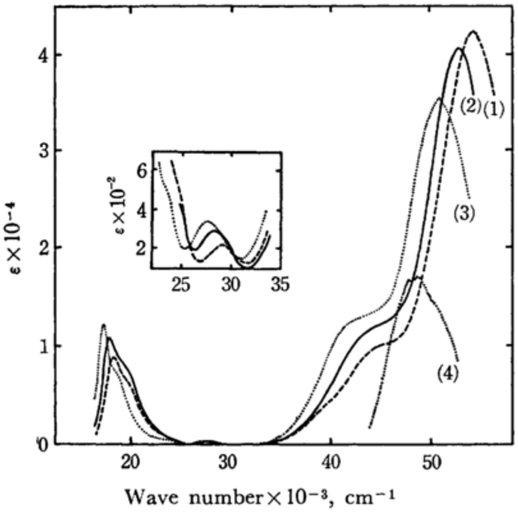

Fig. 1. The absorption spectra of (1) tris(glyoxal-bis-*N*-methylimine)iron(II) tetrafluoroborate, (2) tris(biacetyl-bis-*N*-methylimine)iron(II) tetrafluoroborate, (3) tris(biacetyl-bis-*N*-butylimine)iron-(II) tetrafluoroborate in an aqueous solution and (4) biacetyl-bis-*N*-butylimine in an ethanol solution.

appearing near 18000 cm^{-1}, which is the origin of the intense color, has received much attention. On the other hand, an intense band near 50000 cm^{-1} with a moderately intense shoulder has not attracted any attention, and nothing has been reported of it, probably because of the difficulty of the measurement. It should be noted that there are two shoulder bands which are difficult to observe. One appears in all cases near 25000 cm^{-1} with molar extinction coefficient of ∼400, whereas the other is observed only with tris(glyoxal-bis-*N*-methylimine)iron(II) ion at ∼38000 cm^{-1}.

The observed spectrum of the ligand, biacetyl-bis-*N*-butylimine, is also shown in Fig. 1. The spectrum of the free ligand was measured in an ethanol solution, which well accorded with the result of Barany *et al.*[7)]

Theoretical Consideration and Calculation of Electronic Structure

The structures of an α-diimine molecule and a tris(α-diimine)iron(II) complex are shown in Figs. 2 and 3 together with the coordinate systems used. Since no experimental data of their geometrical structures were reported, it was assumed that the C–N and the C–C bond distance in the conjugated system were 1.37 and 1.46 Å, respectively, and also the angle between the C–N and the C–C bond was 120°.

The method of theoretical treatment was already described for the acetylacetonato complexes of transition metals.[5)] The outline of the calculation will be given below. The integral values characteristic for the present complex ions, however, will be discussed in detail.[*3]

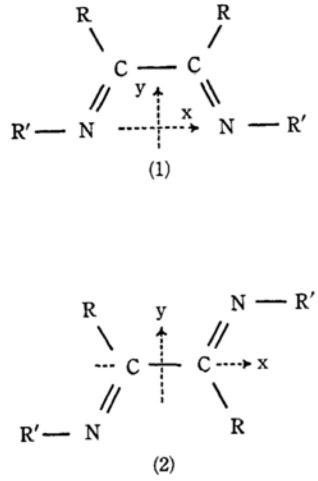

Fig. 2. Structure of α-diimine in cis form (1) and trans form (2). R=H, R′=CH_3, glyoxal-bis-*N*-methylimine; R=CH_3, R′=CH_3, biacetyl-bis-*N*-methylimine; R=CH_3, R′=C_4H_9, biacetyl-bis-*N*-butylimine.[*2]

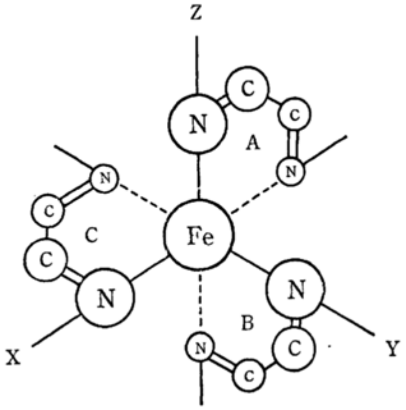

Fig. 3. The geometrical structure of tris(α-diimine)iron(II) complex and the coordinate system adopted. The Fe–N bond distance was assumed to be 2.00 Å. Only metal ion and chelate rings are shown.

SCF MO and the Lower Excited States of α-Diimine. α-Diimine molecule has four electrons in its π electron system which is made of two

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[*2] The IUPAC nomenclatures of glyoxal-bis-*N*-methylimine, biacetyl-bis-*N*-methylimine and biacetyl-bis-*N*-butylimine are *N, N′*-dimethyl-1, 2-ethanediimine, *N, N′*-dimethyl-2, 3-butanediimine and *N, N′*-dibutyl-2, 3-butanediimine, respectively.

[*3] 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 5020E at the University of Tokyo.

TABLE 1. SCF MO AND ITS ORBITAL ENERGY (ε) OF α-DIIMINE IN CIS AND TRANS CONFORMATION

	Sym.	ε, eV	Coefficients of AO's			
			N	C	C′	N′
Cis conformation (C_{2v})						
φ_1	b_2	−14.034	0.4611	0.5361	0.5361	0.4611
φ_2	a_2	−12.010	−0.6170	−0.3454	0.3454	0.6170
φ_3	b_2	−2.428	−0.5361	0.4611	0.4611	−0.5361
φ_4	a_2	0.575	0.3454	−0.6170	0.6170	−0.3454
Trans conformation (C_{2h})						
φ_1	a_u	−14.212	0.4757	0.5231	0.5231	0.4757
φ_2	b_g	−12.068	−0.6163	−0.3466	0.3466	0.6163
φ_3	a_u	−2.637	−0.5231	0.4757	0.4757	−0.5231
φ_4	b_g	0.513	0.3466	−0.6163	0.6163	−0.3466

carbon 2pπ AO's and two nitrogen 2pπ AO's. The nitrogen atom may be in an sp^2 hybrid valence state so that the lone-pair electrons in sp^2 hybrid AO's make a coordinate bond with a metal ion.

Following Pariser-Parr-Pople's treatment,[9,10] self-consistent field molecular orbitals (SCF MO's) were calculated. Then, the energies and the wave functions of lower excited states were determined by taking into consideration the configuration interaction (CI) between all singly-excited configurations. The valence state ionization potentials (I) and the electron affinities (A) were obtained from the table given by Pilcher and Skinner[11] as follows:

$I=11.22$ eV and $A=0.62$ eV for carbon, and

$I=14.51$ eV and $A=1.20$ eV for nitrogen.

On the zero-differential overlap approximation, the core resonance integrals between adjacent AO's were calculated with the relation,

$$\beta_{ij}=\frac{S_{ij}}{S_0}\beta_0 \tag{1}$$

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.*,[12] the core resonance integrals were determined to be

$$\beta_{\mathrm{CC}}=-2.130\,\mathrm{eV} \text{ and } \beta_{\mathrm{CN}}=-1.947\,\mathrm{eV}.$$

α-Diimine molecule is considered to exist in preferred trans conformation in a free state, but in cis conformation when chelated in the metal complex. To examine the geometrical effect, the calculation of SCF-CI was carried out for both cis and trans conformations.

The calculated SCF MO's are shown in Table 1. The results of the calculation of the configuration interaction are summarized in Tables 2 and 3.

Barany *et al.*[7] reported that biacetyl-bis-*N*-butylimine showed the $\pi\rightarrow\pi^*$ absorption spectrum, at 207 mμ (5.99 eV) with the molar extinction coefficient of 17000. From the observed spectrum the oscillator strength of the band was determined to be ∼0.5.

As can be seen from Tables 2 and 3, the excitation energy and the intensity calculated for the first excited state, especially, those of the trans conformation, are both in reasonable agreement with those of the observed band.[*4] The lowest excited state is mainly composed of the $\varphi_2\rightarrow\varphi_3$ configuration in both conformation. The lowest transition is antisymmetric in cis conformation with respect to the symmetry plane perpendicular to the plane of the α-diimine molecule (x-polarization, see Fig. 2).[*5]

SCF Calculation of the Ligand in the Complex. The MO's of α-diimine obtained above are self-consistent with respect to the field of the free molecule. For the ligands in the complex ion, however, the effects of the electrostatic potential fields caused by the other ligands and the metal ion are considerably strong and must be taken into account in the SCF calculation, so that the MO's used for the calculation of the electronic

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

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

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

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

[*4] Using the β_{CN} value larger than that evaluated by Eq. (1), the better agreement between the calculated and the observed results was obtained for the free ligand molecule but not for the ligand in the metal complex. It may be due to either the inaccuracy of the assumed interatomic distances or the essential difference of C-N bond character between in a free state and in a chelated state (see the discussions given in Refs. 4 and 13).

13) T. Ito, N. Tanaka, I. Hanazaki and S. Nagakura, *Sci. Repts. Tohoku Univ., First Ser.*, **50**, 168 (1967).

[*5] Moreover, the absorption intensity and excitation energy of cis conformation were calculated to be lower than those of trans conformation, in accord with the original inference of Mulliken for *cis*- and *trans*-butadienes.[14]

14) R. S. Mulliken, *J. Chem. Phys.*, **7**, 21 (1939).

TABLE 2. CALCULATED AND OBSERVED VALUES OF TRANSITION ENERGY (E) AND OSCILLATOR STRENGTH (f) FOR α-DIIMINE

State	Calculated						Observed*	
	Cis conformation			Trans conformation				
	Sym.	E, eV	f	Sym.	E, eV	f	E, eV	f
W_1	B_1	4.58	0.38	B_u	5.02	0.96	5.99	~0.5
W_2	A_1	6.05	0.21	A_g	5.90	0		
W_3	A_1	6.82	0.47	A_g	6.72	0		
W_4	B_1	8.18	0.03	B_u	8.45	0.14		

* Observed value for biacetyl-bis-*N*-butylimine

TABLE 3. WAVE FUNCTIONS OF THE LOWER EXCITED STATES OF α-DIIMINE*

State	Cis conformation	Trans conformation
W_1	$0.1567\Phi(1^{-1}4)+0.9877\Phi(2^{-1}3)$	$0.1213\Phi(1^{-1}4)+0.9926\Phi(2^{-1}3)$
W_2	$0.9706\Phi(1^{-1}3)-0.2406\Phi(2^{-1}4)$	$0.9754\Phi(1^{-1}3)+0.2205\Phi(2^{-1}4)$
W_3	$0.2406\Phi(1^{-1}3)+0.9706\Phi(2^{-1}4)$	$-0.2205\Phi(1^{-1}3)+0.9754\Phi(2^{-1}4)$
W_4	$0.9877\Phi(1^{-1}4)-0.1567\Phi(2^{-1}3)$	$0.9926\Phi(1^{-1}4)-0.1213\Phi(2^{-1}3)$

* $\Phi(i^{-1}j)$ means the one-electron excited configuration from the ith MO to the jth one.

TABLE 4. SCF MO AND ITS ORBITAL ENERGY (ε) OF CHELATED α-DIIMINE IN IRON COMPLEX*

	Sym.	ε, eV	Coefficients of AO's			
			N	C	C′	N′
φ_1	b_2	−23.675	0.5106	0.4892	0.4892	0.5106
φ_2	a_2	−22.067	0.6388	0.3033	−0.3033	−0.6388
φ_3	b_2	−12.246	−0.4892	0.5106	0.5106	−0.4892
φ_4	a_2	−8.925	0.3033	−0.6388	0.6388	−0.3033

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

TABLE 5. LOWER FOUR ENERGY LEVELS AND THEIR WAVE FUNCTIONS OF CHELATED α-DIIMINE IN IRON COMPLEX*

State	Sym.	Energy, eV	f	Wave function
W_1	B_1	4.67	0.34	$-0.1696\Phi(1^{-1}4)+0.9855\Phi(2^{-1}3)$
W_2	A_1	5.92	0.34	$0.9991\Phi(1^{-1}3)+0.0423\Phi(2^{-1}4)$
W_3	A_1	7.15	0.29	$-0.0423\Phi(1^{-1}3)+0.9991\Phi(2^{-1}4)$
W_4	B_1	8.28	0.02	$0.9855\Phi(1^{-1}4)+0.1696\Phi(2^{-1}3)$

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

structure of the metal complex are self-consistent with the distribution of π-electrons in the other ligand, the electrostatic potential field of the central metal ion being taken into account.5) Since the degree of σ-donation caused by the coordination was uncertain, the 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. When the charge of the central metal ion is neutralized or partly neutralized, the σ-hole appears at the coordinated nitrogen atoms. The potential due to the σ-hole was also included in the core part of the Hartree-Fock operator. Its energy was calculated from Roothaan's table,15) using Slater 2s and 2p AO of nitrogen and 2pπ AO of carbon. The parameters in the improved SCF calculation were determined similarly, but varied according to the degree of σ-donation.

Tables 4 and 5 show the results of the SCF-CI calculation obtained for the case when the formal charge of iron is zero. These results were used in the following calculation because of the reason discussed later.*6

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15) C. C. J. Roothaan, "Tables of Two-Center Coulomb Integrals Between 1s, 2s and 2p Orbitals," Special Technical Report of the University Chicago (1955).

*6 The results for the other cases are reported elsewhere.13) The parameters for nitrogen atom used in the calculation of the results given in Tables 4 and 5 are: $I=18.68$, $A=4.52$ and $\beta_{CN}=-1.866$ eV.

The Symmetries of the Electronic Configurations of Tirs(α-diimine)iron(II) Complex. It was found by the measurement of magnetic susceptibility that the electronic spin of tris(biacetyl-bis-*N*-methylimine)iron(II) iodide is singlet in its ground state.[3] Therefore, six electrons of iron(II) may be in 3dπ AO, d_{xy}, d_{yz} and d_{zx} with antiparallel spins.

As we consider explicitly only π-electron systems, tris(α-diimine)iron(II) complexes can be divided into four components, namely, a π-electron system of metal ion and those of the three ligands. By placing π-electrons in the appropriate orbitals, the wave function for the ground configuration can be represented by the equation,

$$G = |(1\bar{1}2\bar{2})^{A}(1\bar{1}2\bar{2})^{B}(1\bar{1}2\bar{2})^{C}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}|$$

where superscripts A, B and C denote the three coordinated α-diimine molecules shown in Fig. 3.

In addition to the ground configuration, eighteen charge transfer (CT) configurations and twelve locally excited (LE) configurations were taken into account, which are given in Table 6.

The CT configuration is constructed by transferring an electron from one of the 3dπ AO's to the vacant MO φ_3 or φ_4 of one of the three ligands. The LE configuration is constructed by exciting an electron in an occupied MO of one of the three ligands to a vacant MO of the same ligand.

Table 6. Singly-excited configurations taken into account for the configuration interaction calculation

Configuration	Orbitals	
	from	to
CT	d_{xy} d_{yz} d_{zx}	φ_3^{A} , φ_4^{A} φ_3^{B} , φ_4^{B} φ_3^{C} , φ_4^{C}
LE	φ_1^{A}	φ_3^{A} and φ_4^{A}
	φ_2^{A}	φ_3^{A} and φ_4^{A}
	Similar eight transitions in ligand B and C	

In a way similar to the ground configuration, the wave function for a CT configuration in which one electron is transferred from d_{xy} to φ_3^{A} is expressed as,

$$CT(d_{xy}\rightarrow\varphi_3^{A}) =$$
$$\frac{1}{\sqrt{2}}\{|(1\bar{1}2\bar{2})^{A}(1\bar{1}2\bar{2})^{B}(1\bar{1}2\bar{2})^{C}\varphi_3^{A}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}| + |(1\bar{1}2\bar{2})^{A}(1\bar{1}2\bar{2})^{B}(1\bar{1}2\bar{2})^{C}d_{xy}\bar{\varphi}_3^{A}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}|\}$$

Similarly, the wave function for a LE configuration in which one electron in φ_2^{A} is excited to φ_3^{A} is expressed as,

$$LE(\varphi_2^{A}\rightarrow\varphi_3^{A}) =$$
$$\frac{1}{\sqrt{2}}\{|(1\bar{1}3\bar{2})^{A}(1\bar{1}2\bar{2})^{B}(1\bar{1}2\bar{2})^{C}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}| + |(1\bar{1}2\bar{3})^{A}(1\bar{1}2\bar{2})^{B}(1\bar{1}2\bar{2})^{C}d_{xy}\overline{d_{xy}}d_{yz}\overline{d_{yz}}d_{zx}\overline{d_{zx}}|\}$$

Other CT and LE configurations are expressed in a similar way. By taking the linear combination of the above-mentioned wave functions, the ground, the CT and the LE configurations are classified into the irreducible representations of D_3 symmetry, which are given below.

A_1:

$$G = G$$

$$CT_1^{A_1} = \frac{1}{\sqrt{6}}\{CT(d_{xy}\rightarrow\varphi_3^{A}) - CT(d_{yz}\rightarrow\varphi_3^{A}) - CT(d_{xy}\rightarrow\varphi_3^{B}) + CT(d_{zx}\rightarrow\varphi_3^{B}) + CT(d_{yz}\rightarrow\varphi_3^{C}) - CT(d_{zx}\rightarrow\varphi_3^{C})\}$$

$$CT_2^{A_1} = \frac{1}{\sqrt{6}}\{CT(d_{xy}\rightarrow\varphi_4^{A}) + CT(d_{yz}\rightarrow\varphi_4^{A}) + CT(d_{xy}\rightarrow\varphi_4^{B}) + CT(d_{zx}\rightarrow\varphi_4^{B}) + CT(d_{yz}\rightarrow\varphi_4^{C}) + CT(d_{zx}\rightarrow\varphi_4^{C})\}$$

$$CT_3^{A_1} = \frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_4^{A}) + CT(d_{yz}\rightarrow\varphi_4^{B}) + CT(d_{xy}\rightarrow\varphi_4^{C})\}$$

$$LE_1^{A_1} = \frac{1}{\sqrt{3}}\{LE(\varphi_1^{A}\rightarrow\varphi_3^{A}) + LE(\varphi_1^{B}\rightarrow\varphi_3^{B}) + LE(\varphi_1^{C}\rightarrow\varphi_3^{C})\}$$

$$LE_2^{A_1} = \frac{1}{\sqrt{3}}\{LE(\varphi_2^{A}\rightarrow\varphi_4^{A}) + LE(\varphi_2^{B}\rightarrow\varphi_4^{B}) + LE(\varphi_2^{C}\rightarrow\varphi_4^{C})\}$$

A_2:

$$CT_1^{A_2} = \frac{1}{\sqrt{6}}\{CT(d_{xy}\rightarrow\varphi_3^{A}) + CT(d_{yz}\rightarrow\varphi_3^{A}) + CT(d_{xy}\rightarrow\varphi_3^{B}) + CT(d_{zx}\rightarrow\varphi_3^{B}) + CT(d_{yz}\rightarrow\varphi_3^{C}) + CT(d_{zx}\rightarrow\varphi_3^{C})\}$$

$$CT_2^{A_2} = \frac{1}{\sqrt{3}}\{CT(d_{zx}\rightarrow\varphi_3^{A}) + CT(d_{yz}\rightarrow\varphi_3^{B}) + CT(d_{xy}\rightarrow\varphi_3^{C})\}$$

$$CT_3{}^{\mathrm{A}_2} = \frac{1}{\sqrt{6}}\{CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{A}}) - CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{A}}) - CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{B}}) + CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{B}}) + CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{C}}) - CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{C}})\}$$

$$LE_1{}^{\mathrm{A}_2} = \frac{1}{\sqrt{3}}\{LE(\varphi_2{}^{\mathrm{A}}\to\varphi_3{}^{\mathrm{A}}) + LE(\varphi_2{}^{\mathrm{B}}\to\varphi_3{}^{\mathrm{B}}) + LE(\varphi_2{}^{\mathrm{C}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$LE_2{}^{\mathrm{A}_2} = \frac{1}{\sqrt{3}}\{LE(\varphi_1{}^{\mathrm{A}}\to\varphi_4{}^{\mathrm{A}}) + LE(\varphi_1{}^{\mathrm{B}}\to\varphi_4{}^{\mathrm{B}}) + LE(\varphi_1{}^{\mathrm{C}}\to\varphi_4{}^{\mathrm{C}})\}$$

E:

$$CT_1{}^{\mathrm{E}} = \frac{1}{2}\{CT(\mathrm{d_{xy}}\to\varphi_3{}^{\mathrm{B}}) + CT(\mathrm{d_{zx}}\to\varphi_3{}^{\mathrm{B}}) - CT(\mathrm{d_{yz}}\to\varphi_3{}^{\mathrm{C}}) - CT(\mathrm{d_{zx}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$CT_2{}^{\mathrm{E}} = \frac{1}{\sqrt{12}}\{2CT(\mathrm{d_{xy}}\to\varphi_3{}^{\mathrm{A}}) - 2CT(\mathrm{d_{yz}}\to\varphi_3{}^{\mathrm{A}}) - CT(\mathrm{d_{zx}}\to\varphi_3{}^{\mathrm{B}}) + CT(\mathrm{d_{xy}}\to\varphi_3{}^{\mathrm{B}}) - CT(\mathrm{d_{yz}}\to\varphi_3{}^{\mathrm{C}}) + CT(\mathrm{d_{zx}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$CT_3{}^{\mathrm{E}} = \frac{1}{\sqrt{2}}\{CT(\mathrm{d_{yz}}\to\varphi_3{}^{\mathrm{B}}) - CT(\mathrm{d_{xy}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$CT_4{}^{\mathrm{E}} = \frac{1}{\sqrt{12}}\{2CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{A}}) + 2CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{A}}) - CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{B}}) - CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{B}}) - CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{C}}) - CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{C}})\}$$

$$CT_5{}^{\mathrm{E}} = \frac{1}{2}\{CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{B}}) - CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{B}}) - CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{C}}) + CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{C}})\}$$

$$CT_6{}^{\mathrm{E}} = \frac{1}{\sqrt{6}}\{2CT(\mathrm{d_{zx}}\to\varphi_4{}^{\mathrm{A}}) - CT(\mathrm{d_{yz}}\to\varphi_4{}^{\mathrm{B}}) - CT(\mathrm{d_{xy}}\to\varphi_4{}^{\mathrm{C}})\}$$

$$LE_1{}^{\mathrm{E}} = \frac{1}{\sqrt{6}}\{2LE(\varphi_1{}^{\mathrm{A}}\to\varphi_3{}^{\mathrm{A}}) - LE(\varphi_1{}^{\mathrm{B}}\to\varphi_3{}^{\mathrm{B}}) - LE(\varphi_1{}^{\mathrm{C}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$LE_2{}^{\mathrm{E}} = \frac{1}{\sqrt{6}}\{2LE(\varphi_2{}^{\mathrm{A}}\to\varphi_4{}^{\mathrm{A}}) - LE(\varphi_2{}^{\mathrm{B}}\to\varphi_4{}^{\mathrm{B}}) - LE(\varphi_2{}^{\mathrm{C}}\to\varphi_4{}^{\mathrm{C}})\}$$

$$LE_3{}^{\mathrm{E}} = \frac{1}{\sqrt{2}}\{LE(\varphi_2{}^{\mathrm{B}}\to\varphi_3{}^{\mathrm{B}}) - LE(\varphi_2{}^{\mathrm{C}}\to\varphi_3{}^{\mathrm{C}})\}$$

$$LE_4{}^{\mathrm{E}} = \frac{1}{\sqrt{2}}\{LE(\varphi_1{}^{\mathrm{B}}\to\varphi_4{}^{\mathrm{B}}) - LE(\varphi_1{}^{\mathrm{C}}\to\varphi_4{}^{\mathrm{C}})\}$$

There is another similar set of ten wave functions with E representation which are orthogonal to the above wave functions.

Configuration Interaction. The matrix elements of the total electronic Hamiltonian between the configurations were calculated in a way similar to the case of the acetylacetonato complex.[*7] The diagonal element of the CT configuration, $E_{\mathrm{CT}(i)}$, is represented by means of the equation,

$$E_{\mathrm{CT}(i)} = I(\text{metal}) - A_{(i)}(\text{ligand}) + \varDelta_{(i)} \qquad (2)$$

where, I(metal) is the valence state ionization potential of 3dπ AO of iron, $A_{(i)}$(ligand), the electron affinity to put an electron into the ith vacant MO of the ligand and $\varDelta_{(i)}$, the electrostatic interaction energy between the electron donor and acceptor. $A_{(i)}$(ligand) may be equal to the orbital energy with sign reversed of the MO to which an electron is transferred. There remains difficulty in the actual evaluation of E_{CT}, because it is very sensitive to the σ-electron distribution and, also, because $A_{(i)}$(ligand) cannot be determined accurately (see the discussion given in Ref. 5).

Figure 4 shows the relation between $E_{\mathrm{CT}(1)}$ and the formal charge of iron, which was roughly evaluated by the calculation of an appropriate two-center repulsion integral with the point charge approximation. Considering the fact that the CT band appears at about 2.2 eV (~18000 cm^{-1}), the formal charge of iron seems to be close to zero though there is some uncertainty in the estimated value of E_{CT}. Therefore, the MO's of the ligands used in the following calculation are those constructed with the condition that the formal charge of iron is zero.

As is evident from the above discussion, the accurate evaluation of E_{CT} is quite difficult. Therefore, in the present calculation, $E_{\mathrm{CT}(1)}$, the diagonal element of CT configurations corresponding to d→φ_3 transition, was treated as a parameter and set to be 1.0 eV. The value of $E_{\mathrm{CT}(2)}$ corresponding to d→φ_4 transition was determined to be $E_{\mathrm{CT}(2)} = E_{\mathrm{CT}(1)} + 3.87$ eV, considering the difference of $A_{(i)}$ and $\varDelta_{(i)}$ between φ_3 and φ_4.

[*7] The details of the matrix elements are shown in Ref. 13.

TABLE 7. WAVE FUNCTIONS AND ENERGIES OF THE LOWER ELECTRONIC STATES OF TRIS(α-DIIMINE)IRON(II) ION

	E, eV*	Sym.	Wave function**
W_0	−1.391	A_1	$-0.8015\,G-0.5797\,CT_1{}^{A_1}+0.1353\,CT_2{}^{A_1}$
W_1	0.784	E	$-0.9720\,CT_1{}^{E}-0.2342\,LE_3{}^{E}$
W_2	0.816	A_2	$-0.9794\,CT_1{}^{A_2}-0.2014\,LE_1{}^{A_2}$
W_3	0.896	E	$0.9896\,CT_2{}^{E}+0.1441\,LE_1{}^{E}$
W_4	4.553	E	$-0.9423\,CT_4{}^{E}-0.3345\,LE_2{}^{E}$
W_5	4.579	E	$0.1855\,CT_1{}^{E}+0.5972\,CT_5{}^{E}-0.7412\,LE_3{}^{E}+0.2441\,LE_4{}^{E}$
W_6	4.701	A_2	$0.9551\,CT_3{}^{A_2}-0.1854\,LE_1{}^{A_2}+0.2268\,LE_2{}^{A_2}$
W_7	4.819	E	$-0.1430\,CT_1{}^{E}+0.7777\,CT_5{}^{E}+0.6095\,LE_3{}^{E}$
W_8	5.318	A_2	$-0.1958\,CT_1{}^{A_2}+0.2258\,CT_3{}^{A_2}+0.9438\,LE_1{}^{A_2}-0.1410\,LE_2{}^{A_2}$
W_9	5.917	E	$0.1440\,CT_2{}^{E}-0.9890\,LE_1{}^{E}$

* The energy of the ground configuration is taken to be zero.
** Only main configurations are written.

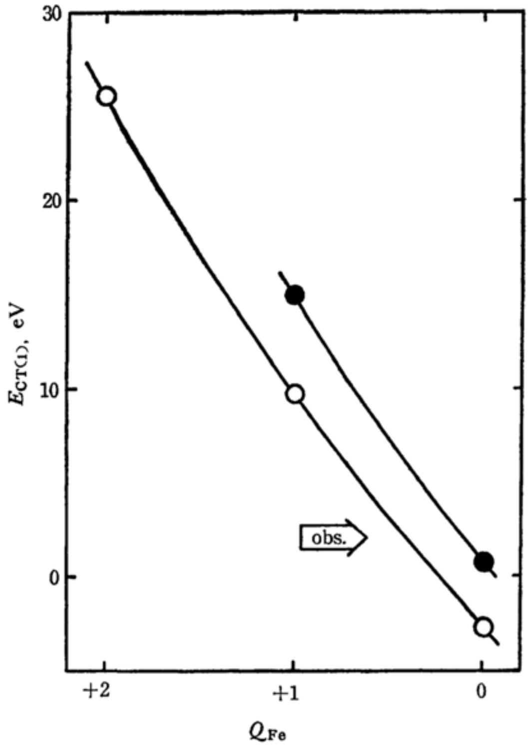

Fig. 4. The relation between $E_{CT(1)}$ and the formal charge of iron, Q_{Fe}, where $E_{CT(1)}$ is the diagonal element of the CT configuration with the lowest energy. ○ and ● correspond to d^n and $d^{n-1}s$ configuration, respectively.

The diagonal elements of LE configurations are expressed as the sum of the excitation energy of the chelated ligand molecule, $E_{LE}(\varphi_i\rightarrow\varphi_j)$, and the additional term including the integral K'_{ij}. The latter is the repulsion integral defined by

$$K'_{ij}=\int\varphi_i{}^{A}(1)\varphi_j{}^{A}(1)\frac{e^2}{r_{12}}\varphi_i{}^{B}(2)\varphi_j{}^{B}(2)\mathrm{d}\tau_{12} \quad (3)$$

The K'_{ij}'s were calculated with the zero-differential overlap and the point charge approximation.*8

The off-diagonal matrix elements between G and CT and between CT and LE were accounted for only by means of β, the core resonance integral between the appropriate 3dπ AO of iron and 2pπ AO of nitrogen. It was evaluated with the relation,16)

$$\beta=-S\frac{I_{Fe}+I_{N}}{2} \quad (4)$$

TABLE 8. COMPARISON OF OBSERVED VALUES WITH CALCULATED ELECTRONIC STRUCTURES OF TRIS(α-DIIMINE)IRON(II) ION

Calculated			Observed*	
Transition from W_0 to	E eV**	f	E, eV**	f
W_1	2.18	0.002	2.19 ~2.4 (shoulder)	0.17
W_2	2.21	0.002		
W_3	2.29	0.357		
W_4	5.94	~0	~5.3 (shoulder) 6.56	
W_5	5.97	0.076		1.5
W_6	6.09	0.024		
W_7	6.21	0.266		
W_8	6.71	0.675		
W_9	7.31	0.655		

* Observed values for tris(biacetyl-bis-N-methylimine)iron(II) tetrafluoroborate in aqueous solutions.
** Transition energy.

[*8] In contrast with the treatment reported previoulsy,5) the LE configuration is constructed with only one kind of singly-excited configuration. Therefore, $E_{LE}(\varphi_i\rightarrow\varphi_j)$'s appearing in the diagonal elements of the LE configurations correspond to the transition energies without CI. The interactions among the LE configurations were taken into account in the calculation of the CI for the whole complex.

16) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

where S is the overlap integral, and I_{Fe} and I_N are the valence state ionization potentials of iron and nitrogen, respectively. The estimation of the overlap integral was made with the aid of the Slater AO of nitrogen and the two-term expanded AO of iron determined by Richardson *et al.*17) It was calculated to be 0.084, using the table given by Jaffé.18) I_{Fe} and I_N are 5.07 eV and 18.68 eV respectively and β amounts to -0.99 eV.

The results obtained by the configuration interaction calculation are shown in Table 7, and the calculated transition energy and oscillator strength are compared with the observed ones in Table 8.

Stabilization caused by the Charge Transfer. According to the present theoretical investigation, the energy of the ground state is lower than that of the ground configuration by 1.39 eV (32.0 kcal/mol). This stabilization is caused by the interaction between the ground and the CT configurations; the contribution of the CT configuration to the ground state amounts to about 30%. This means that the so-called π-back donation from the metal to the ligands is considerably large. This phenomenon may be responsible for the one of the origins of the unusual stability of tris(α-diimine)iron(II) complexes.

Interpretation of the Electronic Spectra

The spectra given in Fig. 1 exhibit a weak absorption band near 28000 cm^{-1} in all tris(α-diimine)iron(II) complexes investigated. The careful measurement also revealed a shoulder band with almost the same intensity near 25000 cm^{-1}. The shoulder and the peak may be assigned to the d→d transitions which correspond to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of the octahedral case, in view of their low intensities and also on the basis of the study reported by Shimura *et al.*19) They found that the absorption frequencies of the iron(II) complex are smaller by 7×10^{13} sec^{-1} than those of the corresponding cobalt(III) complex independent of the kind of ligand, as far as the same kind of absorption bands are compared and both complexes assume the diamagnetic $(3d)^6$ configuration. Any further discussion on these bands is not given, because the authors were concerned with a parity-allowed transition of the π-electron system in the present study.

From the results given in Table 7, it can be concluded that the observed intense band at the visible region is reasonably assigned to the almost pure CT absorption accompanying the π-electron migration from 3dπ AO of iron to the lowest vacant π MO, φ_3, of the ligands.

Since the α-diimine ligands has C_{2v} symmetry in the cis form, the $\pi \rightarrow \pi^*$ transition in the ligand has a transition moment either parallel (x) or perpendicular (y) to the nitrogen-nitrogen direction in the plane of the molecule (see Fig. 2). As has been disucssed by Larsen *et al.*,20) the x-polarized transition in three ligands in the metal complex of D_3 symmetry gives rise to the $A_1 \rightarrow A_2$ and the $A_1 \rightarrow E$ transition, while y-polarized transition, 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, there should appear a single band with its intensity three times as large as that of single α-diimine ligand. On the other hand, if the transition is x-polarized, the intensity ratio of the LE bands corresponding to the $A_1 \rightarrow E$ and the $A_1 \rightarrow A_2$ ought to be 1 : 2. Furthermore, the energy separation between these bands is $6K'_{ij}$ for $\varphi_i \rightarrow \varphi_j$ transition.

The observed spectrum in the ultraviolet region was composed of an intense peak and a moderately intense shoulder at the side of longer wavelengths. In view of their large intensities and energies and also in comparison with the absorption spectrum of the free ligand (see Fig. 1), both of them should be assigned to the lowest LE transitions. In fact, the calculated result predicts that the LE transitions corresponding to the x-polarized excitation $\varphi_2 \rightarrow \varphi_3$ in the ligand appear in this region with splitting by 0.67 eV into the A_2 and E components. The observed spectra really show the splitting, which supports, at least qualitatively, the theoretical prediction. Quantitatively, however, the splitting was found to be nearly twice as large as the calculated value. This discrepancy seems to be explained by considering the mixing of the second CT transition $d \rightarrow \varphi_4$ into the loewst LE transitions. The calculation has revealed that this second CT configuration appears in almost the same energy as the lowest LE configuration and that its mixing especially with the E component of the LE band is significant.*9

Therefore, it seems reasonable to conclude that the main peak results from the LE transition with $A_1 \rightarrow A_2$ symmetry whereas the shoulder is due to the overlap of the $d \rightarrow \varphi_4$ transition and the LE transition with $A_1 \rightarrow E$ symmetry or their mixed states.

The replacement of the alkyl groups (R or R′) attached to the conjugated system of the ligand with a larger alkyl group gives rise to a shift of absorption maxima of both the visible and the

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

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

19) Y. Shimura, N. Matsuoka and T. Yasui, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 635 (1964).

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

*9 Another shoulder band is observed near 38000 cm^{-1} in the spectrum of tris(glyoxal-bis-*N*-methylimine)-iron(II) complex, which may be due to the interaction of CT($d \rightarrow \varphi_4$) and the E component of LE band.

ultraviolet bands toward longer wavelengths, as shown in Fig. 1. Such a frequency shift was also observed for alkyl derivatives of butadiene.[21] Although the sensitivity to the alkyl substitution is different between the visible and the ultraviolet band, the origin of the frequency shift may be the same. It is also said that the larger the substituent is, the lower the energy of the lowest vacant orbital may be.

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21) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," International Series of Monographs on Organic Chemistry ed. by D. H. R. Barton and W. Doering, Vol. 7, Pergamon Press, Oxford (1964), p. 21.