Inorganica Chimica Acta, 15 (1975) 25–32

Studies on the Coordinate Bond. VII. Complexes of Diimines with Iron, Synthesis and Spectral Properties[1,2].

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Received January 15, 1975

In order to investigate the spectral properties of iron diimine complexes a new series of complexes was synthesized and characterized. Their electronic spectra were studied including solid state liquid nitrogen temperature (LNT) measurements. This study showed that in the case of the ferrous complexes three metal to ligand electron transfer (MLET) bands can be observed, in the visible region, although many authors have assigned them to vibrational structure of the main band. The d–d bands in the spectra of the ferrous complexes are discussed. Very intense internal ligand electron transfer (ILET) bands are observed in the UV region and discussed. In the case of the ferric complexes we observed two ligand to metal electron transfer (LMET) bands in the visible region and ILET bands in the UV region. A correlation between the energy of these transitions in the ferrous and ferric complexes is discussed.

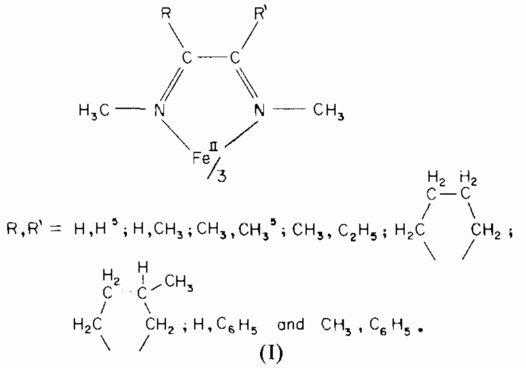
Introduction

In the past years we have been interested in the study of the electronic spectra of ferrous diimine complexes. These spectra show three types of absorption bands which can be attributed to transitions between MO's mainly localized on the central metal atom, MO's mainly localized on the ligands and, at the same time, MO's mainly localized on the ligands and MO's mainly localized on the central metal atom. The last type can be classified as a metal to ligand electron transfer or a ligand to metal electron transfer transition. If one fixes the metal and changes its oxidation state and/or changes regularly the ligands, it is possible to see the behavior of the electronic levels, according to these changes, from the electronic spectra.

In 1953, Krumholz[4] first prepared ferrous complexes with aliphatic diimine ligands, the tris(biacetylbis(methylimine))ferrous iodide, $Fe(BMI)_3I_2$, and the tris(glyoxalbis(methylimine))ferrous iodide, $Fe(GMI)_3$ I_2. The spectra of these complexes resemble the spectra of the similar complexes with phen and dipy as ligands. A strong band in the visible region was observed and assigned, according to Williams[5], to a MLET transition. The strong absorption was related to the presence of a common structural element, a cromophore[6], the functional grouping N=C–C=N. Later[7] Krumholz assigned the double shaped structure of this band to a probable vibrational coupling of the electronic energy levels.

The oxidation of the two compounds prepared by Krumholz[4], in acid media, gives the corresponding ferric complexes as shown by Krumholz and Li Chum in a recent paper[8]. This enables us to study the spectra of these complexes in the oxidized form.

In this work we report the synthesis of a new series of diimine ferrous complexes (I) in order to study their electronic spectra.



(I)

An assignment of the absorption bands is suggested based on the regular variation of the spectra with ligands and on the liquid nitrogen temperature spectra (LNTS). The electronic spectra of the corresponding ferric complexes are reported and assigned. The correlation between results with ferrous and ferric complexes seems to agree with the assignments made.

Experimental

Materials

Solutions of $FeCl_2$ (Baker p.a.) were prepared under nitrogen and treated with iron powder (Merck

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* Deceased.

p.a.) before using to reduce iron(III) present. The methylamine solution used in the synthesis was Eastman Laboratory grade reagent. Solutions for the oxidation procedures were prepared according to reference 8.

Synthesis

The complexes tris(glyoxalbis(methylimine))ferrous perchlorate and tris(biacetylbis(methylimine))ferrous perchlorate were prepared from a modification of the method described by Krumholz[4].

Condensations were performed under nitrogen to avoid oxidation of iron(II) and of the organic reactants in the alkaline media. All analyses refer to materials dried *in vacuo* over P_2O_5 to constant weight.

Tris(methylglyoxalbis(methylimine)) ferrous perchlorate, $[Fe(MMI)_3](ClO_4)_2$

To 5.5 ml of a methylamine solution (630 mmol) was added 21.5 ml of a $FeCl_2$ solution (43 mmol). The mixture was kept in a water bath at 30° C and, under a nitrogen atmosphere, 25 ml of pyruvic aldehyde (160 mmol, Aldrich tech. distilled 95–98° C/700 mmHg) was added dropwise. The mixture was kept in the bath with constant stirring for 1 hour; 60 g of $NaClO_4 \cdot H_2O$ (410 mmol) was added and the mixture was cooled in an ice bath by 4 hours. The precipitate was filtered off, washed with a cold solution of $NaClO_4$ and then with cold water: yield 14.5 g. This product was twice recrystallized from a 0.1 N acetic acid solution; yield 4.0 g. *Anal.* Calcd. for $[Fe(C_5H_{10}N_2)_3](ClO_4)_2$: Fe, 10.17; C, 32.81; N, 15.30; H, 5.51. Found: Fe, 9.96; C, 32.61; N, 15.24; H, 5.48%.

Tris(2,3-pentanedionebis(methylimine))ferrous perchlorate, $[Fe(EMI)_3](ClO_4)_2$

A mixture of 3.0 ml of 2,3-pentanedione (28 mmol, Fluka purum), 9.9 ml of a methylamine solution (114 mmol) and 4.6 ml of a $FeCl_2$ solution (9 mmol) was dissolved in 10 ml of deaerated water and kept in a water bath at 40° C during 90 minutes. The mixture was cooled and a sufficient amount of a 4N $HClO_4$ solution was added to lower the pH from 12 to 4, in order to remove the excess of methylamine, with a strong flow of nitrogen through the solution. A 2N Na_2CO_3 solution was then added to raise the pH to 6. After this treatment the mixture was cooled at 0° C for 18 hours, a tarry precipitate was filtered off and redissolved in 60 ml of 70% ethanol. The solution was filtered, concentrated by evaporation to 1/4 of its initial volume and a precipitate was obtained by addition of diethyl ether at –50° C under nitrogen atmosphere. This precipitation was repeated and the product recrystallized from ethanol; yield 1.5 g. *Anal.* Calcd. for $[Fe(C_7H_{14}N_2)_3](ClO_4)_2$: Fe, 8.82; C, 39.83; N, 13.87; H, 6.68. Found: Fe, 8.80; C, 39.54; N, 13.23; H, 6.54%.

Tris(1,2-cyclohexanedionebis(methylimine))ferrous perchlorate, $[Fe(CMI)_3](ClO_4)_2$

To a solution of 2.1 ml of 1,2-cyclohexanedione (18 mmol, Eastman) in 10 ml of ethanol was added 6.3 ml of a methylamine solution (72 mmol). The mixture was kept for 10 minutes in a water bath at 30° C and 18.0 ml of a $FeCl_2$ solution (6 mmol) was added. The mixture was stirred at 45° C for 30 minutes. After the addition of 20 ml of a solution of $NaClO_4$ (200 mmol) the mixture was concentrated by evaporation to 1/3 of its volume and kept at 0° C for 6 hours. The precipitate was filtered off; yield 3.0 g. The product was twice recrystallized from ethanol 50%; yield 1.4 g. *Anal.* Calcd. for $[Fe(C_8H_{14}N_2)_3](ClO_4)_2$: Fe, 8.34; C, 43.06; N, 12.55; H, 6.32. Found: Fe, 8.28; C, 42.72; N, 12.52; H, 6.24%.

Tris(4-methyl-1,2-cyclohexanedionebis(methylimine))ferrous perchlorate, $[Fe(MCMI)_3](ClO_4)_2$

To 1.5 ml of a methylamine solution (135 mmol) was added 4.0 ml of 4-methyl-1,2-cyclohexanedione (34 mmol, Eastman) dissolved in 20 ml of ethanol. This mixture was kept in a water bath at 30° C for 15 minutes with stirring. Under nitrogen atmosphere 5.8 ml of a $FeCl_2$ solution (12 mmol) was added to the mixture, raising the temperature to 45° C for 15 minutes. After this time the mixture was cooled and the complex precipitated with 10 ml of a $NaClO_4$ solution (100 mmol). The solution was kept 4 hours in an ice bath, the precipitate filtered off and washed with cold water; yield 9.2 g. The product was recrystallized four times from ethanol 50% and dried *in vacuo;* yield 2.0 g. *Anal.* Calcd. for $[Fe(C_9H_{16}N_2)_3](ClO_4)_2$: Fe, 7.85; C, 45.58; N, 11.81; H, 6.80. Found: Fe, 7.81; C, 44.41; N, 11.45; H, 6.69%.

Tris(phenylglyoxalbis(methylimine))ferrous perchlorate, $[Fe(FMI)_3](ClO_4)_2$

Under nitrogen atmosphere and vigorous stirring 8.0 g of phenylglyoxal (52 mmol, Fluka puriss.) dissolved in 50 ml of ethanol was mixed with 13.5 ml of a methylamine solution (155 mmol) and 30 ml of a $FeCl_2$ solution (18.6 mmol). This mixture was kept for 2 hours in a water bath at 30° C. After this time it was cooled in an ice bath and the complex precipitated with 10 ml of a $NaClO_4$ solution (100 mmol). We kept the solution in the ice bath for 2 hours and the precipitate was filtered off, washed with cold water and ethyl ether; yield 8.0 g. This product was recrystallized five times from ethanol 80%; yield 1.4 g. *Anal.* Calcd. for $[Fe(C_{10}H_{12}N_2)_3](ClO_4)_2$: Fe, 7.59; C, 49.00; N, 11.43; H, 4.93. Found: Fe, 7.50; C, 49.11; N, 11.32; H, 4.96%.

Tris(1-phenyl-1,2-propanedionebis(methylimine))ferrous perchlorate, $[Fe(MFMI)_3](ClO_4)_2$

32 ml of an alcoholic solution of 1-phenyl-1,2-propanedione (35 mmol, Eastman) was added to 9.5 ml

of a methylamine solution (109 mmol). This mixture was kept in a water bath at 30° C, under stirring, for 3 hours. After this time we added, under nitrogen atmosphere, 6.7 ml of a $FeCl_2$ solution (13 mmol) raising the temperature to 60° C during 4 hours. After precipitating the complex with 6 ml of a $NaClO_4$ solution (60 mmol) it was kept in an ice bath for 3 hours. The precipitate was filtered off and washed with cold water; yield 7.5 g. The product was recrystallized five times from ethanol 50% and dried *in vacuo;* yield 2.7 g. *Anal.* Calcd. for $[Fe(C_{11}H_{14}N_2)_3](ClO_4)_2$: Fe, 7.18; C, 50.98; N, 10.81; H, 5.45. Found: Fe, 7.06; C, 51.95; N, 10.82; H, 5.48%.

Ferric Complexes

These complexes were obtained from $2 \times 10^{-4} M$ solutions, in $11 M$ H_2SO_4, of the corresponding ferrous complexes by oxidation with a $0.012 M$ solution of Ce(IV) in $11 M$ H_2SO_4. A sufficient amount of the oxidizer was added until the disappearance of the original ferrous complex color (*ca.* ± 2% of the stoichiometric amount). These oxidations were performed in a 3° C water bath in order to minimize decomposition of the ferric complexes.

Spectrophotometric Measurements

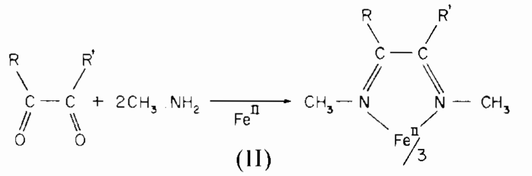
Electronic absorption spectra of the ferrous complexes were obtained on a Cary model 17 recording spectrophotometer in the region ranging from 185 to 1200 nm. They were obtained in 50% ethanol solutions for the visible and near infrared regions and in aqueous solutions for the UV region, at room temperature. These different solutions were used due to the higher solubility of the complexes in 50% ethanol and due to the absorption of UV light by ethanol. Liquid nitrogen temperature (LNT) spectra were measured using a Cary Liquid Helium Dewar and KBr pellets, in the 1200 to 300 nm region. Two of the complexes ($Fe(MMI)_3^{2+}$ and $Fe(FMI)_3^{2+}$) have had their LNT spectra measured in ethanol rigid glass using a Hellma suprasil low temperature cell and the above-mentioned cryostat.

The spectra of the corresponding ferric complexes were measured in a Hitachi–Perkin Elmer model 124 recording spectrophotometer. They were obtained directly from the oxidized complexes solutions, using a Coleman Spectrosil cell with 1.0 cm of path length.

Results and Discussion

Ferrous Complexes

The ferrous complexes studied in this work are formed, in a general way, by the reaction (II) of the corresponding diketone with methylamine, in the presence of a ferrous salt.



(II)

Most of these reactions are not so simple and the appearance of intermediates has been detected in some of them. Curiously, the yield obtained in the synthesis of the complex $Fe(MMI)_3^{2+}$ is strongly influenced by the order of addition of the reagents. If we add them in an order different from that reported, the yield and the purity of the final product are considerably lowered.

The results of the spectral measurements at room temperature of the ferrous complexes are shown in Table I. The values reported for the position of the shoulders were calculated using a computer program which decomposes the spectrum in log–normal components[9, 10]. In Table II we report the solid state LNT spectral results analysed by the same program. Concordance in shoulders positions shows the goodness of the fit of the program. Spectra in ethanol rigid glass confirm these results. The spectra of these complexes, in solution at room temperature (Figure 1a) show a characteristic intense band in the visible region, with two shoulders toward larger energies. This band is shifted to lower frequencies along the series of com-

TABLE I. Energies (in kK) and Intensities ($\varepsilon \times 10^{-3} M^{-1} cm^{-1}$) of the Bands in the Room Temperature Solution Spectra of the Ferrous Diimine Complexes Obtained by Log–Normal Analysis.

Compound	MLET	MLET	MLET	*d–d*	ILET	ILET	ILET
$Fe(GMI)_3^{2+}$	17.97 (8.55)	19.8 (2.9)[a]	24.1 (0.3)[a]	28.41 (0.09)	–	42.9 (6.7)[a]	52.69 (41.6)
$Fe(MMI)_3^{2+}$	17.81 (9.56)	19.7 (2.9)[a]	23.5 (0.4)[a]	28.25 (0.11)	–	42.5 (6.8)[a]	52.76 (44.5)
$Fe(BMI)_3^{2+}$	17.72 (10.6)	19.8 (3.5)[a]	23.5 (0.5)[a]	28.10 (0.55)	–	41.6 (9.3)[a]	52.62 (45.7)
$Fe(EMI)_3^{2+}$	17.50 (10.6)	19.6 (3.8)[a]	23.2 (0.4)[a]	28.40 (0.43)	–	41.8 (7.5)[a]	52.29 (51.9)
$Fe(CMI)_3^{2+}$	17.23 (11.8)	19.2 (3.5)[a]	22.7 (0.4)[a]	28.33 (0.2)	–	41.8 (4.7)[a]	51.92 (48.3)
$Fe(MCMI)_3^{2+}$	17.21 (12.2)	19.2 (3.5)[a]	22.7 (0.4)[a]	28.25 (0.19)	–	41.8 (3.7)[a]	52.00 (59.0)
$Fe(FMI)_3^{2+}$	16.73 (11.1)	19.55 (4.59)	–	28.0 (3.4)[a]	34.57 (20.2)	40.1 (17)[a]	50.26 (85.2)
$Fe(MFMI)_3^{2+}$	16.99 (10.5)	20.08 (4.40)	–	28.01 (3.5)[a]	35.21 (12.4)	41.4 (16)[a]	50.33 (108)

[a] Shoulder.

TABLE II. Energies (in kK) and Normalized Intensities of the Bands in the Solid State LNT Spectra of the Ferrous Complexes.

$Fe(BMI)_3^{2+}$	$Fe(MCMI)_3^{2+}$	$Fe(MFMI)_3^{2+}$	Assignment	
16.40 (0.05)	16.40 (0.05)	16.40 (0.07)	*d–d*,	$^1A_1 \rightarrow {}^3T_2$
17.81 (1.00)	17.19 (1.00)	16.86 (1.00)	MLET,	$^1A_1 \rightarrow {}^1E$
18.60 (0.08)	18.60 (0.09)	18.60 (0.06)	*d–d*,	$^1A_1 \rightarrow {}^1T_1$
20.60 (0.50)	19.51 (0.60)	20.20 (0.55)	MLET,	$^1A_1 \rightarrow {}^1E$
23.28 (0.20)	23.41 (0.10)	21.59 (0.11)	MLET,	$^1A_1 \rightarrow {}^1A_2$
28.30 (0.08)	28.25 (0.15)	28.30 (0.13)	*d–d*,	$^1A_1 \rightarrow {}^1T_2$

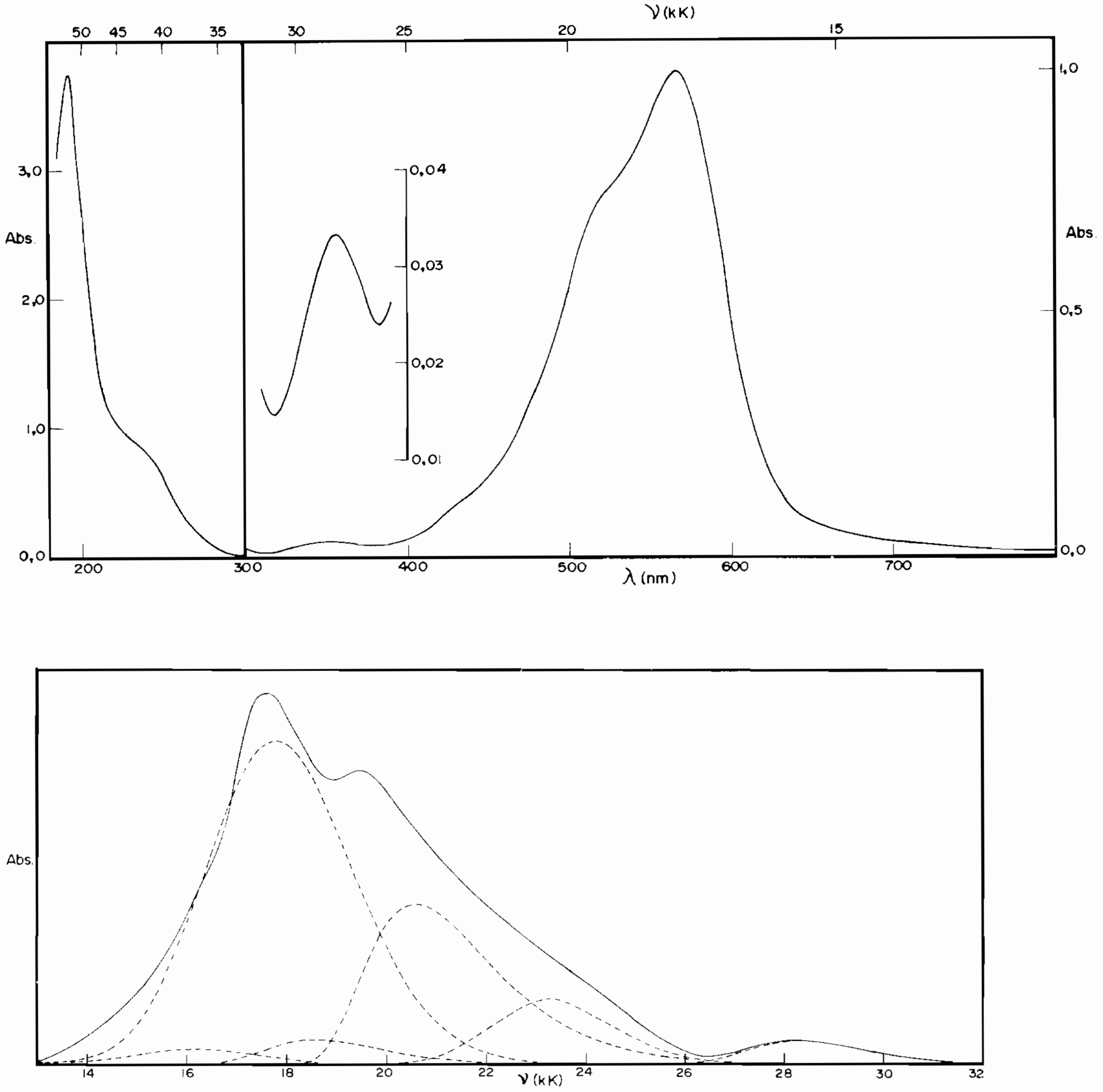


Figure 1. Spectra of the $Fe(BMI)_3^{2+}$ complex; a) room temperature solution spectrum and b) solid state (KBr pellet) liquid nitrogen temperature spectrum (full line) and its log–normal analysis (dotted line).

plexes. When there is a phenyl group in the ligand, as in the case of the complexes with FMI and MFMI as ligands, this band is split into two intense bands (Figure 2a). In the UV spectral region we observed two or three intense bands, depending on the ligand. Another band is observed in the 28 kK region the position of which does not change along the series. In the LNT spectra, obtained in solid state, the visible absorption band is resolved into two intense bands (Figure 1b) with a shoulder in the higher energy region and another in the opposite direction.

ILET bands

The intense bands observed in the region from 33 to 53 kK are assigned to internal ligand electron transfer (ILET) transitions of the type $\pi \rightarrow \pi^*$[11,12,13,14]. In complexed form, the highest symmetry that can be assigned for these ligands is C_{2v}, considering the metal and only one ligand. In this case the ground state is $^1A_1$ corresponding to the $b_2^2a_2^2$ configuration (only π orbitals). Four allowed transitions are possible with excitation of one electron from the b_2 or a_2 π MO's to the b_2 or a_2 π^* MO's. Of these transitions to the

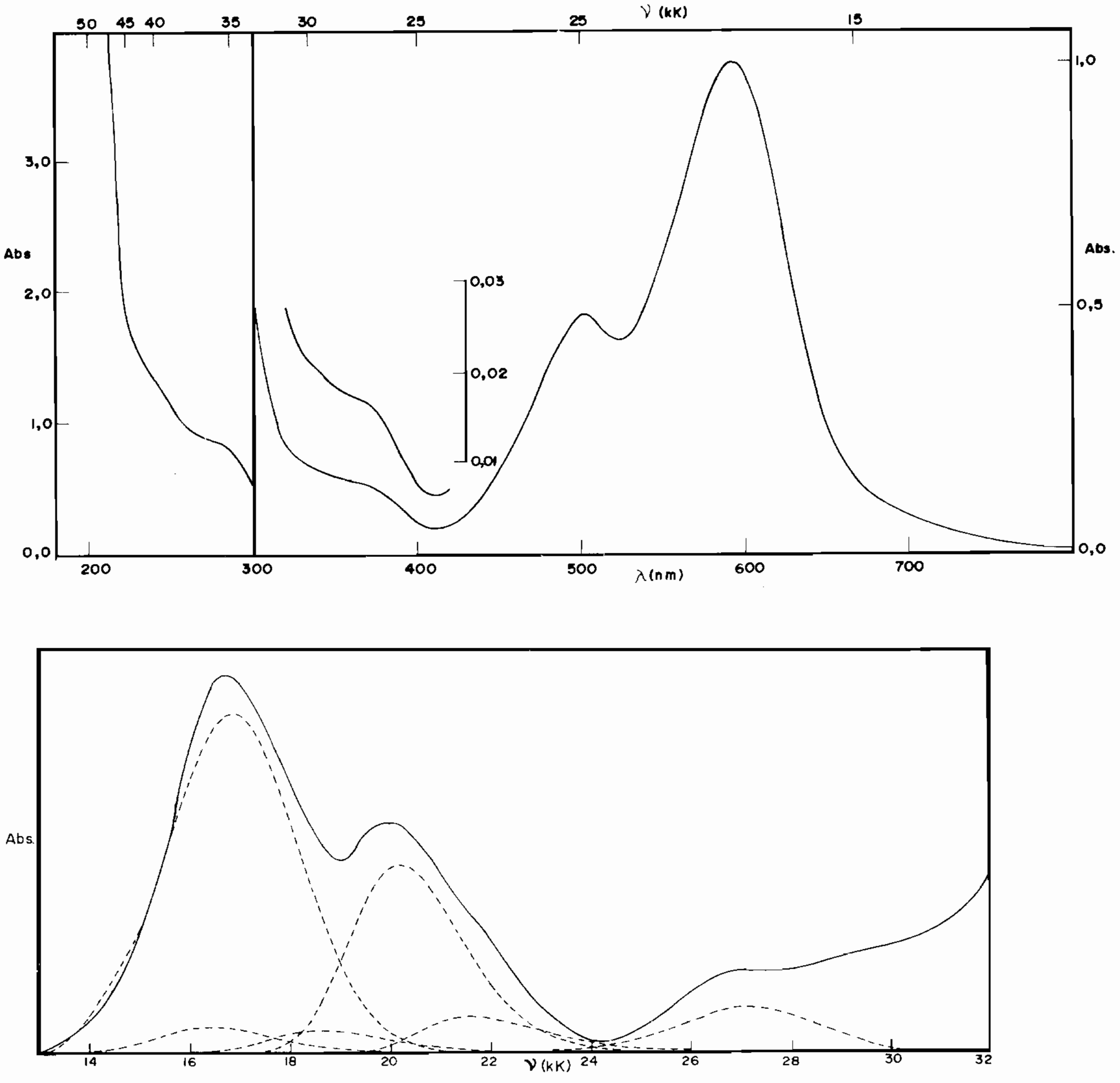


Figure 2. Spectra of the Fe(MFMI)$_3^{2+}$ complex; a) room temperature solution spectrum and b) solid state (KBr pellet) liquid nitrogen temperature spectrum (full line) and its log–normal analysis (dotted line). Absorption in the high energy region is due to KBr.

four excited states, the two more intense are of $^1A_1$ symmetry and the two less intense are of $^1B_1$ symmetry. In the case of the complexes without phenyl groups in the ligands, the more intense band at higher energies can be assigned to the superposition of the two $^1A_1 \rightarrow {}^1A_1$ bands. The observed shoulder at lower energy can be assigned to the first $^1A_1 \rightarrow {}^1B_1$ transition, the other would appear at much higher energy and could not be measured. In the case of the complexes with a phenyl group in the ligands the appearance of a third band suggests that a more complicated model is necessary. The symmetry in this case would be C_s and a very large number of transitions is alowed, precluding therefore the possibility of direct assignments.

MLET bands

The bands observed in the region ranging from 16.7 to 24.1 kK in the spectra of the tris-diimine iron(II) complexes are assigned to metal to ligand electron transfer (MLET) transitions[5, 6, 11, 12, 15, 16]. These transitions involve filled *d* orbitals of the metal and the empty π^* orbitals mainly localized on the ligands. Their intensities suggest that the electron transfer interactions give an important contribution to the ground state of the complexes[12, 17].

The spectra of the complexes $Fe(GMI)_3^{2+}$ and $Fe(BMI)_3^{2+}$ were first published by Krumholz in 1954[4]. Later he assigned the shape of this intense band to a vibrational coupling, assuming six vibrational components for this band[7]. When we measured these spectra at LNT the resolution of the shoulder in an intense band and the pronouncement of the other shoulder suggested to us that the first assignment could be misleading. In addition to these facts the energy separation between these bands (2.8 kK in the $Fe(BMI)_3^{2+}$ case) is too large compared to the 1.6 kK splitting assumed by these authors[7, 18]. The increase of this splitting in the spectra of the phenyl-containing ligand complexes is an additional evidence against the vibrational structure initially proposed by Krumholz and others[7, 18]. The expected lowering of the symmetry in a tris-bidentate complex and the results published by Ito, Tanaka, Hanazaki and Nagakura[12] strongly suggest that we have three MLET transitions. The bands result from the splitting of the t_2 and the lower π^* levels into e,a_1 and e,a_2, respectively, assuming a D_3 symmetry. According to these arguments, the metal to ligand back-donation seems to be responsible for the loss of degeneracy of the t_2 levels of the metal and the π^* levels of the ligands due to the electron-transfer interactions[19]. Using this model and assuming a D_3 point group symmetry we expect two types of MLET transitions: $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$. In this case we are assuming the participation of the lowest unoccupied π^* levels mainly localized on the ligands only. Based on these arguments we can assign the two more intense bands at lower energy to the $^1A_1 \rightarrow {}^1E$ transitions and the high energy shoulder to the $^1A_1 \rightarrow {}^1A_2$ transition. The splitting of the two first bands corresponds to the splitting of the e and a_1 metal levels and the splitting of the first and the third bands corresponds to the splitting of the e and a_2 ligand levels.

The fact that no difference is found in the spectra of the complexes $Fe(CMI)_3^{2+}$ and $Fe(MCMI)_3^{2+}$ shows that the addition of the methyl group in the 4 position of the aliphatic ring does not perturb the electronic energy levels of the complex.

The hypsochromic shift observed when we go from the $Fe(FMI)_3^{2+}$ complex to the $Fe(MFMI)_3^{2+}$ complex seems to be associated to the impossibility of a coplanar structure of the phenyl group with the diimine ring[20]. The methyl group hinders this coplanarity, raising the π^* level energy[21].

d–d bands

In the spectrum of the complex $Fe(BMI)_3^{2+}$ Ito and Tanaka[22] observed an extremely weak shoulder at 11 kK and a band at 28 kK which were assigned by these authors to the $^1A_1 \rightarrow {}^3T_1$ and $^1A_1 \rightarrow {}^1T_2$ transitions, respectively. Palmer and Piper[15] presented strong arguments to assign a band at 11.5 kK in the spectrum of $Fe(dipy)_3^{2+}$ to the $^1A_1 \rightarrow {}^3T_1$ transition. The shift of the much more intense MLET band to lower energies in our series of complexes compared to the same band in the dipy complex is, possibly, the cause of the non detection of the band at 11 kK.

Assuming the Palmer and Piper value for the $^1A_1 \rightarrow {}^3T_1$ energy transition, 11.5 kK, and our measured value for the $^1A_1 \rightarrow {}^1T_2$ allowed transition energy we obtain 10 Dq = 19.0 kK and B = 0.75 kK. Using these values the other two bands would appear at 16.4 and 18.6 kK, corresponding to the transitions to the excited levels $^3T_2$ and $^1T_1$, respectively. The computational analysis of the LNT spectra showed the possibility of the existence of these bands in our spectra. On the other hand the Dq value assumed seems to be reasonable when we compare it with the value of 11.4 kK for the high-spin $Fe(en)_3^{2+}$ complex[23]. According to Jørgensen[24] the ligand field stabilization energy of the low-spin configuration should increase Dq by 40% when we pass from a $^5T_2$ to a $^1A_1$ ground state. In this case the minimum estimated value for 10 Dq in low-spin complexes should be 16 kK.

Ferric Complexes

The oxidation of the ferrous complexes in 11*M* H_2SO_4 solutions with Ce(IV) solutions leads to the corresponding ferric complexes[8]. The high acid concentration is used due to the formation in lower acidities of complex species in which the ligand is oxidized[25]. The ferric complexes formed have a very low stability that makes their isolation in the solid form very difficult.

The absorption spectra of these complexes (Figure 3 and 4) show an intense absorption in the region from 25.6 to 27 kK. This band has a shoulder towards lower energies which is gradually pronounced along the series given in I. Another band appears in the valley between the visible and the UV band. Very intense UV bands were observed in the region from 38 to 50 kK. Due to the high degree of superposition of the bands the log–normal analysis of these spectra gave somewhat worse results in positioning the bands. These are given in Table III.

The observed instability of these complexes might be due to the lesser degree of back-donation in them compared to the ferrous complexes[26]. Magnetic susceptibility measurements of the ferric complexes of phen and dipy at different temperatures showed that delocalization of electrons in the hole in the t_2 subshell in the strong field case is very low[26]. This can be partially applied to our complexes.

LMET bands

The hole in the t_2^5 orbitals of the central metal makes possible the transition of electrons from the highest occupied π MO's (mainly localized on the ligands) to the metal[18,27,28] These LMET bands are observed at higher energy than the MLET bands of the ferrous complexes. The lower stabilization of the metal orbitals can be another argument favoring the lower degree of back-donation in the ferric complexes compared to the ferrous ones. Assuming a D_3 symmetry for these complexes and the participation of only the highest occupied ligand π MO's we could have two allowed transitions, $^2A_1 \rightarrow {}^2A_2$ and $^2A_1 \rightarrow {}^2E$. In fact the first four complexes show these two predicted bands. In the other four we observe a shoulder towards lower energies which is very pronounced in the case of the $Fe(MFMI)_3^{2+}$ complex. The pronouncement of this shoulder can result from the shift of the more intense band. The transition responsible for this shoul-

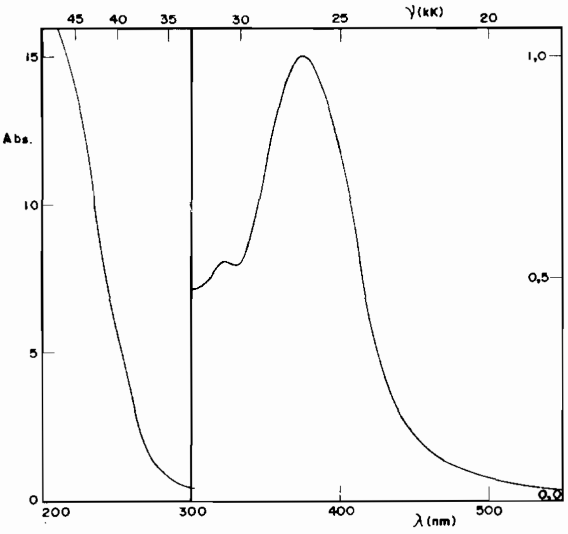


Figure 3. Room temperature solution (H_2SO_4 11 *M*) spectrum of the $Fe(BMI)_3^{3+}$ complex.

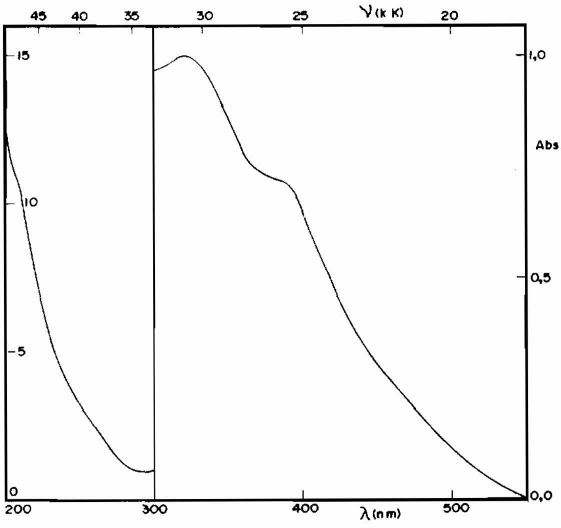


Figure 4. Room temperature solution (H_2SO_4 11 *M*) spectrum of the $Fe(MFMI)_3^{3+}$ complex.

TABLE III. Energies (in kK) and Intensities ($\varepsilon \times 10^{-3} M^{-1}$ cm^{-1}) of the Room Temperature Solution (H_2SO_4 11 *M*) Spectra of the Ferric Diimine Complexes Obtained by Log–Normal Analysis.

Compound	–	–	LMET (?)	LMET	ILET	ILET
$Fe(GMI)_3^{3+}$	–	–	26.96 (2.2)	32.32 (0.3)	39.1 (4.7)[a]	47.0 (14)[a]
$Fe(MMI)_3^{3+}$	–	–	26.70 (2.7)	31.50 (1.8)	39.6 (2.9)[a]	50.0 (32)[a]
$Fe(BMI)_3^{3+}$	–	–	26.75 (3.1)	31.24 (1.9)	39.8 (3.3)[a]	49.8 (55)[a]
$Fe(EMI)_3^{3+}$	–	–	26.40 (2.9)	31.62 (1.6)	41.2 (11)[a]	49.8 (42)[a]
$Fe(CMI)_3^{3+}$	23.6 (3.0)[a]	25.56 (3.2)	27.3 (1.5)[a]	30.6 (1.1)[a]	40.1 (31)[a]	49.5 (74)[a]
$Fe(MCMI)_3^{3+}$	23.6 (2.1)[a]	25.60 (3.4)	27.5 (2.2)[a]	29.9 (1.3)[a]	41.8 (24)[a]	49.5 (39)[a]
$Fe(FMI)_3^{3+}$	21.9 (1.7)[a]	26.2 (3.7)[a]	30.64 (3.8)	–	38.4 (0.5)[a]	48.1 (43)[a]
$Fe(MFMI)_3^{3+}$	21.4 (1.1)[a]	25.6 (3.2)[a]	29.98 (3.8)		39.1 (2.6)[a]	49.5 (47)[a]

[a] Shoulder.

TABLE IV. Comparison of the Sum ($\Sigma(1)$ and $\Sigma(2)$) of the MLET ($\nu_{ML}{}^{2+}(1)$ and $\nu_{ML}{}^{2+}(2)$) and LMET ($\nu_{LM}{}^{3+}(1)$ and $\nu_{LM}{}^{3+}(2)$) Energies with the ILET ($\nu_{IL}(1)$ and $\nu_{IL}(2)$) Energies. Spectra Obtained in H_2SO_4 11 *M* solutions.
$\nu_{ML}{}^{2+}(1) + \nu_{LM}{}^{3+}(1) = \Sigma(1)$ and $\nu_{ML}{}^{2+}(2) + \nu_{LM}{}^{3+}(2) = \Sigma(2)$.

Ligand	$\nu_{ML}{}^{2+}(1)$	$\nu_{ML}{}^{2+}(2)$	$\nu_{LM}{}^{3+}(1)$	$\nu_{LM}{}^{3+}(2)$	$\nu_{IL}(1)$	$\Sigma(1)$	$\nu_{IL}(2)$	$\Sigma(2)$
GMI	18.0	19.8	27.0	32.3	45.0	45.0	53	52.1
MMI	17.8	19.7	26.7	31.5	43.9	44.5	53	51.2
BMI	17.7	19.8	26.8	31.3	43.5	44.5	53	51.1
EMI	17.5	19.6	26.4	31.6	43.1	43.9	52	51.2
CMI	17.2	19.2	25.6	30.6	43.9	42.8	52	49.8
MCMI	17.2	19.2	25.6	29.9	43.9	42.8	52	49.1
FMI	16.7	19.6	26.2	30.6	40.1	42.9	50	50.2
MFMI	17.0	20.0	25.6	30.0	41.5	42.6	51	50.0

der could result from the lowering of symmetry with a consequent splitting of the energy levels. Another possibility is that this shoulder could be due to a *d–d* allowed transition.

ILET bands

As in the case of the ferrous complexes the UV bands in the region up to 35 kK result from the ILET transitions. In this case they appear shifted due to the acidity of the solution used to obtain the spectra. The spectra of the ferrous complexes in the same conditions showed a similar shifting of these bands.

Final Comments

When we compare the sum of the energy of the MLET transitions (ferrous complexes) and the LMET transitions (ferric complexes) we observe that, within the experimental error, they coincide with the energy of the ILET transitions, as shown in Table IV. This fact is in agreement with a very simplified model where the relative energies of the MO levels of the complexes do not change with the oxidation state of the metal.

Acknowledgements

We thank the Coordenação de Aperfeiçoamento do Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support, Dr. Helena Li Chum for her help in the oxidations and Dr. Henrique E. Toma for helpful discussions.

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