Some Comments on the Orbital Pattern in the High-Spin Mixed Ligand Complexes of Iron(II)

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Abstract: The high-spin mixed ligand complexes of iron(II) are discussed in terms of ligand field theory. It is shown that their paramagnetism is due to the strong "π" antibonding effect of the halides (pseudohalides). Another reason is suggested by the electronic spectra, which indicate that the "σ" antibonding power of the ammines is almost equal to that of the halides.

A series of Fe(II) complexes having the general formula [$Fe^{II}a_2b_2$], where a = phen or bipy and b = halides or pseudohalides, has recently been prepared and their paramagnetism reported.[1-5] In all cases, the magnetic moments observed are approximately those predicted for octahedral d^6 systems with four unpaired electrons.

The high moments are very interesting because the organic ammines, such as 1,10-phenanthroline and 2,2′-bipyridyl, are particularly strong ligands and generally form low-spin compounds of the type $Fe^{II}a_3^{2+}$.

It is the purpose of this paper to discuss the origins of the paramagnetic behavior observed with the aforementioned complexes. With this end in view, these chromophores will be analyzed in terms of the ligand field theory. In the first part, some considerations are presented with regard to the orbital pattern, electronic spectra, and condition of diamagnetism. In the last two sections, the results obtained are compared with the spectral and magnetic data.

The reflectance spectra of some Fe(II) compounds have been recorded by Madeja and König[2] and are given schematically in Figure 2. Magnetic measurements can be found in the papers mentioned above.

To apply the ligand field theory, the Fe(II) complexes have been considered as having an octahedral environment with either *trans* or *cis* distortions. The orbital patterns, as deriving from the simple MO interpretation, are represented in Figure 1 where scheme I corresponds to a nearly octahedral environment when there are no differences in the $\sigma(\pi)$ bonds with the "a" and "b" ligands. Here, the orbital energy Δ_o may be regarded as the difference between the "σ" and the "π" antibonding effect of the ligands.

Schemes II–III in Figure 1 correspond to the tetragonal (weak D_{4h}) or *cis* (weak C_{2v}) distortions due to the difference between the $\sigma(\pi)$-antibonding effects of the ligands. In all these schemes, it is considered that the ligands a (phen or bipy) have a σ-antibonding effect stronger than the ligands b (halides or pseudohalides) (δ parameter). It has also been considered that the ligands b have a π-antibonding effect stronger than the ligands a (μ parameter).

These considerations regarding the antibonding power of ligands have been made on the basis of the results obtained for praseo salts.[6,7]

The six electrons arising from the partly filled shell of iron(II) fill up the molecular orbitals represented in all these schemes, giving either diamagnetic (singlet) or paramagnetic (quintet) states. Their energies expressed in Δ_o, Δ_T, Δ_c, δ, μ, and Racah parameters are

$$\begin{array}{lll} \mathrm{I\ (O_h)}\left\{\begin{array}{l} t_2^6\ (^1A_{1g}) \\ t_2^4e^2\ (^5T_{2g}) \end{array}\right. & \begin{array}{l} n + 5B + 8C \\ n + 2\Delta_o \end{array} & \\ \mathrm{II\ (weak\ D_{4h})}\left\{\begin{array}{l} b_2^2e^4\ (^1A_{1g}) \\ b_2^2e^2a_1b_1\ (^5B_{2g}) \end{array}\right. & \begin{array}{l} n + 5B + 8C \\ n + 2\Delta_T + \delta \end{array} & (1) \\ \mathrm{III\ (weak\ C_{2v})}\left\{\begin{array}{l} e^4b_2^2\ (^1A_{1g}) \\ e^3b_2b_1a_1\ (^5E_g) \end{array}\right. & \begin{array}{l} n + 5B + 8C \\ n + 2\Delta_c + \delta + \mu \end{array} & \end{array}$$

where $n = 15A - 35B + 7C$.

For each of these schemes, the excited levels (quintet) at which spin-allowed transitions can take place may be found at

$$\begin{array}{lll} \mathrm{I\ (O_h)}\quad t_2^3e^3\ (^5E_g) & \Delta_o & \\ \mathrm{II\ (weak\ D_{4h})}\left\{\begin{array}{l} b_2e^3a_1b_1\ (^5E_g) \\ b_2e^2a_1^2b_1\ (^5A_{1g}) \\ b_2e^2a_1b_1^2\ (^5B_{1g}) \end{array}\right. & \begin{array}{l} \mu \\ \Delta_T + \mu \\ \Delta_o^h \end{array} & (2) \\ \mathrm{III\ (weak\ C_{2v})}\left\{\begin{array}{l} e^2b_2^2b_1a_1\ (^5B_{2g}) \\ e^2b_2b_1^2a_1\ (^5B_{1g}) \\ e^2b_2b_1a_1^2\ (^5A_{1g}) \end{array}\right. & \begin{array}{l} \mu \\ \Delta_c + \mu \\ \Delta_o^h \end{array} & \end{array}$$

above the ground paramagnetic state, where $\Delta_o^h = \Delta_T + \delta + \mu$ or $\Delta_c + \delta + \mu$.

The conditions of diamagnetism, as resulting from the comparison of both the ground states, singlet, and quintet, are of the form

$$\begin{array}{lll} \mathrm{I\ (O_h)} & \Delta_o > \Pi & \\ \mathrm{II\ (weak\ D_{4h})} & \Delta_T + {}^1/_2\delta > \Pi & (3) \\ \mathrm{III\ (weak\ C_{2v})} & \Delta_c + {}^1/_2(\delta + \mu) > \Pi & \end{array}$$

In all these relations, the quantity $\Pi = 2.5B + 4C$ represents the spin-pairing energy which appears to have a value of[2,8] 12,000–12,500 cm^{-1}.

In the following two sections, we shall attempt to compare these theoretical results with the spectral and the magnetic data. For this purpose, it is convenient to express the orbital energies in the radial parameters of the angular overlap model. Further details regarding this MO approximation may be found else-

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(1) F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).

(2) K. Madeja and E. König, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963).

(3) W. A. Baker, Jr., and H. M. Bobonich, *Inorg. Chem.*, **2**, 1071 (1963).

(4) W. A. Baker, Jr., and H. M. Bobonich, *ibid.*, **3**, 1184 (1964).

(5) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(6) J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, 4981 (1956).

(7) D. S. McClure, *Advan. Chem. Coordination Compds.*, 498 (1961).

(8) M. A. Robinson and D. H. Busch, *Inorg. Chem.*, **2**, 1171, 1178 (1963).

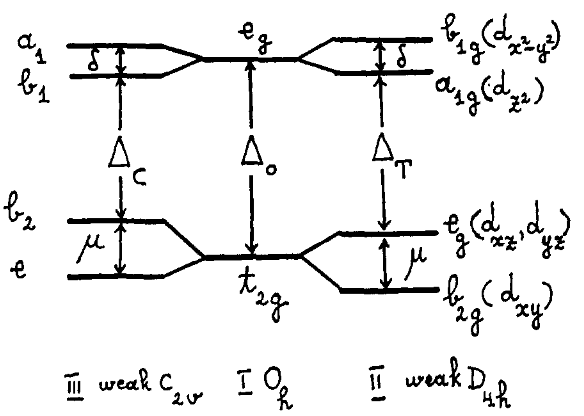

Figure 1. Molecular orbital energy level diagram for octahedral (O_h), tetragonal (D_{4h}), and C_{2v} symmetries.

where.[9,10] Using the angular overlap model, the σ- and π-antibonding energies in $[Ma_2b_2]$ chromophores are as shown in eq 4, where $e_{\sigma(\pi)}$ represents the radial parameters for the $\sigma(\pi)$ bonds with ligands a and b.

$$\begin{array}{ll} \text{weak } D_{4h} & \text{weak } C_{2v} \\ E(a_{1g}) = e_\sigma^a + 2e_\sigma^b & E(a_1) = {}^5/_2 e_\sigma^a + {}^1/_2 e_\sigma^b \\ E(b_{1g}) = 3e_\sigma^a & E(b_1) = {}^3/_2 e_\sigma^a + {}^3/_2 e_\sigma^b \\ E(b_{2g}) = 4e_\pi^a & E(b_2) = 2e_\pi^a + 2e_\pi^b \\ E(e_g) = 2e_\pi^a + 2e_\pi^b & E(e) = 3e_\pi^a + e_\pi^b \end{array} \quad (4)$$

It must be mentioned that the ligands a (phen or bipy) are bidentate, and, for the *cis* $[Ma_2b_2]$ chromophores, the symmetry classes of the D_4 point group have been used.

The Splitting Parameters

By making use of (4), the splitting parameters in Figure 1 are as shown in (5) and the energies of the spin-allowed transitions (2) are

$$\begin{array}{ll} \text{weak } D_{4h} & \text{weak } C_{2v} \\ \delta = 2e_\sigma^a - 2e_\sigma^b & \delta = e_\sigma^a - e_\sigma^b \\ \Delta_T = e_\sigma^a + 2e_\sigma^b - & \Delta_c = {}^3/_2 e_\sigma^a + {}^3/_2 e_\sigma^b - \\ \quad 2e_\pi^a - 2e_\pi^b & \quad 2e_\pi^a - 2e_\pi^b \\ \mu = 2e_\pi^b - 2e_\pi^a & \mu = e_\pi^b - e_\pi^a \end{array} \quad (5)$$

$$\begin{array}{lll} \text{weak } D_{4h} & \left\{\begin{array}{l} {}^5B_{2g} \longrightarrow {}^5E_g \\ \qquad \longrightarrow {}^5A_{1g} \\ \qquad \longrightarrow {}^5B_{1g} \end{array}\right. & \begin{array}{l} \mu = 2e_\pi^b - 2e_\pi^a \\ \Delta_T + \mu = e_\sigma^a + 2e_\sigma^b - 4e_\pi^a \\ \Delta_o^h = 3e_\sigma^a - 4e_\pi^a \end{array} \\ \text{weak } C_{2v} & \left\{\begin{array}{l} {}^5E_g \longrightarrow {}^5B_{2g} \\ \qquad \longrightarrow {}^5B_{1g} \\ \\ \qquad \longrightarrow {}^5A_{1g} \end{array}\right. & \begin{array}{l} \mu = e_\pi^b - e_\pi^a \\ \Delta_c + \mu = {}^3/_2 e_\sigma^a + {}^3/_2 e_\sigma^b - \\ \quad 3e_\pi^a - e_\pi^b \\ \Delta_o^h = {}^5/_2 e_\sigma^a + {}^1/_2 e_\sigma^b - \\ \quad 3e_\pi^a - e_\pi^b \end{array} \end{array} \quad (6)$$

From the first, it may be seen that no matter what kind of distortion is considered, μ or $\delta << \Delta_T$ or Δ_c, and, according to (6), only two transitions occur, the separation being equal to the δ parameter in Figure 1. Indeed, in the spectra of mixed ligand complexes of Fe(II), there are two absorption bands placed in the near-infrared, as shown in Figure 2. As may be seen, the distance between the bands is practically the same in all series of compounds. This distance of about 2000 cm^{-1} is just equal to the splitting caused by the dynamic Jahn–Teller effect[11] in $Fe(H_2O)_6^{2+}$ and strongly suggests that the appearance of two bands in the spectra is due to that effect. In other words, the δ parameter, which should, according to (6), be the distance between the bands, may be practically ignored.

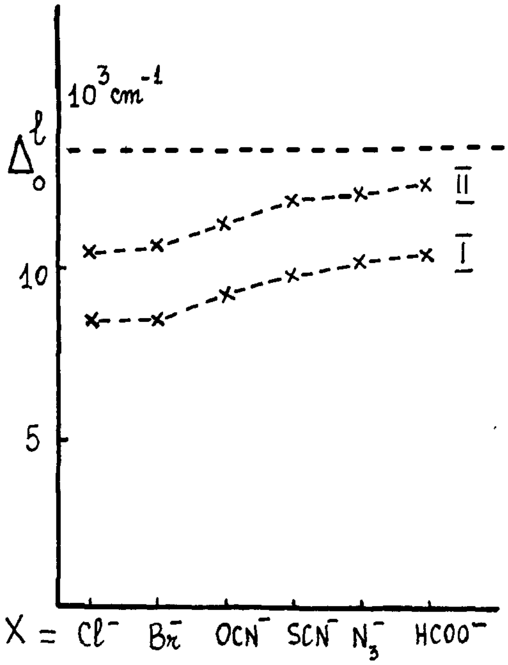

Figure 2. The electronic spectra of $Fe(phen)_2X_2$, where the two absorption maxima are schematically represented by crosses.

Therefore, $e_\sigma^a \simeq e_\sigma^b = e_\sigma$, and the spin-allowed transitions in $[Fe^{II}a_2b_2]$ chromophores have the energies shown in (7).

$$\begin{array}{ll} \text{weak } D_{4h}\ {}^5B_{2g} \longrightarrow {}^5A_{1g};\ {}^5B_{1g} & \Delta_o^h = 3e_\sigma - 4e_\pi^a \\ \text{weak } C_{2v}\ {}^5E_g \longrightarrow {}^5B_{1g};\ {}^5A_{1g} & \Delta_o^h = 3e_\sigma - 3e_\pi^a - e_\pi^b \end{array} \quad (7)$$

It would be interesting to compare these energies with the orbital energy in $Fe(phen)_3^{2+}$. In the angular overlap model, the orbital energy in an octahedral compound is defined by the difference[10]

$$\Delta_o = 3e_\sigma - 4e_\pi \quad (8)$$

According to eq 7 and 8, $\Delta_o^1 = 3e_\sigma^a - 4e_\pi^b$, the orbital energy in $Fe(phen)_3^{2+}$, must be equal to the energy of the spin-allowed transitions in the *trans* $[Fe^{II}a_2b_2]$ complexes having weak D_{4h} distortions. A regularity of this kind has been found in praseo salts.[12] In the tetragonal chromophores, $Co^{III}(NH_3)_4X_2$, the second absorption band (${}^1A_{1g} \rightarrow {}^1A_{2g}$) has an energy, expressed in our parameters $\Delta_o^h - C$, equal to the first band in $Co^{III}(NH_3)_6^{3+}$, *i.e.*, $\Delta_o^1 - C\,({}^1A_{1g} \rightarrow {}^1T_{2g})$.

According to eq 7 and 8, the energy value of the spin-allowed transitions in the $[Fe^{II}a_2b_2]$ chromophores having weak C_{2v} distortions must be lower than the orbital energy in $Fe(phen)_3^{2+}$, since the ligands b have a stronger π-antibonding effect than the ligands a ($e_\pi^b > e_\pi^a$). The last remark seems to be verified by the spectra of some Fe(II) chromophores. As may be observed in Figure 2, the energy of the spin-allowed transitions in $[Fe(phen)_2b_2]$ chromophores is generally lower than $\Delta_o^1 = 13{,}000\ cm^{-1}$, the orbital energy in the parent compound $Fe(phen)_3^{2+}$, which seems to indicate weak C_{2v} distortions in these complexes.

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(9) C. K. Jørgensen, *J. Phys. Radium*, **26**, 825 (1965).
(10) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).
(11) C. Furlani, *Gazz. Chim. Ital.*, 87, 371 (1957).
(12) R. S. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202, 709, 1524 (1965).

Another reason for which the energy of the spin-allowed transitions in [$Fe^{II}a_2b_2$] has a lower value than the orbital enrgy Δ_o^1 in Fe(phen)$_3^{2+}$ may be found in the changes occurring in the radial parameters e_σ^a and e_σ^b. The reduction of Δ_o^h (eq 7) can take place by the lowering or increasing in e_σ^a and e_σ^b values, respectively. We cannot decide at this point which of the causes is most important. However, if the reduction in e_σ^a value is considered to be the main cause, it follows that $e_\sigma^a \simeq e_\sigma^b$, and the δ parameter (eq 5) may be practically ignored.

The Magnetic Behavior

With $\delta = 0$, the conditions of diamagnetism (eq 3) may be written in the form

$$\begin{array}{ll} \text{I}\,(O_h) & \Delta_o > \Pi \\ \text{II (weak } D_{4h}) & \Delta_o^h - \mu > \Pi \\ \text{III (weak } C_{2v}) & \Delta_o^h - {}^1/_2\,\mu > \Pi \end{array} \quad (9)$$

The two last conditions corresponding to the *trans* or *cis* distortions are more difficult to fulfill than the first relation, if $\mu > 0$. One may therefore conclude that the strong π-antibonding effect of the halides or pseudohalides ($\mu > 0$) is responsible for the paramagnetic behavior of the mixed ligand complexes of iron(II).

Let us study some Fe(II) chromophores having C_{2v} distortions. According to eq 5, 7, 8, and 9, we have

$$\Delta_o^1 - {}^3/_2\mu > \Pi \quad (10)$$

where Δ_o^1 is the orbital energy in the low-spin compound Fe(phen)$_3^{2+}$. Assuming that e_σ^a and e_π^a are the same in both $Fe^{II}a_3^{2+}$ and [$Fe^{II}a_2b_2$] chromophores, the μ parameter may be easily found from

$$\mu = e_\pi^b - e_\pi^a = \Delta_o^1 - \Delta_o^h \quad (11)$$

Table I shows the Δ_o^h, μ, and $\Delta_o^1 - {}^3/_2\mu$ values as found from the spectra[2] of some Fe(II) chromophores for which X-ray evidence[4] would indicate *cis* distortions.

Table I

Fe(phen)$_2$X$_2$	Δ_o^h, cm^{-1}	μ, cm^{-1}	$\Delta_o^1 - {}^3/_2\mu$, cm^{-1}
X = Cl$^-$	8,470	4530	6200
Br$^-$	8,470	4530	6200
N$_3^-$	10,200	2800	8800

The μ parameter was estimated from eq 11, where Δ_o^1, the orbital energy in Fe(phen)$_3^{2+}$, has a value of about 13,000 cm^{-1}.

As may be seen from Table I, $\Delta_o^1 - {}^3/_2\mu$ has a lower value than that of the spin-pairing energy Π = 12,500 cm^{-1} and, according to eq 10, the chromophores [Fe(phen)$_2$X$_2$], where X = Cl$^-$, Br$^-$, N$_3^-$, must be paramagnetic.

The condition of diamagnetism is also verified by the diamagnetic compounds. Let us take as an example the diamagnetic chromophores [Fe(phen)$_2$(CN)$_2$]. As has been postulated, on the basis of the infrared data,[13] the cyanide is *cis*, and therefore it must verify the condition in (10).

Since Δ_o^1, the orbital energy in the low-spin compound Fe(phen)$_3^{2+}$, is higher than the spin-pairing energy and since $\mu < 0$ (the π-antibonding effect of the CN groups is negative), $\Delta_o^1 - {}^3/_2\mu$ is much higher than the critical energy of spin pairing. According to (10), the condition of diamagnetism is fulfilled and the complex [Fe(phen)$_2$(CN)$_2$] must be diamagnetic, as shown by the spectral and magnetic measurements.[3]

(13) N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).