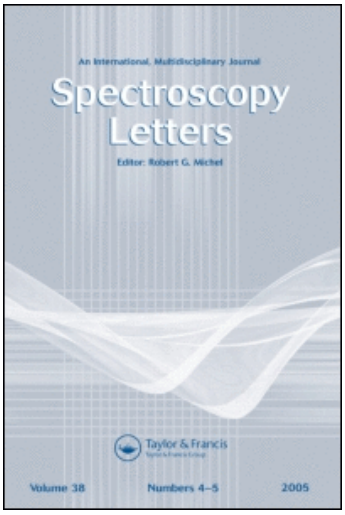

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Electronic Spectra of a Series of Iron(II) α-iminooxime Macrocyclic Complexes Containing Axial N-Heterocyclic Ligands

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ELECTRONIC SPECTRA OF A SERIES OF IRON(II) α-IMINOOXIME MACROCYCLIC COMPLEXES CONTAINING AXIAL N-HETEROCYCLIC LIGANDS

Key words: Charge-Transfer Spectra, Iron-Macrocycles
Iron-N-Heterocyclic Complexes.

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ABSTRACT

The influence of the axial N-heterocyclic ligands on the charge-transfer spectra of a series of iron(II)-iminooxime macrocyclic complexes is reported. Spectral correlations are discussed, based on the deconvolution of the absorption profiles and on the dependence of the charge-transfer energies with the Hammett $\sigma^{+/-}$ substituent parameters.

INTRODUCTION

In biological systems, the structure and activity of the several iron-porphyrin species are strongly dependent on the nature of the axial ligands. Their electronic spectra are dominated by the intense $\pi \rightarrow \pi^*$ transitions in the porphyrin, and little information concerning the metal-ligand interactions can be accessed from the absorption data. In this sense, iron(II)

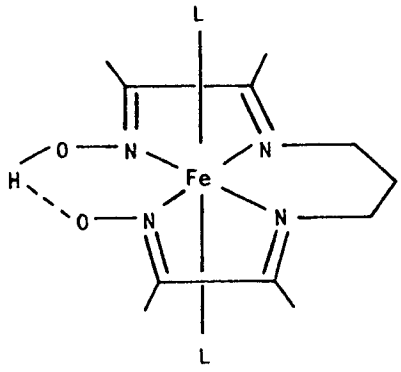

Fig. 1. $[Fe(imox)L_2]^+$

complexes of synthetic macrocyclic ligands provide particularly useful heme model compounds exhibiting less complicated spectra and a great variety of chemical properties, such as oxygen and CO transport,[1,2] ligand reactions[3] and stabilization of unusual oxidation states.[4,5]

In this work we investigated the electronic spectra of a series of iron(II) α-iminooxime macrocyclic complexes of the type $[Fe(imox)L_2]^+$ where imox = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundecane-1,3,8,10-tetraen-11-ol-1-olato (Figure 1) and L = substituted pyridine ligands. A correlation study of the charge-transfer energies with the Hammett $\sigma^{+/-}$ substituent parameters[6,7] was carried out in order to evaluate the electronic effects associated with the axial and equatorial ligands in these heme model complexes.

EXPERIMENTAL

The α-iminooxime ligand was prepared according to the procedures previously published in the literature.[8]

The corresponding $[Fe(imox)(mim)_2]BF_4$ complex, where mim = N-methyl imidazole, was synthesized by mixing 1.9 g (5.5 mol) of $[Fe(H_2O)_6](BF_4)_2$ with 4.4 ml (55 mmol) of mim, in methanol, under an argon atmosphere, followed by the reaction with 1.3 g (5.5 mmol) of the macrocyclic ligand. The solvent was eliminated by rotoevaporation and after dissolving in CH_2Cl_2, the product was adsorbed into a neutral alumina column and eluted with methanol. A dark blue solid was isolated by solvent evaporation, washed with diethyl ether and dried under vacuum. Yield: 34%. Anal. Calcd for $FeC_{19}H_{31}N_8O_2BF_4$: C, 41.8; N, 20.5; H, 5.8%. Found: C, 41.9; N, 21.0; H, 6.0%.

The $[Fe(imox)L_2]^+$ complexes where L = pyridine (py), 4-cyanopyridine (cnpy), 4-bromopyridine (brpy), 4-carboxymethylpyridine (cmpy), 4-pyridinecarboxamide (adpy), 4-acetylpyridine (acpy), 4-chloropyridine (clpy), 4-methylpyridine (pic), 4-tertbutylpyridine (tbpy) and 4-aminopyridine (ampy) were freshly prepared in aqueous solution, by reacting the N-methyl imidazole derivative with a high excess of the corresponding ligands (Aldrich), under an argon atmosphere. All other reagents were of high purity and were used as supplied.

The electronic spectra were recorded on a Hewlett-Packard 8452-A diode-array spectrophotometer. Spectral deconvolution was carried out using a local variation of the SPECSOLV program.[9]

RESULTS AND DISCUSSION

Typical electronic spectra of the $[Fe(imox)L_2]^+$ complexes are shown in Figure 2. The spectra can be deconvoluted into two groups of absorption bands, exhibiting three components each. The first group is observed around 600 nm and is less sensitive to the substituents at the pyridine ligands. In contrast, the

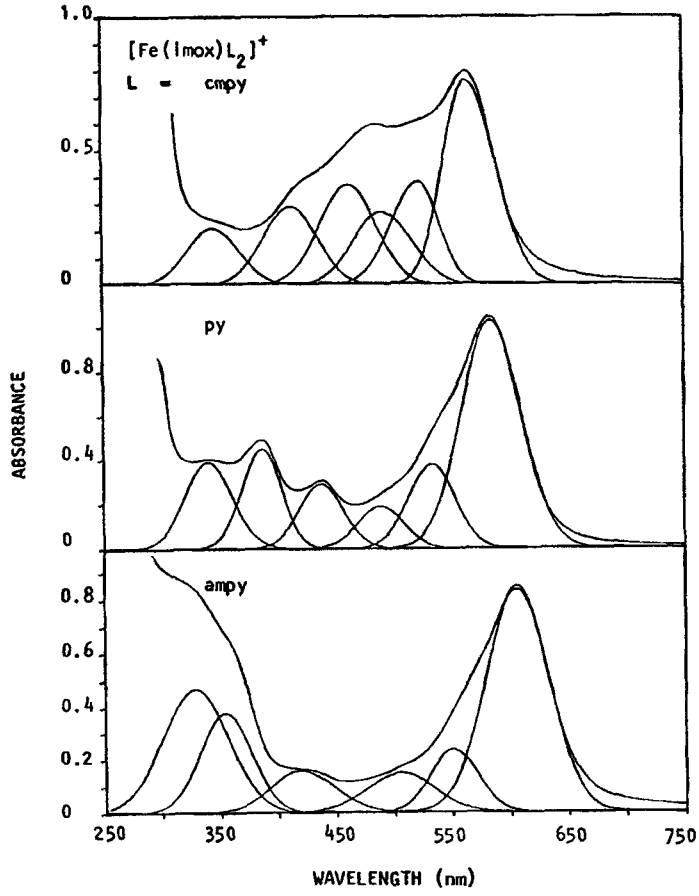

Fig. 2. Gaussian analyses of the electronic spectra of typical $[Fe(imox)L_2]^+$ complexes.

second group is strongly dependent on the axial ligands. This type of behavior is analogous with those reported for related iron(II) macrocyclic complexes[10,11] and is consistent with the assignment of the first group as a metal-to-equatorial ligand charge-transfer transition (MECT), and of the second group, as a metal-to-axial

TABLE 1

Spectral data for the $[Fe(imox)L_2]^+$ complexes[a]

L =		MECT1	MECT2	MECT3	MACT4	MACT5	MACT6
a	cnpy	17.99	19.31	20.83	20.58	23.81	29.24
b	acpy	17.67	19.23	20.58	21.55	23.81	b
c	cmpy	17.73	19.08	20.33	21.55	24.15	28.90
d	adpy	17.61	18.87	20.16	21.74	23.70	29.07
e	brpy	17.42	18.87	20.41	22.52	25.13	28.50
f	clpy	17.42	18.87	20.00	22.62	25.25	28.90
g	py	17.12	18.73	20.41	22.83	25.77	29.41
h	tbpy	17.01	18.59	20.20	23.09	26.04	29.41
i	pic	17.06	18.66	20.24	23.15	26.11	29.59
j	ampy	16.50	18.18	19.76	23.92	28.25	30.49

[a]Wavenumbers (10^3 cm^{-1}) measured in aqueous solution.
[b]Masked by the ligand absorption in the UV region.

ligand charge-transfer transition (MACT). The spectral data for the complexes are shown in Table 1.

It should be emphasized that the components of the first group, here denoted MECT1, MECT2 and MECT3 exibit energy separation very close to 1600 cm^{-1}, practically coinciding with the C=N stretching frequency of 1574 cm^{-1} observed in these complexes. Analogously with the iron(II)-tris(diimine) complexes reported in the literature,[12] we assigned the two high energy components to vibronic transitions within the iron(II)-iminooxime chromophore.

The contrasting dependence of the MECT and MACT energies on the Hammett $\sigma^{+/-}$ substituent parameters for the axial ligands is illustrated in Figure 3. As

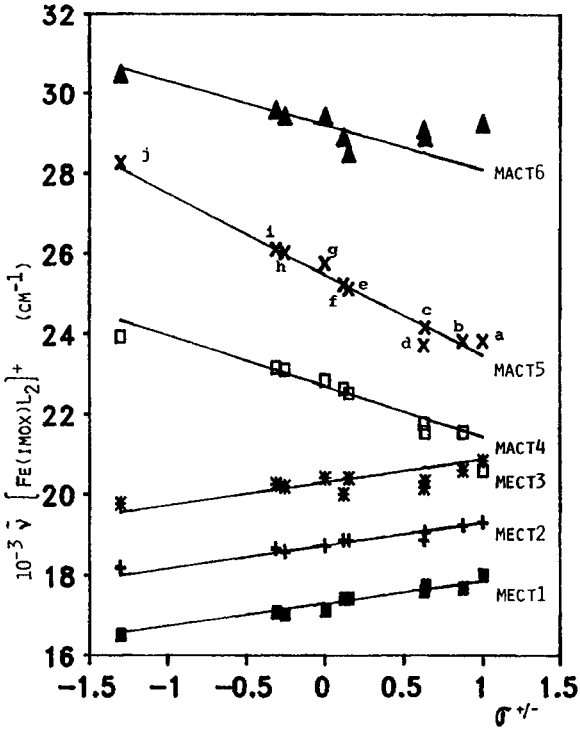

Fig.3. Plots of the MECT and MACT wavenumbers *versus* the substituent $\sigma^{+/-}$ parameters; the ligand labels are shown in Table 1.

expected, the MACT bands are very sensitive to $\sigma^{+/-}$ as a consequence of the direct influence of the substituents on the π^* levels of the pyridine ligands. An electron withdrawing group stabilizes the π^* level, decreasing the energy of the MACT transition. An electron donor group leads to an opposite effect. The dependence of the MECT energies on $\sigma^{+/-}$ is better explained by means of a molecular orbital (MO) scheme, as shown in Figure 4.

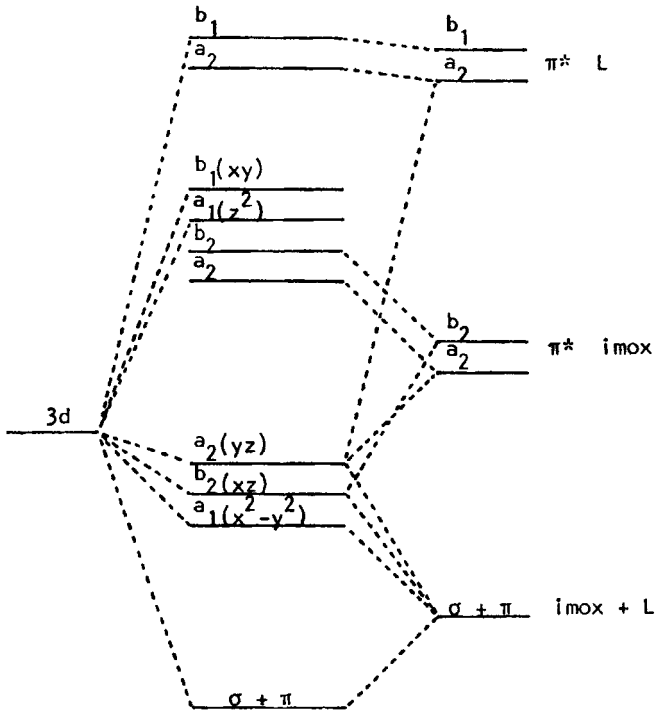

Fig. 4. Qualitative molecular orbital diagram for $[Fe(imox)L_2]^+$ complexes.

The qualitative MO scheme was based on SCF-Xα-SW calculations for an analogous iron(II)-diimine macrocyclic complex, of D_{2h} symmetry.[12] In our case the symmetry is C_{2v} and the corresponding group theory representations were derived from D_{2h} using appropriate correlation tables.[14] The highest occupied MOs exhibit strong metal d_π character, namely d_{yz} (a_2), d_{xz} (b_2) and $d_{x^2-y^2}$ (a_1). The lowest unoccupied MOs may be represented by the a_2 and b_2 π^*-levels of the macrocyclic ligand, or by the metal d_{z^2} (a_1), d_{xy} (b_1)

levels, or by the b_1 and a_2 π^*-levels of the N-heterocyclic ligands.

According to the proposed MO scheme, the occupied metal $d_{yz}(a_2)$ orbital interacts simultaneously with the empty a_2 π^*-orbitals of the equatorial and axial ligands, in a competitive way. The $d_{xz}(b_2)$ and $d_{x^2-y^2}(a_1)$ orbitals can only play a minor role, exhibiting a very poor overlap with the π-orbitals of the equatorial and axial ligands. It has been shown that the metal-ligand interaction is an important factor contributing to the dipole transition moment,[15] which is responsible for the intensities of the electronic spectra. Therefore, the observed MECT band is consistent with the $d_{yz}(a_2) \rightarrow \pi^*(a_2)$ transition.

The MACT bands can arise from the excitation of the metal $d_{yz}(a_2)$ to the pyridine a_2 and b_1 π^*-orbitals. Considering that the axial ligands can exibit free rotation in solution, the d_{xz} orbital can strongly interact with the pyridine $\pi^*(a_2)$ orbitals. Therefore, the $d_{xz}(b_2) \rightarrow \pi^*(a_2)$ transition is also very probable. Since the $d_{xz}(b_2) \rightarrow \pi^*(b_1)$ transition is forbidden by symmetry, the three MACT bands observed in the spectra can be ascribed to the $d_{yz}(a_2) \rightarrow \pi^*(a_2)$, $d_{yz}(a_2) \rightarrow \pi^*(b_1)$ and $d_{xz}(b_2) \rightarrow \pi^*(a_2)$ transitions.

The interaction between the metal and ligand orbitals is expressed by the ressonance integral β. When the interaction is weak, β is practically negligible, and the CT excitation energies correspond to the energy separation between the metal and ligand π-orbitals. In this case, the slope of the plots of the MACT wavenumbers versus $\sigma^{+/-}$ reflects the direct influence of the substituents on the π^* levels of the pyridine ligands. However, when the interaction is strong, the β term leads to an increase of the CT

energies.[16] In this way, the slope of the plots of the CT wavenumbers versus $\sigma^{+/-}$ becomes smaller than in the case of electronic transitions involving weakly interacting orbitals.

In Figure 3, one can see that the slopes of the MACT4 and MACT6 plots are smaller than that for the MACT5 plot, as expressed by the linear equations:

$$E_{MACT4}\ (10^3\ cm^{-1}) = -1.26\ \sigma^{+/-} + 22.70$$
$$E_{MACT5}\ (10^3\ cm^{-1}) = -2.02\ \sigma^{+/-} + 25.50$$
$$E_{MACT6}\ (10^3\ cm^{-1}) = -1.10\ \sigma^{+/-} + 29.20$$

Therefore, the MACT4 and MACT6 transitions should involve strongly interacting orbitals, and are consistent with the $d_{yz}(a_2)$ or $d_{xz}(b_2) \rightarrow \pi^*(a_2)$ transitions. On the other hand, the MACT5 band is consistent with the $d_{yz}(a_2) \rightarrow \pi^*(b_1)$ transition, involving weakly interacting orbitals.

The stabilization of the metal d_π orbitals due to the interaction with the axial N-heterocyclic ligands, is also reflected in the slope of the plots of the MECT wavenumbers versus $\sigma^{+/-}$, as expressed by the equations:

$$E_{MECT1}(10^3\ cm^{-1}) = 0.57\ \sigma^{+/-} + 17.30$$
$$E_{MECT2}(10^3\ cm^{-1}) = 0.57\ \sigma^{+/-} + 18.75$$
$$E_{MECT3}(10^3\ cm^{-1}) = 0.57\ \sigma^{+/-} + 20.30$$

If the stabilization is negligible, the slope should be close to zero.

In conclusion, the interaction between the metal and the macrocyclic ligand is strongly influenced by the axial ligands, and vice-versa. As the π-acceptor properties of the axial ligands increase, the bonding between the metal and the macrocyclic ligand becomes weaker. On the other hand, when the macrocycle is a strong π-acceptor ligand, the complex will exhibit less affinity for axial π-acceptor ligands.

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