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ZINDO/S Calculations and Resonance Raman Spectra of the Bis(2,6-diacetylmethyliminepyridine)iron(II) Complex

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Dedicated to Professor Oswaldo Sala on his 70th birthday

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O espectro eletrônico do complexo bis(2,6-diacetilmetilimina piridina)ferro(II) consiste de duas bandas intensas em 490 e 590 nm e uma série de ombros ou bandas fracas na região do visível. As duas bandas principais foram atribuídas, com base em cálculos semiempíricos ZINDO/S, a transições de transferência de carga envolvendo dois conjuntos de orbitais d_{π} do metal, com simetria b_1 e e , e um único orbital π^* de simetria a_2 , deslocalizado sobre o ligante poliimínico. A atribuição foi corroborada pelos perfis de excitação Raman ressonante dos diversos modos vibracionais apresentados pelo complexo. A estrutura ondulada do espectro eletrônico foi atribuída a componentes vibrônicos, como anteriormente descrito na literatura.

The electronic spectrum of the bis(2,6-diacetylmethylimine pyridine)iron(II) complex consists of two strong bands around 490 and 590 nm and a series of shoulders or weak bands in the visible region. Based on ZINDO/S calculations, the two major bands were assigned to iron(II)-to-polyimine, charge-transfer transitions involving two sets of metal d_{π} orbitals of b_1 and e symmetry, and a single π^* orbital of a_2 symmetry spread over the polyimine ligand. The assignment was corroborated by the resonance Raman excitation profiles of the various vibrational modes for the complex. The typical structure of the electronic bands was ascribed to vibronic components, as previously reported in the literature.

Keywords: *resonance Raman spectra, iron(II)-polyimine spectra, electronic spectroscopy*

Introduction

The characteristic red color of iron complexes with bipyridine and phenantroline ligands was first reported by Blau¹ nearly a hundred years ago. In 1952, Sone² proposed the existence of an iron(II)-diimine chromophore, which was confirmed by Krumholz³ one year later. The strong absorption band observed around 500 nm in this type of complex was assigned by Williams⁴ to a charge-transfer (MLCT) transition from the metal (t_{2g})⁶ levels to a π^* level located on the diimine ligand. This band is typically asymmetrical, exhibiting a shoulder in the high energy region.

The assignment of the shoulder or second band was rather controversial. Krumholz⁵ considered the possibility of two MLCT bands involving distinct π^* levels, but concluded that the vibronic interpretation was more plausible, since the typical energy separation of $1.5 \times 10^3 \text{ cm}^{-1}$ was

very close to the stretching frequency of the C=N group. In contrast, several authors⁶⁻⁸ preferred to ascribe the second band to a low symmetry ligand field splitting. Later, a similar interpretation was also considered by Krumholz and coworkers⁹, based on the fact that for several iron(II)-diimine complexes, the energy separation between the absorption bands exceeded 3000 cm^{-1} , therefore being too high for a vibronic coupling mechanism. In 1977, however, this proposal was negated by Clark *et al.*¹⁰, and the shoulder observed for symmetric iron(II)-tris(diimine) complexes was ascribed to a vibronic transition, based on the analysis of the resonance Raman excitation profiles.

Here we investigate the electronic spectra of the bis(2,6-diacetylmethyliminepyridine)iron(II) complex, $[\text{Fe}(\text{damipy})_2]^{2+}$, shown in Fig. 1. This complex exhibits a very complicated absorption profile, suggesting the involvement of several π^* levels or low symmetry ligand

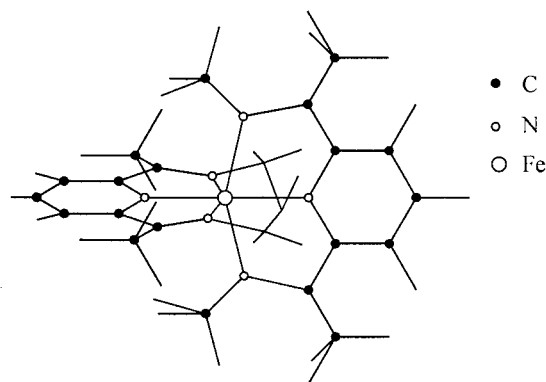


Figure 1. MM⁺ optimized configuration for the [Fe(damipy)₂]²⁺ complex.

field splittings, in addition to possible vibronic interactions. In order to evaluate this point, ZINDO/S calculations and resonance Raman studies were performed.

Experimental

The synthesis and analytical characterization of the [Fe(damipy)₂](BF₄)₂·2H₂O complex have been previously reported in the literature¹¹. Electronic spectra were recorded on a Guided Wave model 260 fiber optics instrument or on a Hewlett-Packard model 8452-A diode array spectrophotometer. Spectral deconvolution was carried out using the Grams 386 software package, employing Gaussian functions, which are particularly suitable for electronic transitions. Resonance Raman spectra were recorded on a Jobin Yvon U1000 spectrometer, fitted with an RCA C31034A-02 photomultiplier tube, using excitation lines from both Kr⁺ and Ar⁺ lasers. A spinning cell for solids was employed for the measurements. The laser power was kept around 40 mW for the sample, and the spectral slit was typically 7 cm⁻¹. The measurements were carried out by dispersing the solid complex in NaCl (diluent) and NaNO₃ (internal standard). Intensities were taken as peak areas and reported as relative to the intensity of the nitrate Raman band at 1053 cm⁻¹; in the case of band overlapping, deconvolution (Grams 386) was performed using Lorentzian line shapes, as are usually employed for vibrational transitions.

Quantum mechanical semi-empirical calculations were carried out using Hyperchem 4.5 from Hypercube and an IBM microcomputer with a 100 Mz Pentium microprocessor.

Results and Discussion

The electronic spectrum of the [Fe(damipy)₂]²⁺ complex, including deconvolution analysis, is shown in Fig. 2. The diffuse reflectance spectrum of the solid is also illustrated for comparison purposes in Fig. 2.B, nearly coinciding with that measured in solution, except for the broadening effect usually observed for powder measurements. Two strong bands are most evident in the spectra at

490 (log ε = 3.9) and 590 nm (4.0), in the characteristic region for the iron(II)-to-diimine charge-transfer transitions⁵. In addition, several shoulders or weak bands are apparent around 535, 560, 615, 650 and 700 nm.

A spectral simulation, based on ZINDO/S¹² semi-empirical quantum mechanical calculations, is also shown in Fig. 2A. The geometry of the complex was optimized by molecular mechanics (MM⁺) calculations, using Hyperchem 4.5 default parameters for transition metal ions, at a refinement level of 0.0001 Kcal mol⁻¹ Å⁻¹. The optimized geometry, shown in Fig. 1, exhibits a rigorous D_{2d} symmetry. ZINDO/S calculations were performed for the optimized configuration with 154 electrons occupying 77 orbitals, assuming a low spin state for the metal center (spin multiplicity = 1) and a restricted Hartree-Fock approach. Configuration interaction was limited to three occupied and

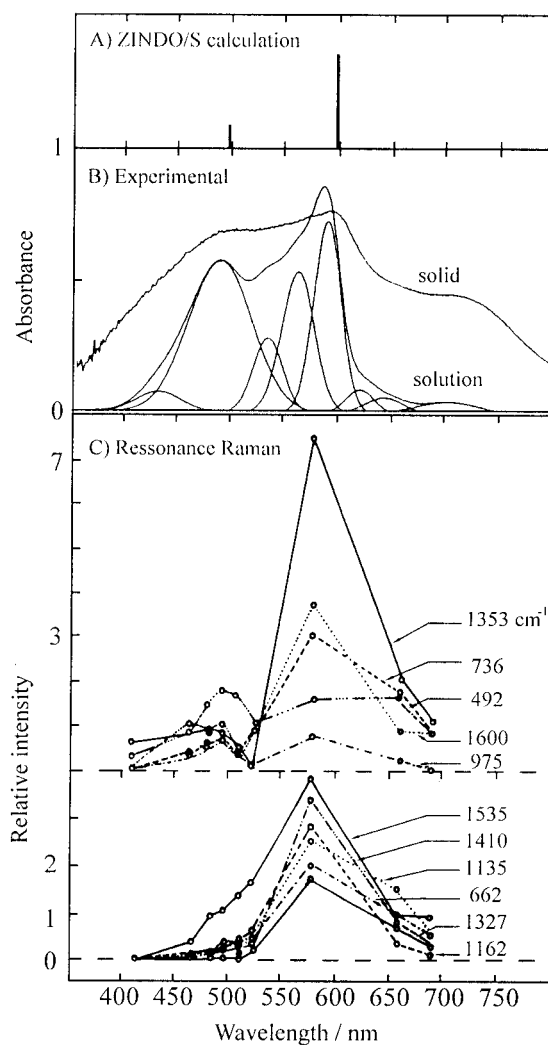


Figure 2. A) Theoretical (ZINDO/S) and B) experimental electronic spectra of the [Fe(damipy)₂]²⁺ complex (solid = reflectance, solution = absorption measurement); C) typical resonance Raman excitation profiles for several vibrational peaks.

three unoccupied orbitals. The calculations were repeated, assuming a constant σ - σ overlap weighing factor of 1.267 (default) and a variable π - π factor. The two electronic bands at 490 and 590 nm were accurately fitted using a π - π factor of 0.350, as shown in Fig. 2.A.

The theoretical electronic transition at 587 nm involves the occupied MO level 77, which essentially corresponds to the iron d_{xy} orbital of b_1 symmetry, and the empty MO level 80, which is a π^* orbital of a_2 symmetry spread over the polyimine ligand. The theoretical electronic transition at 494 nm involves a degenerate set of occupied MO levels, (MO number 75 and 76); essentially corresponding to the iron d_{xz} and d_{yz} orbitals of e symmetry, and the same MO level 80 of the polyimine ligand. These two electronic transitions, $b_1 \rightarrow a_2$ and $e \rightarrow a_2$, are allowed by symmetry, in the parallel and perpendicular directions, respectively. The calculated oscillator strengths for the two bands, 0.81 and 0.19, were rather qualitative, since the vibronic functions were not appropriately included the transition dipole integrals. Several other theoretical transitions can be found above 770 nm or below 350 nm, but exhibit negligible oscillator strengths (< 0.01). Therefore, according to the ZINDO/S calculations, the occurrence of the two electronic bands is associated with the ligand field splitting of the iron(II) d orbitals in a D_{2d} symmetry.

In order to improve the understanding of the excited states involved in the electronic spectra of the $[\text{Fe}(\text{damipy})_2]^{2+}$ complex, a detailed resonance Raman investigation was carried out, using a number of excitation wavelengths, as shown in Fig. 3.

The enhanced peaks at 1600 (ν CC py), 1535 (ν C=N imine), 1410 (ν CC,CN py), 1353 (ν CC,CN + δ CCH py), 1327 (ν CC,CN + δ CCH, py), 1162 (δ CCH), 1135 (δ CCH), 975 (ring breath), 736 (ring def.out-of-plane), 662 (ring def. in-plane), and 423 cm^{-1} (δ ring) can be ascribed to the pyridine and polyimine vibrational modes, and at 492 cm^{-1} to a predominantly metal-ligand vibration (ν Fe-N), through analogy to the previous studies of normal coordinate analysis and spectroscopy of tris(dimine)iron(II) complexes and related species^{10, 13-15}.

The excitation profiles for the vibrational peaks (Fig. 2C) exhibit maximum enhancement at the 590 nm band, and a weak or negligible enhancement at the second electronic band at 490 nm. This result is consistent with the ZINDO/S calculations, which predict a much less intense band at 490 nm. The most strongly enhanced peaks correspond to the polyimine (ν C=N) and pyridine ring vibrations at 1535 and 1600, 1353 cm^{-1} , respectively, indicating that the chromophore group is spread over the pyridine-imine bonds, as expected from the MO calculations for the complex. Furthermore, the lack of contrasting excitation profiles for the various enhanced vibrational peaks cor-

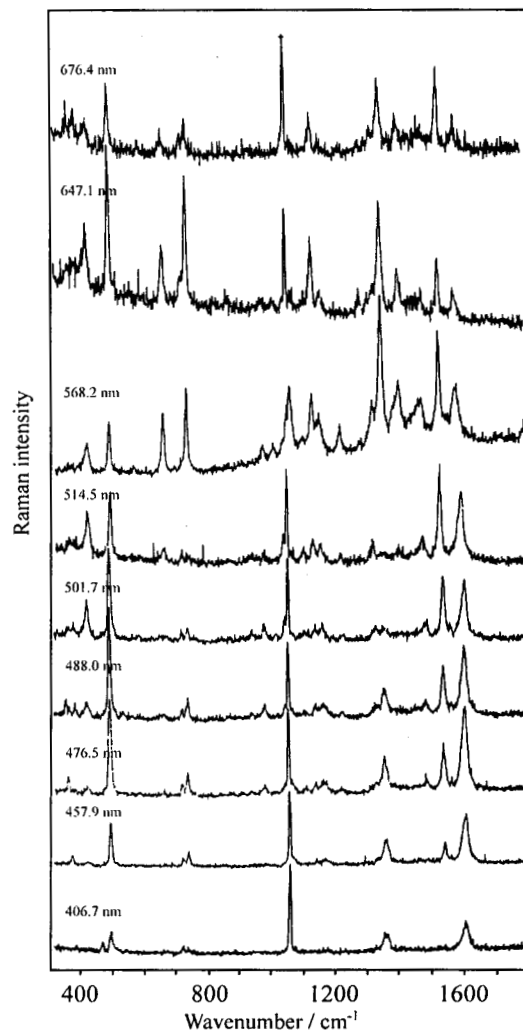


Figure 3. Resonance Raman spectra of the $[\text{Fe}(\text{damipy})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ complex (solid) dispersed in NaCl, in the presence of NaNO_3 as the internal standard (\uparrow), and recorded at several excitation wavelengths.

roborates the involvement of the same LUMO level in both electronic transitions.

Conclusions

According to the ZINDO/S calculations and the resonance Raman behavior, a single LUMO level located on the pyridine-imine ligand is involved in the MLCT spectra of the $[\text{Fe}(\text{damipy})_2]^{2+}$ complex in the visible region. The occurrence of two bands at 490 and 590 nm can be theoretically explained in terms of the ligand field splitting of the metal d_π orbitals in a D_{2d} symmetry. The various shoulders or weak bands in the 540 - 650 nm region do not exhibit distinct excitation profiles, corresponding to a series of vibronic components, in agreement with the work of Clark *et al.*¹⁰. Therefore, the contribution of ligand field splittings and vibronic components should be taken into account in the discussion of the electronic spectra of the iron(II)-polyimine complexes.

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