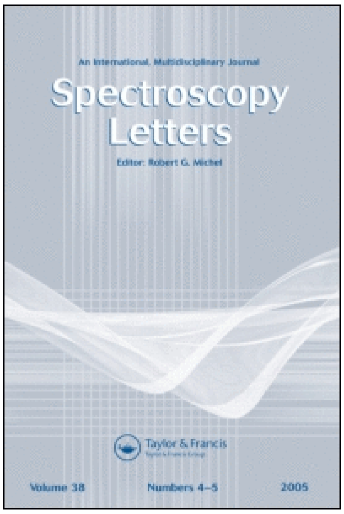

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ELECTRONIC AND RAMAN SPECTRA OF AN IRON-DIOXIMATO POLYMER

Key Words: Raman Spectra, Iron-dioximato Complexes, Pirazine Polynuclear Complexes.

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ABSTRACT

Electronic and resonance Raman spectra are reported for the $[Fe(Hdmg)_2(clpz)]_n$ polymer (clpz = 2-chloropyrazine, Hdmg = dimethylglyoximato anion). Excitation at the absorption bands in the visible region led to a selective enhancement of vibrational modes of the Hdmg and clpz ligands, allowing the characterization of the metal-to-macrocycle and metal-to-axial ligand charge-transfer transitions.

INTRODUCTION

Bridged macrocyclic metal polymers have recently been investigated as part of efforts to discover new types of low-dimensional solids exhibiting interesting electronic and magnetic properties.[1-4] The most intensively studied systems are derived from metallophtalocyanines with bridging ligands such as pyrazine, tetrazines, and diisocyano-benzenes. The visible-uv spectra of these polymers are dominated by the intense Q-bands around 640 nm and the B-band around 315 nm, which are due to transitions of the phthalocyaninato moiety.[1] For this reason, little information on the electronic structure of the metal ion has been obtained in these systems. The use of less conjugated macrocyclic species, such as the bis(dimethylglyoximato)iron(II) complex, would be more appropriate for this purpose, allowing the detection of ligand field and charge-transfer transitions which are not accessible in the metallophthalocyanines. Along this line, we investigated the electronic structure of a new chloropyrazine bridged bis(dimethylglyoximato) iron(II) polymer, based on visible-uv, Mossbauer and resonance Raman spectroscopy.

EXPERIMENTAL

The $[Fe(Hdmg)_2(clpz)]_n$ compound (Hdmg = dimethylglyoximato or diacetyldioximato anion, clpz = 2-chloropyrazine) was synthesized by reacting 5 ml of methanol solution containing 0.6 g (3.5 mmol) of iron(II) acetate, with 0.82 g (7 mmol) of dimethylglyoxime and 2 g (17 mmol) of 2-chloro pyrazine previously dissolved in 25 ml of methanol. The synthesis was carried out under an argon atmosphere. After 20 min the solution was filtered and the violet-brown solid washed with 10 ml of methanol. The product was dried under vacuum. Anal. Calcd for $C_{12}H_{16}N_6O_4ClFe$: C, 36.0; H, 4.2; N, 20.9. Found: C, 37.1; H, 4.0; N, 20.7.

Physical Measurements

The electronic spectra of the complex in the visible and uv region were recorded on a Hewlett-Packard model 8452-A diode-array spectrophotometer.

Resonance Raman spectra were recorded on a Jarrell-Ash instrument, using Spectra-Physics argon and krypton ion lasers. The measurements were carried out with the solids dispersed in compressed pellets with a supporting medium of sodium sulfate (1:100) and placed in a spinning cell, to avoid local heating and decomposition of the complex. The relative intensities were measured as peak heights with respect to the sulfate Raman band at 1000 cm^{-1}. The evaluation of the depolarization ratios for the Raman peaks was precluded by the photodecomposition of the complexes in solution.

Mossbauer measurements were carried out on an Elscint constant acceleration spectrometer, using a Rh (^{57}Co) source. The Mossbauer absorbers were prepared by sealing the sample powders in lucite holders. Metallic iron was used as a standard for velocity calibrations and as a reference material for isomer shifts.

RESULTS AND DISCUSSION

The $[Fe(Hdmg)_2(clpz)]_n$ compound was practically insoluble in solvents such as chloroform; however, the solubility increased dramatically in the presence of an excess of the 2-chloropyrazine ligand, due to the formation of the monomeric $[Fe(Hdmg)_2(clpz)_2]$ complex. The analogous pyrazine phthalocyanineiron(II) complex[1] $[Fe(Pc)(pz)_2]$ also readily splits off a pyrazine ligand in chloroform to form the polymer $[Fe(Pc)(pz)]_n$. In this case, monomeric species has only been observed in the presence of a 10^6 fold excess of pyrazine.

In general, the pyridine and pyrazine iron(II)-dioximato complexes exhibit two characteristic electronic bands in the visible, corresponding to the metal-to-axial ligand and metal-to-equatorial ligand

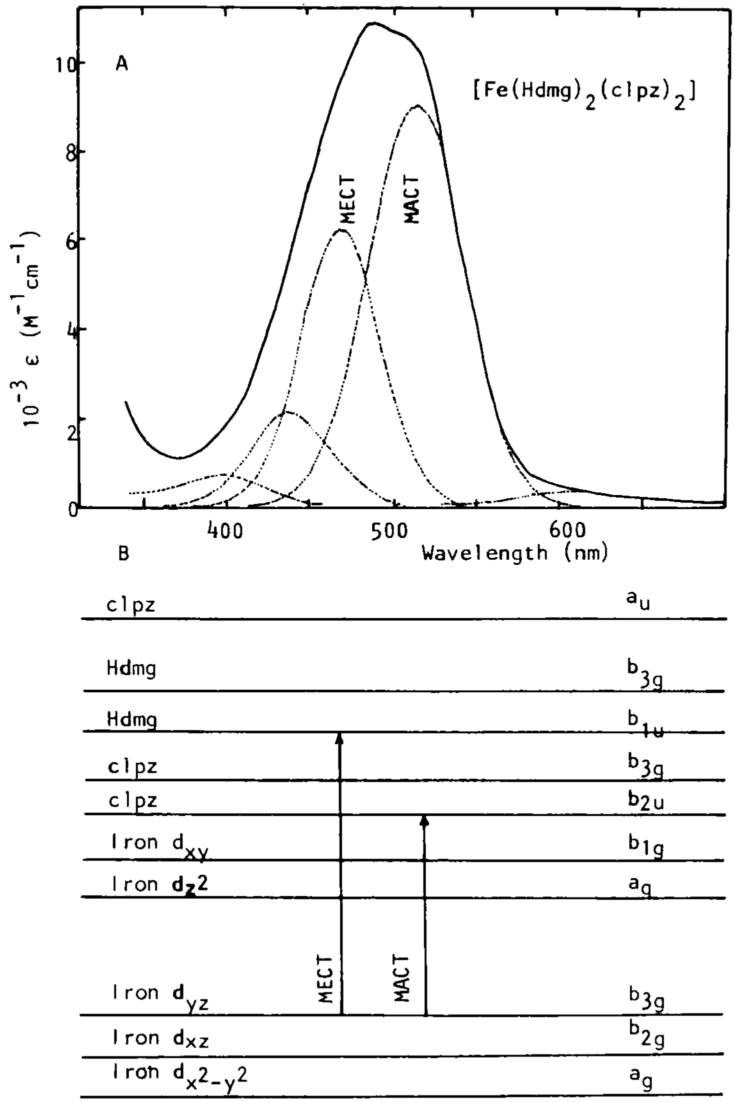

Fig. 1. (A) Electronic spectrum and (B) qualitative molecular orbital diagram for the $[Fe(Hdmg)_2(clpz)_2]$ complex ($CHCl_3$ solution, [clpz] = 0.10 M, Gaussian analyses are shown in dotted lines).

charge-transfer transitions,[5-9] here denoted MACT and MECT, respectively. The electronic spectrum of the monomeric $[Fe(Hdmg)_2(clpz)_2]$ complex is illustrated in Figure 1.A. Strong absorption bands observed at 512 nm (log ε = 3.96) and 470 nm (3.80) were ascribed to the MACT and MECT transitions, respectively, by analogy to the related examples in the literature.[5-9]

The electronic spectrum of the solid $[Fe(Hdmg)_2(clpz)]$ complex differs from that of the monomeric species, as shown in Figure 2.A, exhibiting strong absorptions at 550 and 480 nm. The changes in the absorption bands can not be ascribed to solid state effects, since only small bathochromic shifts have been observed in the spectra of the solid $[Fe(Hdmg)_2L_2]$ monomeric complexes, where L = py (pyridine) and dmpz (2,6 dimethylpyrazine), with respect to those obtained in $CHCl_3$ solutions.[8,9] The large bathochromic shift and the intensification of the MACT band are consistent with the formation of pyrazine bridges, as previously observed in complexes[10] of the type $[(NH_3)_5Ru(pz)\{Ru(NH_3)_4(pz)\}_nRu(NH_3)_5]^{(2n+4)}$.

The assignment of the MACT and MECT bands can be suggested with the help of the qualitative molecular orbital (MO) diagram shown in Figure 1, based on SCF-Xα-SW calculations for an analogous iron(II)-diimine macrocyclic complex.[11] The highest occupied MOs exhibit strong metal d_π character, namely, d_{yz} (b_{3g}), d_{xz} (b_{2g}) and $d_{x^2-y^2}$ (a_g), considering a D_{2h} symmetry. The lowest unoccupied MOs may be represented by the metal d_{z^2} (a_g), d_{xy} (b_{1g}) levels, as well as by the b_{1u}, b_{3g} π-levels of the macrocyclic ligand, and by the b_{2u}, b_{3g} π-levels of the axial N-heterocyclic ligands.

The d_{yz} $(b_{3g}) \rightarrow \pi^*(b_{2u}$ N-heterocycle) and dyz $(b_{3g}) \rightarrow \pi^*(b_{1u}$ macrocycle) transitions are symmetry

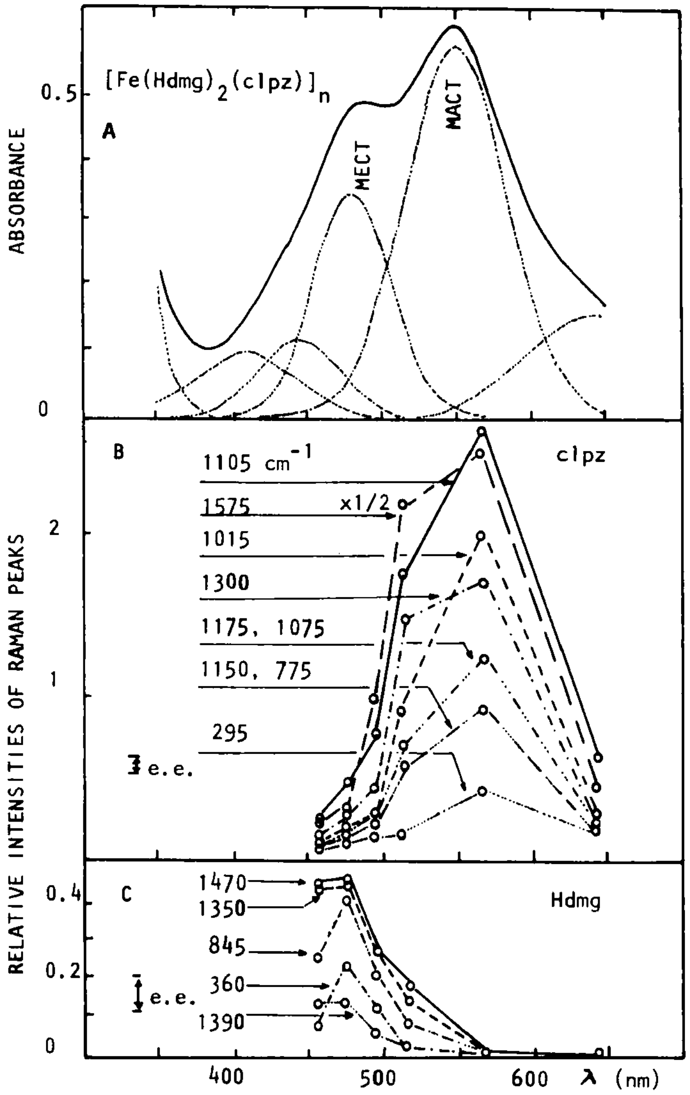

Fig. 2. (A) Electronic spectrum of the [Fe(Hdmg)$_2$(clpz)]$_n$ polymer dispersed in Nujol (Gaussian analyses are shown in dotted lines) and resonance Raman excitation profiles for vibrational peaks of the coordinated (B) clpz and (C) Hdmg ligands. (e.e. = estimated error)

allowed and can be associated with the MECT and MACT bands respectively, in the visible region. The MECT band in the [Fe(Hdmg)$_2$L$_2$] complexes usually exhibits a shoulder on the high frequency side, analogous to the vibronic side band previously reported in iron(II)-tris(diimine) complexes.[12] This band was detected by Gaussian analysis, at 438 and 447 nm, in the electronic spectra of the [Fe(Hdmg)$_2$(clpz)$_2$] and [Fe(Hdmg)$_2$(clpz)]$_n$ complexes, respectively.

The less intense bands at 620, 400 nm and 630, 405 nm, respectively, for the [Fe(Hdmg)$_2$(clpz)$_2$] and [Fe(Hdmg)$_2$(clpz)]$_n$ complexes, are related to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field transitions in an octahedral microsymmetry, as previously reported for several low-spin iron(II)-macrocyclic complexes.[13]

The Mossbauer spectrum of the [Fe(Hdmg)$_2$(clpz)$_n$] complex consisted of a well defined doublet, which was accurately fitted using two Lorentzian lines. The isomer shift referred to metallic iron, and the quadrupole splitting, at 300 K, was 0.204 (± 0.005) and 1.819 (± 0.005) mm.s^{-1}, respectively. Similar values were obtained for the monomeric [Fe(Hdmg)$_2$(dmpz)$_2$] complex, under identical conditions, e.g., 0.216 and 1.803 mm.s^{-1}. These results are consistent with a hexacoordination environment around the metal ion in the [Fe(Hdmg)$_2$(clpz)]$_n$ compound, as expected for a linear pyrazine bridged structure.

Resonance Raman spectra of the [Fe(Hdmg)$_2$(clpz)]$_n$ polymer obtained at several excitation wavelengths are shown in Figure 3. The vibrational peaks of the Hdmg and clpz ligands were selectively enhanced according to two types of excitation profiles, as illustrated in Figures 2.B,C. The strong resonance Raman scattering indicates that the electronic transitions are electric dipole allowed.[14] The excitation profiles are consistent with two chromophore groups in the polymer.

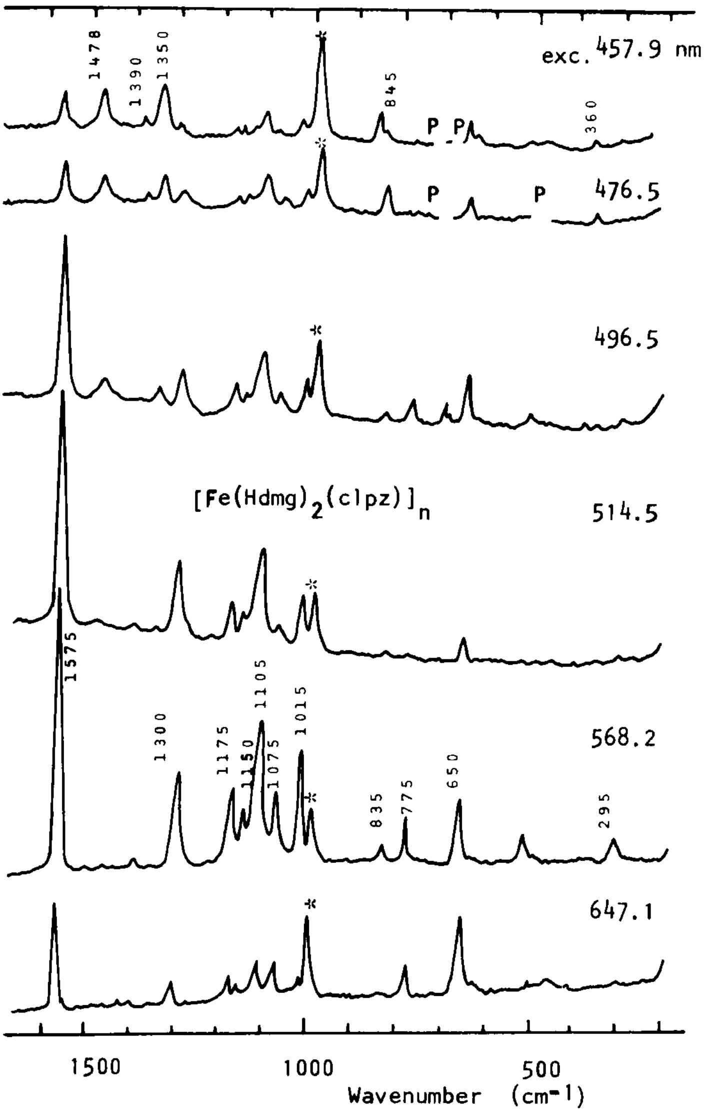

Fig. 3. Raman spectra of the [Fe(Hdmg)$_2$(clpz)]$_n$ polymer dispersed in Na_2SO_4 pellets (1:100), at several excitation wavelengths (* = SO_4^{2-} peaks, P = plasma lines)

The peaks at 1575, 1300, 1175, 1150, 1105, 1075, 1015, 775 and 650 cm^{-1} exhibited maximum enhancement at the low energy charge-transfer band, correlating with the vibrational peaks at 1561, 1287, 1176, 1158, 1135, 1046, 1009, 760 and 654 cm^{-1} in the Raman spectra of the 2-chloropyrazine ligand.[15] This means that the absorption band at 550 nm in the $[Fe(Hdmg)_2(clpz)]_n$ polymer is associated with the iron(II)-clpz chromophore, supporting the assignment of a MACT transition. The enhanced peaks correspond to the vibrational modes of a′ symmetry of clpz, suggesting the contribution of the A term in the resonance Raman theory.[14] The peak at 1575 cm^{-1} was the most strongly enhanced, corresponding to the ring stretching vibration. The peaks at 1300-1075 cm^{-1} are associated with composite CC, CN and ring-H in plane deformation vibrations; the peak at 1015 cm^{-1} is characteristic of a ring breathing vibrational mode, and the peaks at 775 and 650 cm^{-1} can be ascribed to ring deformation vibrations of clpz. The vibrational peak at 295 cm^{-1} was selectively enhanced at the MACT band and can be tentatively assigned to the Fe-N(clpz) vibration.

The vibrational peaks at 1470, 1390, 1350, 845 and 360 cm^{-1} belong to the iron-Hdmg chromophore.[7] They were selectively enhanced according to excitation profiles coinciding with the absorption band at 480 nm (Figure 2.C), in agreement with the assignment of a MECT transition. Normal coordinate analysis for related dioxime complexes[16] has shown that the peaks in the 1470-1350 cm^{-1} region have a large contribution from the C-C and C-N stretching modes of the α-diimine group. The vibrational frequency of 1470 cm^{-1} coincides with the difference of about 1500 cm^{-1} between the Gaussian components at 447 and 480 nm, in Figure 2, and may be indicative of vibronic coupling, as proposed by Clark et al.[12], for the tris(diimine)iron(II) complex. The vibrational peak at 845 cm^{-1} involves nearly equivalent contributions from the N-O and $C-CH_3$ stretching modes. The peak at 360 cm^{-1} can be tentatively assigned to a metal-N(Hdmg) stretching vibration, by analogy to the literature.[16]

In conclusion, the identities of the iron(II)-Hdmg and iron(II)-clpz chromophores were nearly preserved in the polymer. The main changes were observed in the axial direction, along the interacting iron(II)-clpz groups in the linear chain polymer. This interaction was responsible for the decrease in the energy of the MACT band, reflecting a smaller band gap in the polymer, but not enough to produce great changes in the electrical conductivity, around 10^{-9} S cm^{-1}, observed for this type of system.[3,4]

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