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Uv-Vis Spectra and Fluorescence Properties of Two Iminooxime Ligands and Their Metal Complexes: Optical Band Gaps†

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ABSTRACT

In this study, UV-Vis and fluorescence properties of two iminooxime ligands and their complexes, which have been previously synthesized, were investigated. UV-Vis. spectrum of the HL, $H_2L'.H_2O$ and their complexes were measured in chloroform and $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$, CT→M, d→d transitions were determined. Fluorescence properties of the complexes of HL and $H_2L'.H_2O$ were studied at room temperature. Measurement results showed that all the complexes display intraligand ($\pi\rightarrow\pi^*$) fluorescence. The optical behavior of the complexes of HL and $H_2L'.H_2O$ were investigated using optical reflectance and transmittance measurements. The optical band gaps, which turned out to depend significantly on the metal coordination were calculated by optical absorption method. The analysis of the optical absorption data revealed optical direct transition with band gaps of 3.8 - 4.1 for all of the complexes.

Key Words: *UV-Vis. spectra, fluorescence properties, optical band gaps*.

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1. INTRODUCTION

Many Schiff base derivatives, containing substituted oxime, have been synthesized, characterized in detail and used for complexation with some transition metal ions, in literature, because of different properties and different application areas [1,2]. α-Iminooximes are species like these ligands [3,4]. One of these different properties is showing luminescent properties of some α-iminooximes and their complexes.

Luminescent compounds are attracting much current research interest because of their many applications including emitting materials for organic light emitting diodes, light harvesting materials for photo catalysis and fluorescent sensors for organic or inorganic analyties [5]. Further, luminescent metal complexes are a fascinating class of molecules that have found applications in many areas such as light emitting devices (LED) [6].

Considerable interest has been shown in the synthesis and study of molecular complexes, which may behave like semiconducting materials or at least show high conductivities. Optical and electrical properties of the metal complexes have become an increasingly interesting area of semiconducting and optical materials because these materials possess great potential for device applications such as Schottky diode, solid state devices and optical sensor. The study of optical absorption of metal complexes, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of these materials. The data transmittance and reflectance can be analyzed to determine optical band gaps. It is possible to determine indirect and direct transition occurring in band gap of the metal complexes by optical absorption spectra [7].

In the present work, we obtain two iminooxime ligands and their Ni(II), Co(II), Co(III), Cu(II) and Zn(II) complexes. We are to investigate UV-Vis. spectra and fluorescence properties of these complexes that this information would be helping the researchers towards applying these materials in light emitting devices (LED). We have investigated optical properties of these complexes that this information would be helping the

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researchers towards applying these materials in optical communication and optical devices.

2. EXPERIMENTAL

(2E)-3-aza-1-(hydroxyimino)-2,4-diphenylpent-2-ene, HL, (3E)-3-aza-5-(hydroxyimino)-1,4-diphenylpent-3-en1-ol mono hydrate, $H_2L'.H_2O$ and their Ni(II), Co(II), Co(III), Cu(II) and Zn(II) complexes were synthesized by literature procedure[8]. For the ligands and their complexes, suggested structures are given in Figure 1. Luminescent spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer. The optical absorption spectra and the UV-Vis spectra were recorded between 190 and 900 nm wavelength using Ati-Unicam UV2 UV-Vis spectrophotometer at room temperature.

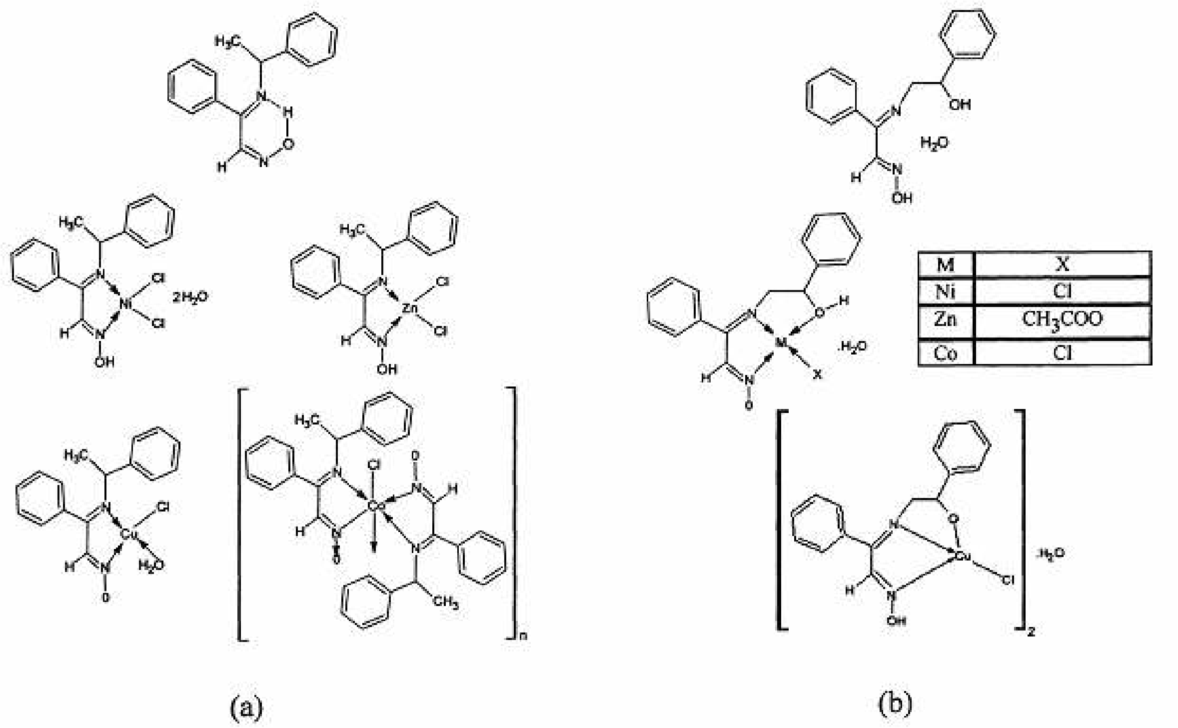


Figure 1. (a) Suggested structure of HL ligand and its complexes (b) Suggested structure of $H_2L'.H_2O$ ligand and its complexes.

3. RESULT AND DISCUSSION

3.1. Electronic Spectra Measurements

The electronic spectra of the HL, $H_2L'.H_2O$ and their complexes were recorded in chloroform at room temperature. UV-Vis spectra date of ligands and complexes are given Table 1. Some spectrums of complexes are seen in Figure 2. Electronic absorption spectral data of showed $\pi \rightarrow \pi^*$ transitions related to benzene ring at 205–256 nm. In the HL ligand and its complexes, imine $\pi \rightarrow \pi^*$ transitions at 275-299 nm and imine $n \rightarrow \pi^*$ transitions at 323-334 nm. Complexes of Ni(II), Co(III) and Cu(II) revealed less intense shoulder at 521, 568 and 632 nm assigned to d→d transitions of the metal ions, respectively. The spectra of all the complexes showed intense band between 395-422 nm, which could be associated with metal to ligand charge transfer transitions. In the $H_2L'.H_2O$ ligand and its complexes, imine $\pi \rightarrow \pi^*$ transitions at 268-280 nm and imine $n \rightarrow \pi^*$ transitions at 310-341 nm. Complexes of Ni(II), Co(II) and Cu(II) revealed less intense shoulder at 630, 492 and 714 nm assigned to d→d transitions of the metal ions, respectively. The spectra of all the complexes showed intense band between 397-428 nm, which could be associated with metal to ligand charge transfer transitions. In the complexes, imine $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions were shifted to longer wavelengths as a consequence of coordination when binding with a metal, confirming the imine nitrogen was coordinated to the metal atom [9].

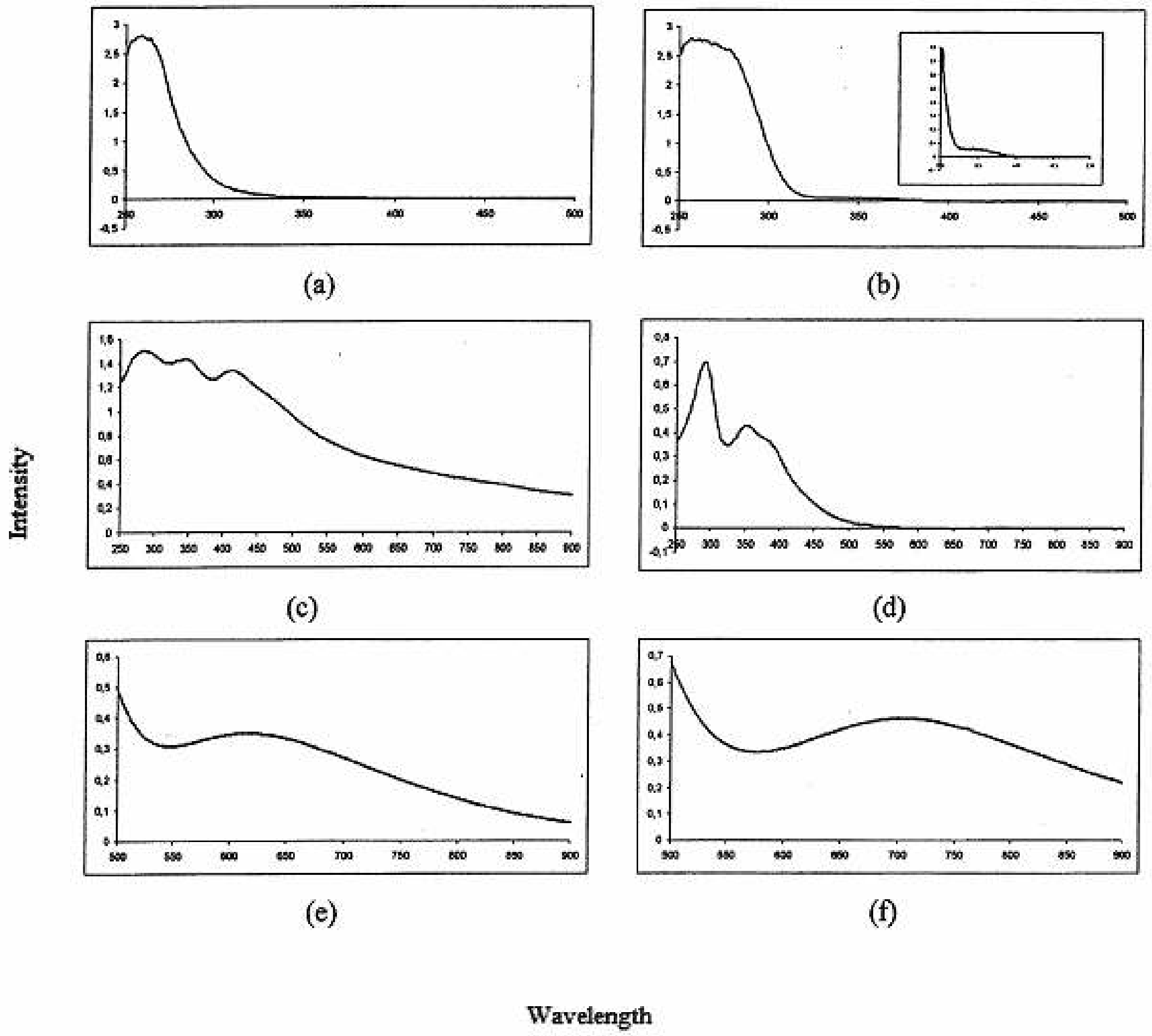


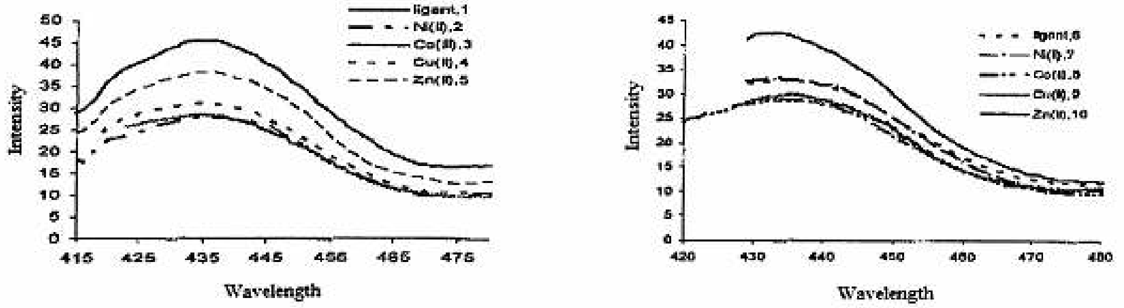
Figure 2. UV-Vis spectra in chloroform; a) HL, b) $H_2L'.H_2O$, c) Cu(II) complex of HL, d) Co(II) complex of $H_2L'.H_2O$, e) d→d transition of Cu(II) complex of HL, f) d→d transition of Cu(II) complex of $H_2L'.H_2O$.

Table 1. Electronic spectral data of HL, $H_2L'.H_2O$ and their complexes.

Compounds	d→d	CT→M	λ_{max}, nm (ε, 10^4 L mol^{-1} cm^{-1})		
			azomethine group		phenyl group
			n→π*	π→π*	$\pi\to\pi^*$
HL (1)	—	—	—	275(2.32)	207(1.54), 231(1.27)
$[NiHLCl_2].2H_2O$ (2)	521(0.010)	400(1.20)	334(1.55)	286(1.48)	201(2.39), 225(1.17)
$[Co(L)_2Cl]_n$ (3)	568(0.014)	407(1.26)	345(1.84)	299(2.12)	204(5.55), 255(2.70)
$[CuLClH_2O]$ (4)	632(0.036)	422(1.81)	337(2.00)	294(2.07)	201(1.64), 224(1.27)
$[ZnHLCl_2]$ (5)	—	395(1.12)	323(1.72)	282(2.28)	203(1.73), 241(1.48)
$H_2L'.H_2O$ (6)	—	—	341(0.02)	268(1.30)	205(1.43), 256(1.32)
$[NiHL'Cl].H_2O$ (7)	630(0.013)	399(1.50)	352(1.55)	275(1.28)	208(1.63), 256(0.98)
$[CoHL'Cl].H_2O$ (8)	492(0.010)	409(1.76)	354(1.84)	280(1.72)	207(1.76), 256(1.02)
$[Cu_2(HL')_2Cl_2].H_2O$ (9)	714(0.047)	428(1.96)	350(2.00)	270(1.98)	210(1.36), 256(1.27)
$[ZnHL'CH_3COO]$ (10)	—	397(1.08)	310(2.12)	272(1.79)	208(1.52), 256(0.96)

3.2. Fluorescence Spectra Studies

The fluorescence properties of the HL, $H_2L'.H_2O$ and their complexes (1-10) were studied at room temperature (298 K) in solid state. The fluorescence spectra of ligands and complexes are appeared in Figure 3. All the eight complexes of HL and $H_2L'.H_2O$ exhibited blue photoluminescence with a maximum emission around 435 and 440 nm upon excitation at 375 and 380 nm. All these fluorescent emissions may be assigned to the intraligand fluorescence since the free ligand exhibited a similar emission at 434 and 438 nm, respectively, under the same condition. The enhancement of fluorescence for 2-5 and 7-10 compared with the free ligand (1 and 6) under the same conditions may be attributed to the bridge connection of the ligand to metal atoms, which enhanced its conformational rigidity and decreased the non-radiative energy loss [10]. The emission observed in the complexes is tentatively assigned to the (π→π*) intraligand fluorescence [11].



(a) (b)

Figure 3. (a) Fluorescence spectra of HL and its complexes, 1-5 (b) Fluorescence spectra of $H_2L'.H_2O$ and its complexes, 6-10.

3.3. The Optical Band Gap of Thin Films

The thin films of the compounds were prepared by evaporating the solvent from a solution of the compounds with subsequent drying of the films deposited on glass substrates. The solution of the compounds was homogenized for 3h and was rotated for homogenous mixing. The thicknesses of the films were determined as about 1 μm with Mettler Toledo MX5 microbalance by using weighing method.

As known, the valuable information about optical band gap is provided by study of fundamental absorption edge. In the absorption process, a photon excites an electron from a lower to a higher energy state which is called an absorption edge. The absorption coefficient was obtained from the transmittance and reflectance spectra of the films using relationship [12],

$$\alpha = \frac{1}{t}\ln\left(\frac{T}{(1-R)^2}\right) \tag{1}$$

where t is thickness of the film. Absorption in these films occurs by excitation of electrons from the filled states to empty ones. The optical absorption edge was analyzed by the following relationship [13],

$$\alpha h\nu = A(h\nu - E_g)^m \tag{2}$$

where A is a constant, m value is respectively 1/2 and 2 for direct and indirect transitions and E_g is the optical band gap. In order to determine optical band gap of the films, we applied the models for both direct and indirect transitions. For this, the $(\alpha h\nu)^2$ (direct transitions) and $(\alpha h\nu)^{1/2}$ (indirect transitions) vs hν were plotted. From these results, it was concluded that the absorption in the films corresponds to a direct energy gap. The plots for direct transitions are shown in Figure 4 and 5. The linear portion of the plots at the absorption edge confirms that the thin film has a direct optical band gap.

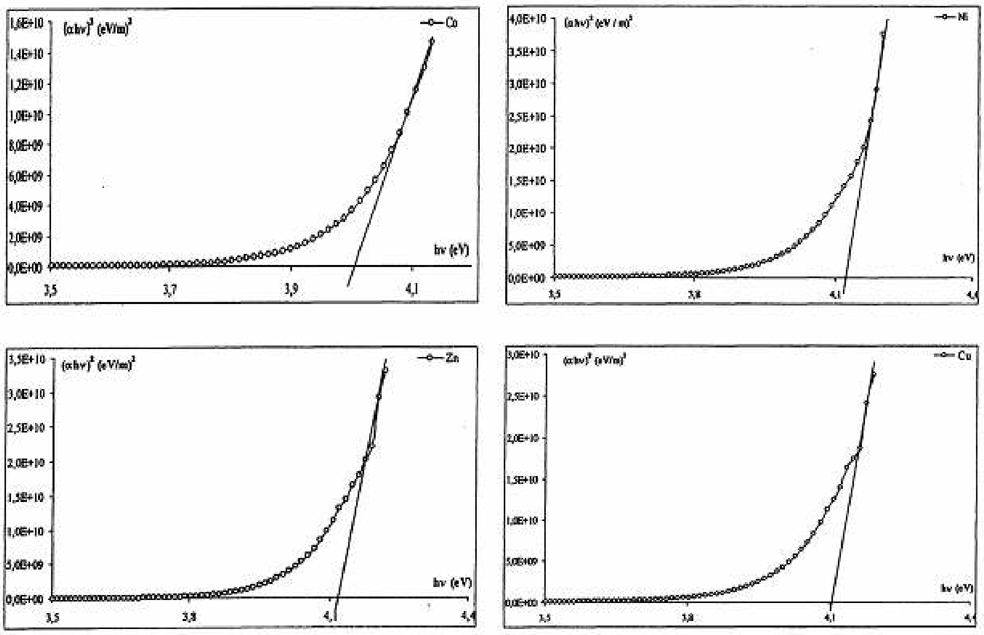


Figure 4. The plots of $(\alpha h\nu)^2$ vs. hν of the films (complexes of HL, 2-5).

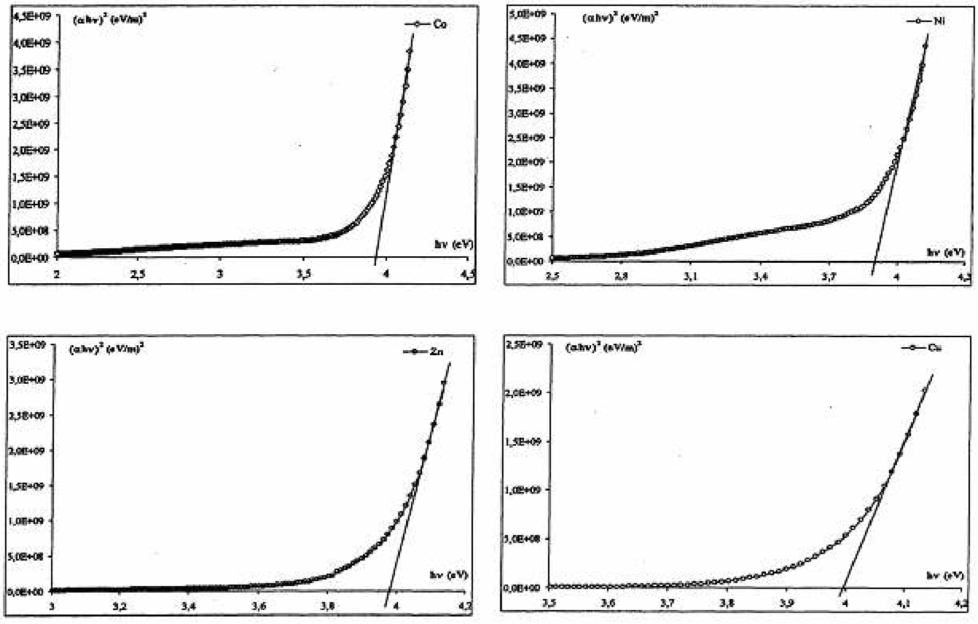


Figure 5. The plots of $(\alpha h\nu)^2$ vs. hν of the films (complexes of $H_2L'.H_2O$, 7-10).

When the optical band gaps were compared with each other, their order follows Co(III)<Ni(II)<Zn(II)<Cu(II) for 2-5 and Ni(II)<Co(II)<Zn(II)<Cu(II) for 7-10. It is observed that E_g values do not show any certain trend according to atomic number of the metal ion, in which the atomic number follows order of Co(II)<Ni(II)<Cu(II)<Zn(II).

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