SYNTHESIS AND PHOTOLYSIS OF SOME TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGAND DERIVED FROM ETHYLENEDIAMINE AND SALICYCALDEHYDE

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Abstract:
This study deals with the preparation of Schiff- base ligands from the reaction of salicaldehyde with ethylenediamine in the ratios 1:1 of ligand (1) and 1:2 of ligand (2). Their metal complexes with ions Fe (II), Co (II), Ni (II), and Cu (II) were also prepared. The electronic spectrum of all these complexes and the IR spectrum were studied. The ratios of dissociation of these complexes were investigated via radiation by using mercury lamp in the wavelength of 365 nm. It is noticed that these complexes dissociate slowly during the process of radiation.

Key word: Schiff- base ligands, Electronic spectra , Structural Formulas, Photolysis.

Introduction
Schiff bases are an important class of ligands in coordination chemistry and have extensive application in different fields [1-3]. Schiff bases derived from (2-hydroxy benzal) are well known polydentate ligands [4-5]. The tetradentate Schiff bases are interesting complexing reagents because they form highly stable metal chelate compounds with a limited number of metal ions [e.g., Cu(II), Ni(II), Co(II), Co(III), Fe(II), Fe(III), Pd(II), Pt(II), VO(II), UO2(II)]. [6-10]. Spectral properties; electrochemical behavior and potential applications were investigated [11,12]. And the physicochemical properties and Mass spectra of transition metals complexes were discussed [13-15]. They have wide-range of applications in analytical chemistry since they provide simple and inexpensive way for determination of several organic and inorganic substances by HPLC [16,17]. These compounds were used as antifungal, antibacterial and antitumor agents.
Experimental
Preparation of Schiff base ligands and complexes:

The Schiff base ligands were prepared by the condensation of ethylenediamine (0.1 mol) with (0.1 mol) 2-hydroxy benzal in ethanol (50 ml) (L1), and with (0.2 mol) 2-hydroxy benzal in ethanol as a solvent (50 ml) (L2), the mixture was refluxed for 2 hr, after cooling the precipitated ligand was filtered and recrystallized from ethanol and dried in a vacuum dessicator [24]. The Schiff base complexes were prepared by dissolving (0.002 mol) from L1 or L2 in 50 ml ethanol, a solution of the metal ions Fe(II), Co(II), Ni(II) or Cu(II) (0.002 mol) in 20 ml ethanol was added with continuous stirring, the mixture was refluxed for 2 hr, after cooling the precipitated complexes were filtered and recrystallized from ethanol and dried in a vacuum dessicator.

Physical measurements:

- IR spectra for the ligands and complexes obtained using CsI disks 4000 - 200 Cm\(^{-1}\) on Shimadzu FT-IR – 8700 spectrophotometer. UV-Visb. Spectra 1100-200 nm. Range were obtained in ethanol on a Cintra 5 spectrophotometer and the melting point were recorded by using an Electrothermal Melting Point Apparatus.

Photolysis:

The photolysis of the complexes were carried out in ethanol solution of complexes (1 X 10\(^{-3}\)Mol/L) in quartz spectrophotometric cell at room temperature by using chromate – vue C_75 UVP and a light source (Hg lamp) with 365 nm. UV- Visb. Spectra were recorded for these complexes after various irradiation time.

Results and Discussion.

Electronic spectra:

Through molecular Structure of Ligand (L1, L2), it would be expected that electronic transition of n → π* of –C=N- group, and electronic transition of π → π* of C=N group as well as aromatic ring.

Figures (I and II) showing ultra-violent spectrum of legands (L1), (L2) respectively. An absorbance band reveals at 407-406 nm. this band caused by charge transition between C=N and conjugated benzene ring. It is also the cause of the yellowish orange color of these components. The band at 317-316 nm. may be caused by electronic transition n → π* belongs to C=N: .For the transform at 264-265nm, it may be caused by electronic transition of π → π* of double bonds in C=N and the aromatic ring. A red displacement reveals an absorbance of the ring due to the consequence between this ring and C=N [25].

The ultra–violet spectrum conjugation shows Nickle complex (Figure III) highly absorbance band at 400nm and shoulder band at 450nm. These two bands caused by charge transition between C=N and d-orbital in metal. While the band at 317-316 electronic transition n → π* in the ligand whose hardness is lowered in the complex because the electron pair of nitrogen atom uniforming with metal. Besides, electronic transition band π → π* of Ligands reveals in complexes at 268-250 nm. slight absorbance band reveals at complex spectrum. This band differs in position depending on the differences of complex, as shown in table (1)

FTIR –Spectrum:

The study of FTIR – spectra of different complexes and Ligands refer to the frequency of –OH the
latter at (3450-3430) cm\(^{-1}\), but disappears in complexes. This indicates that H\(^+\) is out of the crystal lattice and the bonding metal ion by oxygen atom [26]. The C=N frequency value at 1660-1650 cm\(^{-1}\) differs in complexes 1630;1650 cm\(^{-1}\) [27]. New absorbance bond appeared at 451-430 cm\(^{-1}\) and 405-389 cm\(^{-1}\) refers to bond frequency M-N and M-O respectively [26]. Table (2) shows IR spectrum of absorbance bands for the prepared complexes:

Structural Formulas:

UV spectrum and FTIR spectrum of the formed complexes, were determined expected to be:

\[
\text{ML1} \\
M= \text{Fe(II), Co(II), Ni(II), Cu(II)}
\]

\[
\text{ML2} \\
M= \text{Fe(II), Co(II), Ni(II), Cu(II)}
\]

Photolysis:

It has been showed that all the complexes affected by light used at 365 nm. (5.58 \times 10^{-19} \text{ J}) . The continuous falling of absorbance spectrum for these complexes with irradiation time is as shown in figure (IV) for Ni L2 complex. The rate constant for photolysis has been studied by using first order for reactant \([28]\).

\[
\text{Ln} \left( \frac{A_t}{A_0} \right) = -kt
\]

A\(_0\), A\(_t\) is complex absorbance at the beginning time and after t respectively and (k) is the rate constant as shown in fig. (V) for Ni-L2 complex. determined \([28]\). Table (III) shows rate constants for different complexes by photolysis at 365nm at any time. These vales indicating that the photolysis speed of the complexes is at close range except that of iron complexes is found to be the highest moreover, cobalt complexes do not dissolve in the used solvent. the study of the spectrum of IR of irradiated complexes figure (VI) show the appearance of broad band (3200-3300 cm\(^{-1}\)) which indicates a dissociation of these complexes and the leaving group NH\(_2\) from the metal. There is also a change on the shape of the bands at (1000-1700 cm\(^{-1}\)) especially the band at (1620 cm\(^{-1}\)) which belongs to the frequency of group C=N in the complex. A shoulder band is noticed at (1620-1650 cm\(^{-1}\)) approximately. This confirms to the frequency of band C=N before the formation of the complex. This shows a dissociation of the complex. It is clear that the period of irradiation leads to the dissociation of the complex. The constants of the dissociation rate indicate the slow rate of the process of dissociation.

REFERENCES


### Table (1): Physical properties for ligands and complexes

<table>
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<th>No</th>
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<th>Fusion range cm⁻¹</th>
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<td>Orange</td>
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<td>Green</td>
<td>330 dec</td>
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### Table (2): FTIR spectra band of the ligands and metal complexes

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### Table (3): Rate constant for complexes photolysis

<table>
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<td>0.0185</td>
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$y = -0.0183x - 0.0432$

$R^2 = 0.9691$

**Figure (1):** Electronic spectrum of ligand-1 (L1)

**Figure (2):** Electronic spectrum of ligand-2 (L2)

**Figure (3):** Electronic spectrum of the complex Ni-L2

**Figure (IV):** Spectra changes during photolysis of (Ni-L1) with irradiation time

**Figure (5):** First order plot for photolysis Ni-L2 complex

**Figure (6):** IR spectra of (Ni-L1) a: Before irradiation, b: After irradiation
أکل دوداعی و رشد تی لپاره مبتنی بر شرایط زیستی و قابلیت

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- :کر علی

1:1 که دیده شد که علت سبب شد که علی از نظر از حدودی در کتک cherished ژیت

Cu(II) Cu(II) Cu(II) Cu(II)

Cu(II) Cu(II) Cu(II) Cu(II)

Cu(II) Cu(II) Cu(II) Cu(II)

Cu(II) Cu(II) Cu(II) Cu(II)

Cu(II) Cu(II) Cu(II) Cu(II)