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

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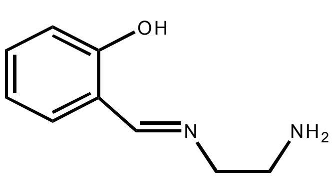
Abstract:

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 (11), Co (11), Ni (11), and Cu (11) 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.

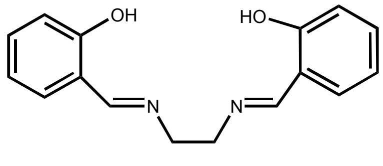
Key word: Schiff- base ligands, Electronic spectra , Structural Formulas, Photolysis.

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 tetra dentate 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), UO_2(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. due to theirs biological activity [18,19]. A few reports are in the literature regarding photochemical [20] , photolysis and thermo gravimetric studies on Cu(II) complexes of *N*-salicylideneaniline and its derivatives were reported [21-23] .However , this work aims at the synthesis of two Schiff base ligands , 2-hydroxy benzal with ethylendiamin (1:1) (L1) and (2:1) (L2) , and their complexes with metal ions Fe(II) , Co(II) , Ni(II) and Cu(II) . The photolysis behavior was followed by irradiating the solutions of complexes by using alight source of (365nm.)



L1



L2

Expermental

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 asolvent (50 ml) (L2) , the mixture was refluxed for 2hr , after cooling the precipitated ligand was filtered and recrystalized 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 50ml 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 continues stirring , the mixture was refluxed for 2h , after cooling the precipitated complexes were filtered and recrystalized 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^{-4}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 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)

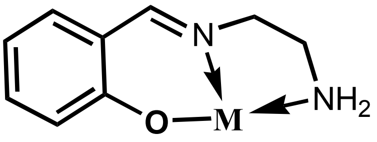
FTIR –Spectrum :

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 out ;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 :

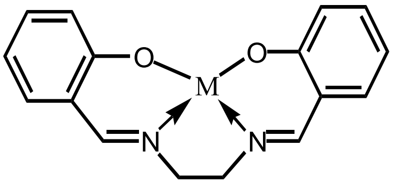
Structural Formulas:

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



ML1

M= Fe(II) , Co(II) , Ni(II) , Cu(II)



ML2

M= 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 × 10^{-19} 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] .

$$\mathrm{Ln}\,(A_t \;/\; A_o) = -kt$$

A_o , 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 morever , 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.

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Table(1) : physical properties for ligands and complexes

No	Complexes code	Absorbance bandcm^{-1}	Color	Fusion range c°
1	L1	-	Yellow	192-194
2	FeL1	406	Brown	300 dec
3	CoL1	630	Purple	192-194
4	NiL1	541	Orange	300 dec
5	CuL1	571	Green	330 dec
6	L2	-	Yellow	220-222
7	FeL2	412	Red	300 dec
8	CoL2	656	Green	218-220
9	NiL2	545	Purple	334-336
10	CuL2	569	Green	308-310

Table(2) : FTIR spectra band of the ligands and metal complexes

No	Complexes code	C=N cm^{-1}	M-N cm^{-1}	M-O cm^{-1}
1	L1	1650	-	-
2	FeL1	1605	444	391
3	CoL1	1600	450	397
4	NiL1	1620	433	401
5	CuL1	1632	445	359
6	L2	1657	-	-
7	FeL2	1600	445	359
8	CoL2	1607	451	393
9	NiL2	1623	430	405
10	CuL2	1629	441	389

Table(3) : Rate constant for complexes photolysis

No	Complex code	K (h^{-1})
1	FeL1	0.0308
2	CoL1	-
3	NiL1	0.0183
4	CuL1	0.0181
5	FeL2	0.0312
6	CoL2	-
7	NiL2	0.0186
8	CuL2	0.0185

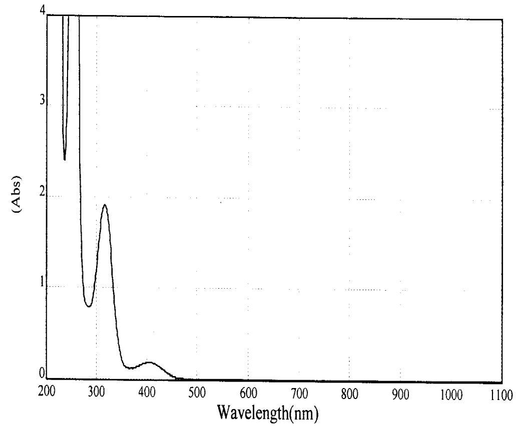
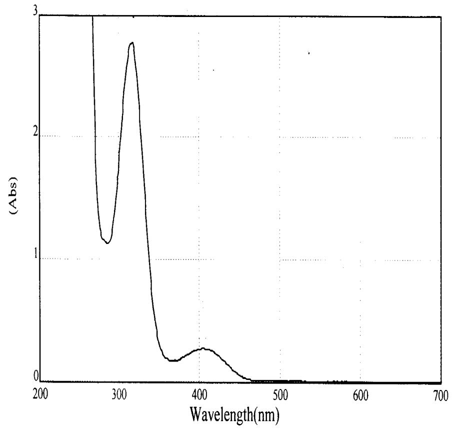


Figure (1):Electronic spectrum of ligand- 1 (L1)



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

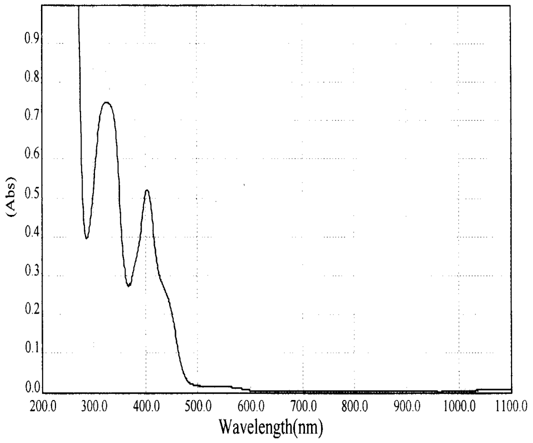


Figure (3) : Electronic spectrum of the complex Ni-L2

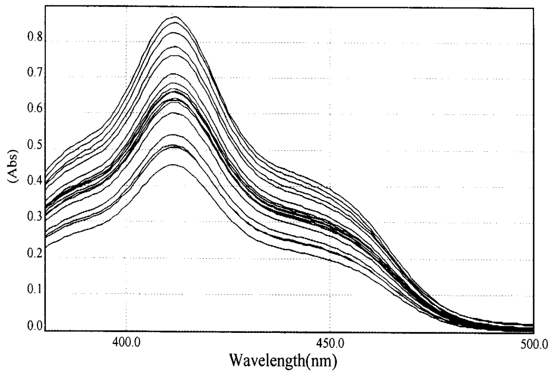


Figure (IV) : Spectra changes during photolysis of (Ni-L1) with irradiation time

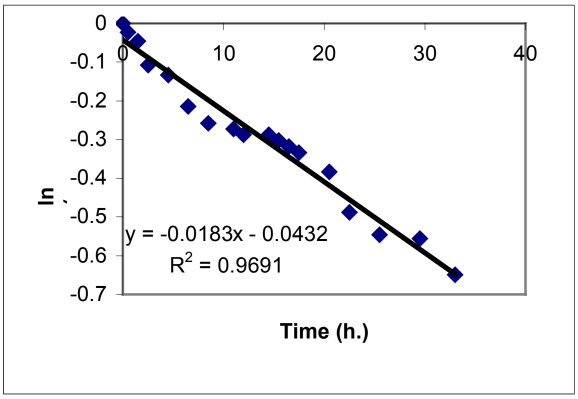


Figure (5) : First order plot for photolysis Ni-L2 complex

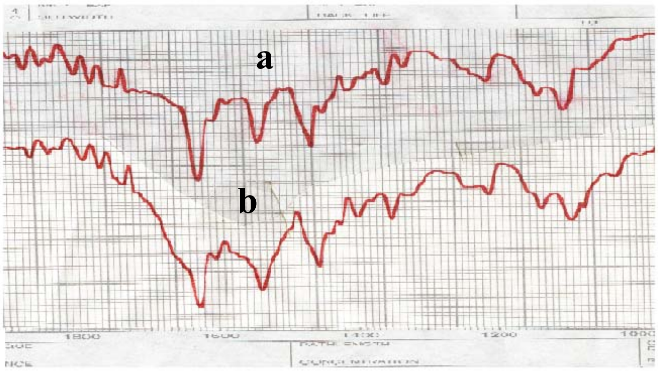


Figure (6) : IR spectra of (Ni-L1) a: Before irradiation , b: After irradiation

تحضير ودراسة التحلل الضوئي لبعض معقدات العناصر الانتقالية مع مشتقات قواعد شيف للاثلين ثنائي الامين مع السالسالديهايد

قيس ارزيك ابراهيم ، وليد فرج الهيتي* ومحمد عبد الكريم طلك

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الخلاصة:-

تم في هذا البحث تحضير ليكاندات قواعد-شيف من تفاعل السلساديهايد والاثلين داي امين بنسبة 1:1 لليكاند الأول L1 وبنسبة 1:2 لليكاند الثاني L2 .كما وحضرت معقداتها الفلزية للايونات Fe(II)، Co(II)، Ni(II)، Cu(II) . تم دراسة الطيف الالكتروني لجميع المعقدات كذلك طيف الأشعة تحت الحمراء ودرست سرع تفكك هذه المعقدات بالتشعيع باستخدام مصباح زئبقي بطول موجي 365 نانو متر ،لوحظ أن هذه المعقدات تتفكك ببطئ أثناء التشعيع .