Copper (II) and Nickel (II) Chelates of Schiff base Derived from 1, 5-diglutraldehyde with *ortho*-phenylene diamine

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Abstract: A Schiff-base ligand derived from *ortho*-phenelyene diamine and 1,5-diglutraldehyde and its transition metal chelates with Cu (II) and Ni (II) have been synthesized. The prepared Schiff-bases were characterized by IR, UV-Visible and CHN. The electrical properties of the prepared Schiff-bases were studied and the maximum value of the conductivity was $4.153*10^{-4}ohm^{-1}.cm^{-1}$ after doping with I_2.

Keyword*: Schiff-bases Complexes, Electrical Properties, ortho-phenylene diamine*

Introduction

The condensation of an amine and an aldehyde to give an imine is well known to be reversible; removal of water to drive this reaction to completion is often essential to obtain a good yield [(1)]. This condensation has been used by many researchers to form both small and large macrocycles, usually template with transition metals**.** When this ligand is bound to transition metals, they form coordination complexes that can be useful for catalysis and can have very interesting optical properties [(1, 2)].

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases of *o*-phenylenediamine and its complexes have a variety of applications including biological, clinical and analytical [(3, 4)]. Earlier work has shown that some Schiff-base complexes showed increased activity when administered as metal chelates rather than as organic compounds, and that the coordinating possibility of *o*-phenylenediamine has been improved by condensing with a 1,5-diglutraldhyde [(5)]. This ligand system has nitrogen donor site. It coordinates with the metal ion in a didendate manner through the enolisable imine or azomethine nitrogen atoms of the Schiff base. The present study has prepared two types of Schiff-bases complexes Cu (II) and Ni (II).

Experimental

A-Chemicals

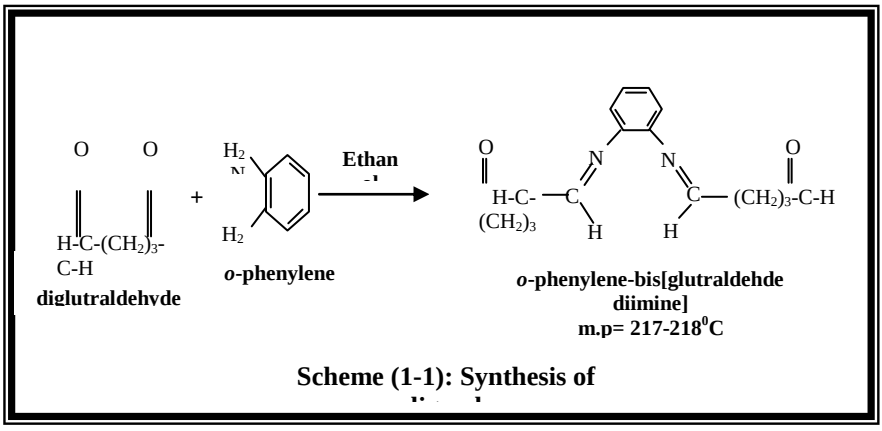
1, 5-diglutraldehyde (BDH), *ortho*-phenylenediamine (Fluka), Lithium hydroxide mono hydrate (Fluka), Ethanol absolute (BDH), Cupper acetate monohydrate (Fluka), Nickel acetate dihdrate (Fluka) and water distillation.

B- Instruments

1. IR-Infrared photometer (U-1500) made by (HITACH) in the range (4000-500)cm^{-1} from the College of Education-Department of Chemistry- Basrah University.
2. UV-Visible spectrophotometer made (Lab Med.Inc), U.S.A the range (300-800)nm from the College of Education-Department of Chemistry- Basrah University.
3. Elemental analysis (CHN) from the College of Science-Tehran University.
4. Electrical conductivity (Voltmeter, Power Supply, Resistance, Temperature recorded and Measured Sample Cell) was used under vacuum in the College of Education-Department of Chemistry-Basrah University.

Synthesis of the Ligand

1.00g (0.01mole) 1,5-diglutraldehde was added to a solution of 1.08g (0.01mole) *ortho*-phenylenediamine in 30ml ethanol. The mixture was stirred for 3hours at 50^0C. The product then collected by filtration, washed several times with methanol and recrystallized from hot ethanol and dried under vacuum[6]. The melting point of yellow crystals found to be 217-218^0C and the yield product (80%).



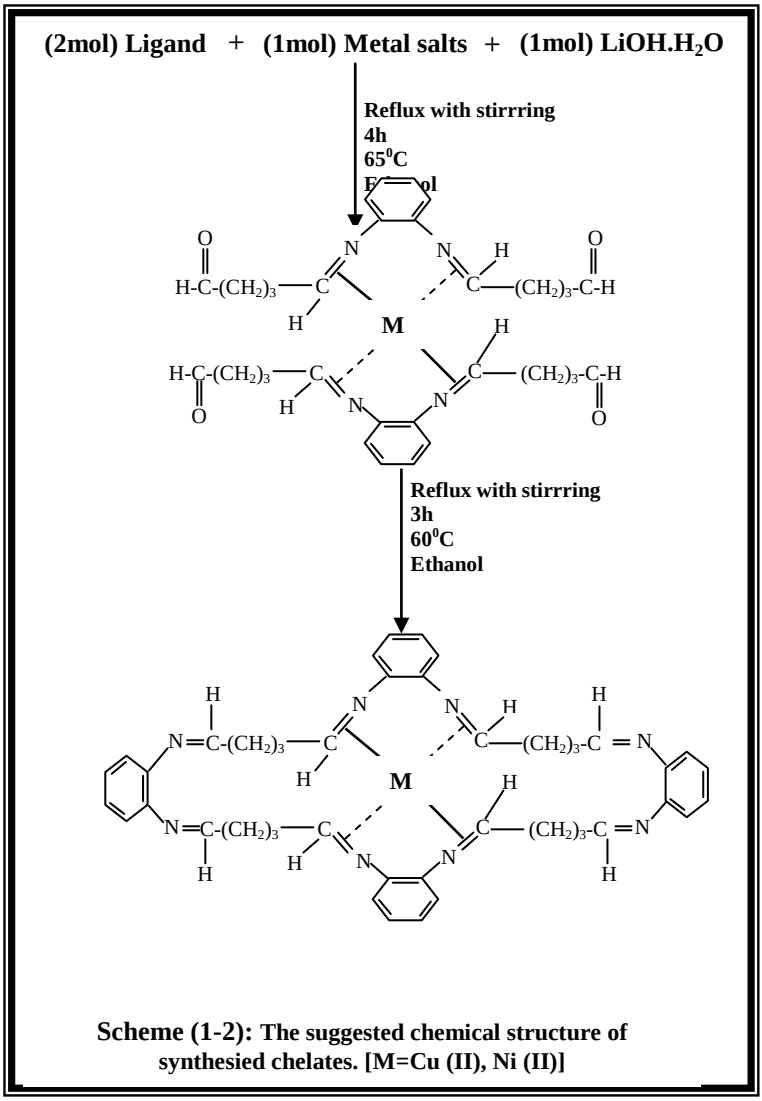
Scheme (1-1): Synthesis of

Synthesis of Copper (II) and Nickel (II) Schiff base Chelates

2.72g (0.01mole) ligand, 0.59g (0.005mole) cupper acetate or (1.06g (0.005mole) nickel acetate) and 0.21g (0.005mole) $LiOH.H_2O$ were dissolved in 30ml ethanol. A mixture was stirred and refluxed at 65^0C for 4hours. The products were collected by filtration and then washed several times with hot ethanol and dried under vacuum. After that the products were reacted with *o*-phenylene diamine at ratio mole (2:1) [amine: chlates] with stirring and refluxing at 60^0C for 3hours [6, 7]. The suggested structures to the chelates are shown in Scheme (1-2). The products found to be decomposed at $>350^0$C [7].

Cu-Chelate is dark brown solid [yield (87%)].

Ni-Chelate is brown solid [yield (83%)].



Scheme (1-2): The suggested chemical structure of synthesied chelates. [M=Cu (II), Ni (II)]

Electrical Measurements

The electrical properties of Schiff-base chelates were measured in Chemistry Department-Education College by conductive instrument consist of temperature recorder, power supply, voltmeter, resistance and sample cell were used under vacuum and the sample was in the form of disc and covered in two sides by silver pain.

The electrical conductivity was increased with iodine doping and temperature due to the prepared Schiff-base chelates which have semiconductive properties. The Schiff-base chelates were dissolved in carbon tetrachloride and the doped with iodine at ratio [1:6] [Chelates: Iodine]. The mixture was refluxed with stirring at 60^0C for 48hours. The product was filtered and dried under vacuum at 110^0C [8].

Results and Discussion

The Schiff base ligand and chelate complexes were identified by IR spectrophotometer. The main bands were noted in Schiff base ligand at 1710cm^{-1} and 1660cm^{-1} which may be attributed to C=O group and –C=N- group respectively, in addition to many of bands at 3065cm^{-1}, 2900-2850cm^{-1},1600-1580cm^{-1}, 1370cm^{-1} and 1200-1000cm^{-1} due to C-H aromatic, C-H aliphatic, -C=C-, C-H bending and C-C respectively [8]. The IR-spectra of the Cu(II) and Ni(II) chelates were observed new principle absorption bands at 1637cm^{-1} and 1633cm^{-1} which may be attributed to coordinate with metals and *o*-phenylen diamine. The shifting of this group band to lower frequency compared with free ligand Schiff base about 23cm^{-1} and 27cm^{-1}, in addition to disappear the band which is returned to C=O group. Besides many bands were noted in spectra of chelates 3070cm^{-1}, 2950-2870cm^{-1}, 1600-1580cm^{-1}, 1365-1360cm^{-1} and 1100-1250cm^{-1} due to C-H aromatic, C-H aliphatic, C=C, C-H bending and C-C respectively.

New band which is not present in the spectrum of free Schiff base appeared at 625-620cm^{-1} is attributed to M-N

Schiff-base	Wave numbers cm^{-1}							
	C-H (aromatic)	C-H (aliphatic)	C=C	C=O	C-C	C=N	M-N	C-H (bending)
Ligand	3065	2870	1580	1710	1200	1660	-	1370

vibration. The band of M-N vibration is support the involvement of nitrogen atom in chelating with the metal ions [9, 10]. The all mentioned bands were shown in Table (1).

Table (1): Selected IR data for Schiff-base ligand and metal chelates

Cu-Chelate	3070	2945	1550	-	1180	1637	625	1365
Ni-Chelate	3070	2940	1560	-	1175	1633	620	1360

In the UV-Visible spectra of ligand show one absorption band at 420nm which may be attributed to (π-π^*) transition [a_2u b_1u] while the Cu(II) and Ni(II) chelates appeared red shift compared with free ligand. The Cu(II) and Ni(II) chelates appeared absorption bands at 570nm and 550nm respectively, the deference in the wave length is 150nm and 130nm due to coordination of metal with ligand, in addition to the appearance of two as an new bands for Cu(II) and Ni(II) complexes at 740nm and 720nm respectively, and these bands refer to the (d-d*) transitions because of the electronic transitions as (t_2g eg) which in conformity with square-planar (dsp^2) geometries [10, 11], the U.V-Visible spectrum proximity of chelates is due to the used elements which have the same valance and they are from the same transition cycle. The Schiff-base of metal complexes do not contain CH_3COO^- anions, which is a coordinate with elemental analysis results for the complexes [11], as shown in Table (2).

The elemental analysis (C, H, N) shows the practical and theoretical values in Table (2).

Table (2): The value of CHN for Schiff-base ligand and metal chelates

The measurements of electrical conductivities were shown in Table (3). The maximum conductivity of doped Schiff-base chelates were $4.153*10^{-4}ohm^{-1}.cm^{-1}$ and the Figure (1) show electrical conductivity to the prepared Schiff-base chelates at different temperatures $(30\text{-}110)^0C$ and show the increased of conductivity with increasing of temperatures may be attributed to presence of metals (d-d*) transition, this state was like semiconductors properties.

Schiff-base	Theoretical Value %			Practical Value %		
	C	H	N	C	H	N
Ligand	70.5	7.35	10.2	70.3	7.41	10.0
Cu-Chelate	70.2	6.38	14.9	70.0	6.50	14.8
Ni-Chelate	70.7	6.43	15.0	70.5	6.37	15.2

The form octahedral geometry (dsp^2) was increased in transitions between the energy plains so this indicates to the increase of the electrical conductivity [8]. The Schiff-base for chelates was used in electrical field such as diode, transistor and photocells.

$$\ln \sigma = \ln \sigma_o - \frac{\Delta E}{2KT} \quad \ldots\ldots (1)$$

Where **σ** is the conductivity at temperature **T**, σ_o is the pre-exponential conductivity**,** Δ**E** is the intrinsic band gap and **K** is Boltzmann constant.

Table (3): The value of electrical conductivity for Schiff-base ligand and metal chelates

Schiff-base	Conductivity ($ohm^{-1}.cm^{-1}$) before doping	ΔE (eV) before doping	Conductivity ($ohm^{-1}.cm^{-1}$) after doping	ΔE (eV) after doping
Ligand	$4.981*10^{-6}$	0.0412	$1.964*10^{-5}$	0.0326
Cu-Chelate	$7.321*10^{-5}$	0.0305	$4.153*10^{-4}$	0.0247
Ni-Chelate	$5.661*10^{-5}$	0.0384	$1.973*10^{-4}$	0.0263

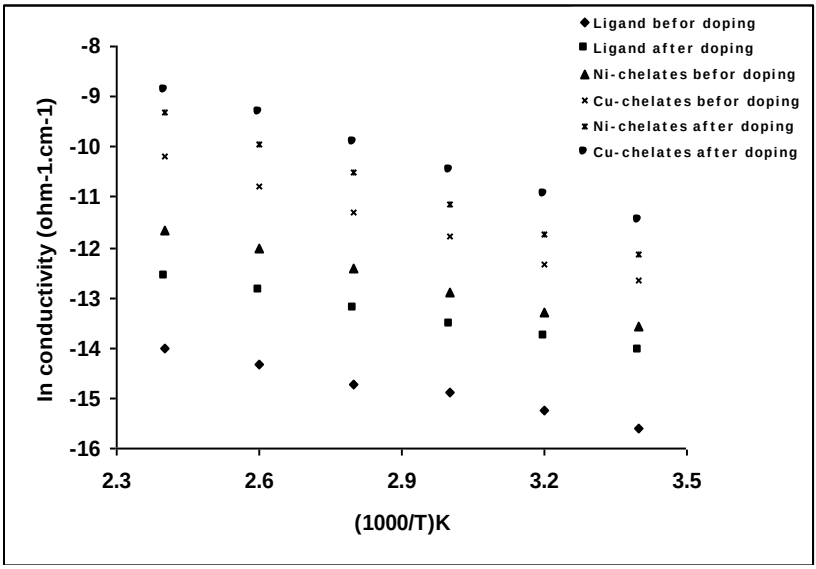


Figure (1): The electrical conductivity of Ligand and Metal-chelates before and after doping

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