MULTIDENTATE LIGANDS AND METAL
COMPLEXES DERIVED FROM NINHYDRIN AND
ETHYLENEDIAMINE

Graduate Project (CHEM.774)

Asnake Lealem Berhanu

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Addis Ababa University  
School Of Graduate Studies  

Multidentate Ligands And Metal Complexes Derived From Ninhydrin And Ethyldiamine

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____________________________
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Decleration
I the undersigned confirm that the results reported in this work were obtained by research carried out by me under the supervision of my Advisor in the faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2006-2007. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my Advisor, who is the principal scientist responsible for any publication. Furthermore if the work is published the institutional address given should be that of the Chemistry Department, AAU.

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This project work has been submitted for examination with my approval as a university advisor.

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July 26, 2007
Multidentate Ligands And Metal Complexes Derived From Ninhydrin And Ethylenediamine

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By
Asnake Lealem Berhanu

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List of abbreviations

1. AAS= Atomic Absorption Spectroscopy
2. Cal = Calculated
3. DMF = Dimethylformamide (CH$_3$)$_2$NCH=O)
4. DMSO= Dimethylsulfoxide (CH$_3$)$_2$S=O)
5. EDTA= ethylenediamine tetraacetic acid
6. en = Ethylenediamine
7. Exp = Experimental
8. IR = Infrared
9. Str. = stretching
10. UV-Vis = Ultraviolet – visible
11. Vib. = Vibration
Abstract
A new Cu(II) chelate formed by the derivatization of the ninhydrin with ethylenediamine (en) in the presence of CuCl2 .2H2O, was synthesized by template procedure in ethanolic medium. The purity of the complex was established by thin layer chromatography and sharp melting point. The complex was characterized on the basis of chemical analysis, conductivity, IR spectroscopy, UV-vis spectroscopy, and magnetic susceptibility studies. The results suggest the formation of a 1:2 condensed product between ninhydrin and ethylenediamine, which behaves as neutral NNONN donor towards Cu(II). This new pentadentate ligand resulted in the formation of a novel metal chelate of the formula [MLCl]Cl.2H2O with a proposed stereochemistry of distorted/elongated octahedron.
1. Introduction

In the middle of the 18th century, an artist’s pigment known as Prussian blue was first prepared when sodium carbonate and animal excrement were heated together in an iron pot. It is now known that Prussian blue is a coordination compound which may be prepared by the action of iron(III) ion with K₄Fe(CN)₆. Early workers termed the substance such as Prussian blue “complex compounds” and this name has persisted. Even today the term complex compound is used synonymously with the term coordination compound. A large variety of chemical substances may be classified as coordination compounds. In aqueous solution, all metal ions acquire water of hydration and become aqua complex ions. Coordination compounds play an essential role in chemical industry and society in general.

In living organisms, two important coordination compounds play significant roles, one is chlorophyll in green plants and the other is hemoglobin in the blood of vertebrate animals. Chlorophyll, which is vital to photosynthesis in plants, is a magnesium complex and hemoglobin which carries oxygen to animal cells, is an iron complex.¹

1.1 Multidentate ligands

Multidentate ligands play an important role in coordination chemistry and catalyst design. An attractive multidentate ligand is a tri anionic tetradentate ligand of the tripodal [X₃E] type (X = N, O, S; E = N, P), which had led to unique structures and patterns of reactivity. The degree of interaction between the metal center and the neutral E atom can exert a profound influence on the reactivity of the resulting complexes.²

Ligands that can bind to a metal through only one donor atom at a time, are unidentate. Many ligands that can bind simultaneously through more than one donor atom are called polydentate. Of the polydentate, those that bind through two, three, four, five or six donor atoms are called bidentate, tridentate, tetradentate, pentadentate and hexadentate, respectively. The resulting complexes, consisting of the metal atom or ion and polydentate ligands, are called chelate complexes.³
Polydentate ligands whose structures permit the attachment of two or more donor sites to the same metal ion simultaneously, those closing one or more rings, are called chelate ligands. Thus both of the ligands shown in fig. 1 and 2 are bidentate ligands, but only ethylenediamine is a chelate.4

![Figure 1 Ethylenediamine derivatives](image1)

![Figure 2 Ethylenediamine](image2)

Some polydentate chelate ligands

![Acetylacetonato ion (acac-)](image3)

![N,N-diethylthiocarbamate ion](image4)

![2,2’-Dipyridyl(dipy)](image5)

![o-phenylenedibismethylarsine (diars)](image6)
A large number of multidentate ligands have been synthesized and investigated for metal binding characteristics. Several such ligands possessing \(-\text{C}=\text{N}\) or azomethine grouping are known as Schiff bases. These are compounds containing an imino or azomethine group (\(\text{R}-\text{C}=\text{N}\)) and are usually formed by the condensation of primary amine with an active carbonyl compounds.

Schiff bases which are effective as coordinating ligands have a functional group \(-\text{OH}, \text{NH}_2, \text{SH}, \text{etc.}\), sufficiently near site of condensation so as to form five or six membered chelate ring on reaction with metal ion.

Because of the great synthetic flexibility of Schiff base formation, many ligands of varied structural types can be and have been synthesized and their ligational properties have been extensively studied. Salicylaldehyde was the carbonyl precursor first used by Pfeiffer and Tsumaki for the synthesis of bases. Some important classes of ligands derived from salicylaldehydes are shown in fig.3 in the anionic form.⁵
1.2 Chelates And Their Stability

1.2.1 What is chelate effect?
This is an effect which is observed when water molecules (or other simple ligands) around the central metal ion in an aqua complex are replaced by multidentate like EDTA or a bidentate ligand like 1, 2- diaminoethane(en).

Compare what happens if two water molecules around a [Cu(H₂O)₆]²⁺ ion with either two ammonia molecules or one molecule of 1,2-diaminoethane was replaced.

Figure 4 Coordination mode of NH₃ and en

This second structure is known as a chelate, from a Greek word meaning a crab's claw. One can picture the copper ion as being nipped by the claw of the 1, 2-diaminoethane molecule. Chelates are much more stable than complex ions formed from simple monodentate ligands. The overall stability constants for the two ions are shown in table 1.

Table. 1 Stability constant

<table>
<thead>
<tr>
<th>Ion</th>
<th>logK</th>
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<tr>
<td>[Cu(NH₃)₂(H₂O)₄]²⁺</td>
<td>7.86</td>
</tr>
<tr>
<td>[Cu(H₂O)₄(en)]²⁺</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The reaction with the 1,2-diaminoethane could eventually go on to produce a complex ion [Cu(en)₃]²⁺. Simplifying the structure of this:
The overall stability constant $\log K$ is 18.7.

Another copper-based chelate comes from the reaction with EDTA.

![Figure 6 the EDTA$^{4-}$ ion](image)

This also has a high stability constant $\log K$ is 18.8.

Studies on the metal complexes have shown that a chelate (a complex ion involving multidentate ligands) is more stable than the metal complexes formed by unidentate ligands. This is known as the **chelate effect**.

### 1.2.2 The reason for the chelate effect

Compare the two equilibria below, the one with the 1,2-diaminoethane (en) has the higher stability constant (for values, see above).

\[
[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O
\]

\[
[Cu(H_2O)_6]^{2+} + \text{en} \rightleftharpoons [Cu(H_2O)_4(\text{en})]^{2+} + 2H_2O
\]
The enthalpy changes of the two reactions are fairly similar. One might expect this because in each case two bonds between copper and oxygen atoms are breaking and replacing them by two bonds between copper and nitrogen atoms. If the enthalpy changes are similar, what causes the difference in the extent to which the two reactions happen? Entropy is most easily thought of as a measure of disorder. Any change, which increases the amount of disorder, increases the tendency of a reaction to happen.

If you look again at the two equilibria, one might notice that the 1,2-diaminoethane equilibrium does lead to an increase in the disorder of the system (an increase in its entropy). There are only two species on the left-hand side of the equation, but three on the right.

\[
[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4(en)]^{2+} + 2H_2O
\]

One can obviously get more disorder out of three species than out of only two.

Compare that with the other equilibrium. In this case, there is no change in the total number of species before and after reaction, and so no useful contribution to an increase in entropy.

\[
[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O
\]

In the case of the complex with EDTA, the increase in entropy is very pronounced.

\[
[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2+} + 6H_2O
\]

Here, the numbers of species present are increasing from two on the left-hand side to seven on the right. You can get a major amount of increase in disorder by making this change.

Reversing this last change is going to be far more difficult in entropy terms. One would have to move from a highly disordered state to a much more ordered one. That isn't so likely to happen, and so the copper-EDTA complex is very stable.
Complexes involving multidentate ligands are more stable than those with only unidentate ligands in them. The underlying reason for this is that each multidentate ligand displaces more than one water molecule. This leads to an increase in the number of species present in the system, and therefore an increase in entropy. An increase in entropy makes the formation of the chelated complex more favourable.

1.3 Reaction of aldehyde and ketones with primary amines

Reaction that begins with nucleophilic addition to aldehyde and ketones is their reaction with primary amines, compounds of the type -RNH₂ or -ArNH₂. In the first stage of the reaction the amine adds to the carbonyl group to give a species known as a carbinolamine. Once formed, the carbinolamine undergoes dehydration to yield the product of the reaction, an N-alkyl or N-aryl-substituted imine:

\[
\text{RCR'} + R''\text{NH}_2 \xrightarrow{\text{Addition}} \text{RCR'}\text{H} \xrightarrow{\text{Elimination}} \text{RCR'}\text{R''} + \text{H}_2\text{O}
\]

N-substituted imines are called Schiff’s bases after Hugo Schiff, a German chemist, who described their formation in 1864.

Aldehyde and ketones can be converted to Schiff bases (imines) by an acid catalyzed reaction with primary amine.

\[
\text{C}=\text{O} + \text{H}^+ \xrightarrow{\text{RNH}_2} \xrightarrow{\text{OH}} \xrightarrow{\text{-H}^+} \text{C}=\text{NR} + \text{H}_2\text{O}
\]
Imine forming reactions are extremely important in the synthesis of multidentate ligands and in the formation of macrocyclic ligands, that is, ligands that are at least tetradentate and that can completely encircle the metal ions. Aldimines (the ligand in ‘A’, it would be called a ketimine if formed from a ketone) constitute an important class of ligands, particularly as it is possible to interchange nitrogen substituents by a transamination reaction, the process connecting ‘A’ to ‘B’.

Figure 9 Coordination of Cu(II) with Nitrogen and Oxygen
1.4 Ninhydrin

Ninhydrin was first made in 1910 by the English chemist Siegfried Ruhemann, who also investigated its reaction with amines and amino acids to form a colored compound known as Ruhemann's Purple (RP).

Figure 10  Ruhemann's purple formation

Ninhydrin  Ruhemann’s purple(RP)

Or 2,2-dihydroxy-1,3-indanedione

Ninhydrin is the 2-hydrate of indane-1,2,3-trione. It reacts with $\alpha$-amino acids to yield highly colored product. 1,2,3-Triketohydrindane forms a stable hydrate known as ninhydrin. In Contact with the skin, it produces a rather long-lasting purple decoloration.9,10

Figure 11  Hydrated ninhydrin

In acid, most aldehydes form non isolable hydrates (gem-diols). The exception is hydrate ninhydrin. The exceptional properties are due to the strong electron withdrawing groups on $\alpha$C(alpha carbon) which destabilize an adjacent carbonyl group because of the repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion. Therefore, the hydrate of the middle carbonyl group of ninhydrin removes the
repulsions. The stability of the diols is probably due to unfavorable dipole-dipole repulsion in the parent carbonyl compounds.\textsuperscript{11,12,13}

Figure 12 Stable diols formed by ninhydrin

Ninhydrin, is used to detect ammonia or primary and secondary amines. When reacting with these free amines, a deep blue or purple color is evolved. Ninhydrin is most commonly used to detect fingerprints, as amines left over from peptides and proteins (terminal amines or lysine residues) sloughed off in fingerprints react with ninhydrin.

Ninhydrin is also used in amino acid analysis of proteins. Most of the amino acids are hydrolyzed and reacted with ninhydrin except Proline; also, certain amino acid chains are degraded. Therefore, separate analysis is required for identifying such amino acids that either react differently or don't react at all with ninhydrin.\textsuperscript{14}

1.5 Template Synthesis

A metal ion such as Ni(II) can be used to assemble a group of ligands which then undergo a condensation reaction to a macrocyclic ligand. A condensation reaction is a reaction in which a bond is formed between two molecules, and a small molecule-often H\textsubscript{2}O-is eliminated. The template effect, can be applied to produce a surprising variety of macrocyclic ligands. The most generally useful condensation reaction is the Schiff’s base condensation of an amine and a ketone, of which an example is

$$(\text{CH}_3)_2\text{C}=\text{O} + \text{H}_2\text{NCH}_3 \rightarrow (\text{CH}_3)_2\text{C}=\text{NCH}_3 + \text{H}_2\text{O}$$

The trouble with such condensation reaction is that they often give unwanted side product, and a metal ion can play a useful role in directing the reaction toward the desired ligand product or aiding in its isolation.

A good example of a synthesis that uses the template effect is the condensation reaction between 2,3-butanedione molecule and 2-aminoethenethiol molecules to Ni\textsuperscript{2+}. The mixture undergoes condensation to give the square-planar Ni(II) complex shown as the first product
in the equation below

\[
\text{CH}_3\text{COOCOCH}_3 + 2\text{NH}_2\text{CH}_2\text{CH}_2\text{SH} + \text{Ni}^{2+} \rightarrow \text{Ni}^{2+} \quad \text{Ni}^{2+} \quad \text{Ni}^{2+} \\
\text{-2H}^+ \\
\]

**Figure 13  Square planar Ni(II) complex**

Any reaction of this type may be called a template synthesis because the ligand is assembled attached to the Ni(II). Template effect, in forming of macrocyclic ring is favored by the presence of a cation of appropriate size that can serve to hold the partially formed ligand in position as the remainder of the ring is synthesized.

### 1.6 Complex formation

The formation of the metal complex is dictated by its stability. This stability of the metal complex depends both on the metal ion and the ligand. In general, stability of the complex increases with decreasing size and increasing electron affinity of the central metal. Thus highly polarizing transition metal ions have greater tendency to form complex, regardless of the nature of the ligand, the stability of the bivalent transition metal complexes increase in the order \(\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}\).  

### 1.7 The chemistry of copper complexes.

The chemistry of Cu(II) ion is considered in this work. Cu(II) will be presented in terms of its \(d^9\) configuration. The (+II) state is the most stable and important for copper. The cupric ion \(\text{Cu}^{2+}\) has electronic configuration \(d^9\) and has an unpaired electron. Its compounds therefore are colored and paramagnetic. Distorted octahedral arrangement is common in copper compounds with two long bonds and four short ones. The distortion occurs because the \(d_z^2\) orbital is doubly occupied, whilst the \(d_{x^2-y^2}\) orbital is only singly occupied, and this prevents the ligands approaching along the \(+z\) and \(-z\) directions from coming close to the copper as those approaching along \(+x\), \(-x\), \(+y\) and \(-y\).
consequence of Jahn-Teller distortion and is electronic in origin. Four coordinate planar complexes are also known.

The Cu (II) ion with its d⁹ configuration as stated above is highly susceptible to Jahn–Teller distortion. In the tetrahedral arrangement also Jahn-Teller distortion is operative, in spite of the fact that large spin-orbital coupling constants might produce sufficient splitting of ²T₂ ground state. Octahedral complex without any distortion are expected to have only one d-d absorption band corresponding to ²E₉ → ²T₂₉ transition. In the axially elongated tetragonal distortion three absorption bands corresponding to the transition ²B₁₉ → ²A₁₉, ²B₁₉ → ²B₂₉, ²B₁₉ → ²E₉ are observed. Tetragonal complexes are expected to give a single broad band corresponding to ²T₂ → ²E transition in the near IR region. The ground term in the square planar geometry is ²B₁ and three d-d bands corresponding to transition ²B₁₉ → ²B₂₉, ²B₁₉ → ²A₁₉, ²B₁₉ → ²E₉ are observed.¹⁸,¹⁹

1.7.1 Complex formation of Cu(II) with N-& O donor ligands.

A facile synthesis of 2-formyl-1,8-naphthalenediol is reported. Its potential as a general precursor for the preparation of unsymmetrical multidentate chelating ligand systems based on 1,8-naphthalenediol is demonstrated by the synthesis of the dinucleating ligand (H₄L=N,N'-bis(2-(1,8-naphthalenediol)methylidene)propylenediamine). One Cu II ion is coordinated by a N₂O₂ compartment of L and the other Cu II ion is coordinated by an O₄ compartment of L while they are bridged by two aryloxide functions of L.²⁰

![Figure 14 Dinuclear bis(phenoxide)-bridged Cu(II) complex](image-url)
The potentially pentadentate Schiff bases of the type fig.15 act as bistridentate ligands with respect to a single metal center giving dinuclear Cu(II) complex shown in the fig16 below.5

![Figure 15 Pentadentate Schiff's base](image1)

![Figure 16 Bis-tridentate dinuclear Cu(II) complex](image2)

1.8. Ethylenediamine

1.8.1 Physical and chemical properties of ethylenediamine
NH₂—CH₂—CH₂—NH₂, 1, 2—diaminoethane, ethylenediamine is colorless at room temperature having the characteristic smell of an amine.
It has a melting point of 11.1°C and a boiling point of 116.9°C at 1 atmosphere.

1.8.2 Acid—base properties of ethylenediamine
Ethylenediamine is extremely soluble in water and in the majority of organic solvents. In aqueous solution it reacts with water giving rise to the two equilibria
Nevertheless, ethylenediamine can, rarely, exhibit also acid properties. Thus, for example, with Pt (IV) it forms the complex \([\text{Pt}(\text{en})_3]^{+4}\) which is capable of loosing up to three protons. This tendency to release hydrogen atoms in the form of protons can be enhanced by electrophilic substitution on the nitrogen.

### 1.8.3 Coordinating properties of ethylenediamine

Ethylenediamine forms a large number of complexes with many different metal ions. It usually acts as a bidentate ligand. The five—membered chelate ring in ethylenediamine complexes can exist in two different conformations: gauche symmetric, (Fig. (17a)) or with an asymmetric conformation (Fig. (17b)). The former is the most common and the bond angle \(N—M—N\) is almost always about 85°.

![Figure 17](image)

**Figure 17** Coordination mode of en

### 1.8.4 The equilibria of complex formation

Ethylenediamine strongly interacts with water molecules and each nitrogen atom binds a water molecule by means of a hydrogen bond of the type \(N...H—O—H\). During the formation of the metal complexes, these water molecules together with others from the first and second hydration spheres of the metal are removed. Although little is known
about the hydration of the complexes of ethylenediamine, it has been shown that the two hydrogen atoms bonded to the nitrogen carry a partial positive charge in the complex and are, therefore, able to form bonds of the type:

\[ \text{N-H}^+ \cdots \text{δ-} \text{OH}_2 \]

The formation of complexes with ethylenediamine leads, especially in the first step, to the liberation of some water molecules so that an increase in entropy (\(\Delta S^0\) positive) would be expected to be associated with this process. In general, this compensates for the decrease in entropy translational, rotational and vibrational, which accompanies the formation of the chelate ring. The formation of the first complex is always characterized by a positive entropy term. This term is larger, the more stable the complex. This is due to an extensive liberation of water molecules. This process becomes less pronounced in the following steps and the entropy of formation therefore diminishes until it finally becomes negative.

The typical spectrum of complexed ethylenediamine with N-H bands at 1565 cm\(^{-1}\), 1290 cm\(^{-1}\) and at 770 cm\(^{-1}\) was reported.\(^{21,22}\)

1.9 **Objective of the present study**

The objective of this study is to condense the ninhydrin with ethylenediamine and to promote complex formation of the product with copper(II) through template synthesis. The template synthesis of materials has received widespread attention recently since this technique allows the preparation of materials with a controlled architecture.\(^{23}\)

As ninhydrin has three exocyclic carbonyl functions and ethylenediamine has two primary amine functions, the condensation may be in 1:1, 1:2 and 1:3 mole ratios or may lead to the formation of cyclic or polymeric condensed products. It is worthwhile to examine, in what way Cu\(^{2+}\) ion can direct the condensation process, while forming a metal chelate(s) as the final product(s).

The metal chelate(s) has been studied using conductivity, IR spectral, UV-vis spectral and magnetic susceptibility data.
2. Experimental, results and discussion

2.1 Instrumentation and methods

Chemicals and Reagents
All chemicals used were of AnalaR (A.R). The reagents used were copper chloride, silver nitrate, ethylenediamine and ammonia solution, chloroform, DMSO, methanol, Distilled water, de-ionized water, ethanol, nitro methane

Instrumentation
The melting point of the Cu (II) complex was recorded using IA 9200 digital melting point apparatus.
The metal content was estimated on a Buck Scientific AAS model 210 VGP.
The conductivity of the complex was obtained on Bench conductivity meter (EC 214).
The magnetic susceptibility of the metal complex was determined using a magnetic Susceptibility Balance MSB Auto, (Sherwood Scientific). Pascal constant were used for diamagnetic corrections.
IR spectrum in the region 4000 to 400 cm$^{-1}$ was recorded in KBr medium on a Perkin Elmer spectrum BX spectrometer.

Method
The metal complex was synthesized by the method known as template synthesis.
The metal percentage was estimated by decomposing and digesting the complex with HNO$_3$ and then by dissolving the residue in de- ionized water to make a solution of a known concentration. The metal content was estimated from the solution by an atomic absorption spectrometer using Cu lamp at 324.7nm (slit width 0.7nm).
For chloride test a weighed quantity of the complex was digested in HNO$_3$ and was subsequently dissolved in HNO$_3$. 1% AgNO$_3$ solution was added until AgCl precipitated completely. The contents were digested on steam bath and the precipitate was filtered through a previously dried and weighed sintered crucible. The filtered precipitate was dried to a constant weight at 110$^0$C.
The conductivity of the Cu(II) complex was measured in freshly prepared solution using nitromethane.
The UV-vis spectrum was recorded by dissolving the Cu(II) complex in the nitro methane. The spectrum was recorded twice by varying the concentration.

The magnetic susceptibility measurement of the powdered sample was recorded at 21°C.

To relate the gram susceptibility with molar susceptibility the following relation was used

\[ \chi_M = \chi_g \cdot M_m \]

\[ \mu_{\text{eff}} = 2.83 \chi_M T^{1/2} \]

Where \( \chi_g \) is the measured gram susceptibility, \( \chi_M \) is molar susceptibility, T is temperature in Kelvin.

\( \mu_{\text{eff}} \) is the effective magnetic moment in Bohr magnet, \( M_m \) is molecular mass of the complex.

From the effective magnetic moment value obtained, the number of unpaired electron was calculated by using the relation

\[ \mu_{\text{eff}} = [n(n+1)]^{1/2} \]

Where n is number of unpaired electron.

Diamagnetism is attributed to the interaction of closed shell electrons with an applied magnetic field. All substances, even paramagnetic substances contain some closed shell of electrons. Consequently, paramagnetic substances have a negative (diamagnetic) contribution to their net susceptibility. In most cases, this diamagnetic contribution is only a small fraction of the total susceptibility, but in accurate work is necessary to correct the measured susceptibility (\( \chi_M^{\text{corr}} \)) for the diamagnetic contribution. We use the relation

\[ \chi_M^{\text{corr}} = \chi_M - \chi_{\text{dia}} \]

Because the diamagnetic contribution, \( \chi_{\text{dia}} \), is always negative, the corrected molar susceptibility is always greater than the uncorrected value.

Purity of the Cu(II) complex was concluded from thin layer chromatography (TLC) and its sharp melting point. For TLC, the complex was dissolved in nitro methane.
2.2 Synthesis of Cu(II) complex using template procedure

The metal complex was synthesized by the following procedure:
Different mole ratios of the metal, ninhydrin and ethylenediamine were used to synthesize the Cu (II) complex, and the one which gives more or less good yield compared with the others is the one following mole ratio 1:1:2.or 0.23gm (1.4mmol) of CuCl₂.2H₂O, 0.5gm (2.8mmol) of ninhydrin and 0.1mL (1.4mmol) of ethylenediamine. Ninhydrin was first dissolved in ethanol and ethylenediamine was added to it while stirring. The reaction mixture was stirred for 2 hours to obtain a pink thick solution and then an ethanolic solution of Cu(II)Cl₂.2H₂O was added. Immediate color change to brown was observed and precipitation of a brown product started. The pH of the medium was observed to drop from 8 to 5. The reaction mixture was then refluxed for another 4 hours. A brown product that finally separated was left overnight and was filtered under suction and washed repeatedly with ethanol.

The melting point of the complex is 205°C and it shows some color change around 98°C. Yield : 28%
- Color:- Brown
- Melting point: 205°C
- Yield (%) = 28

2.3 Result and discussion

General
Physical properties, purity, solubility, metal analysis, molar conductance, electronic spectral and magnetic susceptibility of the Cu(II) complex will be discussed. The complex of Cu(II) is colored . The compound is stable to atmospheric conditions at room temperature and is insoluble in most common organic solvents.
2.3.1 Purity and solubility

The Cu(II) complex shows only one spot on the TLC indicating the complex formed was pure. This is also confirmed by sharp melting point of the complex. The Cu(II) complex was insoluble in most common organic solvents, like DMSO, DMF, ethanol, methanol, chloroform, but soluble on heating in nitromethane.

2.3.2 Metal Analysis

The metal percentage was obtained from atomic absorption spectral measurement and related calculations. The experimental metal percentage of 14.88 % was close to the calculated value of 15.12% for the formula CuCl₂C₁₃H₁₆O₃N₄ or CuCl₂C₁₃H₁₆ON₄.2H₂O or CuCl₂L.2H₂O where C₁₃H₁₆ON₄ corresponds with a 1:2 condensation product between ninhydrin and ethylenediamine.

2.3.3 Chloride

The percentage of chloride obtained from experimental results (16.87) is also in close agreement with the calculated value(17.00 %) which is matches with the molecular formula CuLCl₂.2H₂O.²⁴

2.3.4 Molar conductance

The relation \( \Lambda_M = 1000L/M \) is used to calculate the molar conductance (\( \Lambda_M \)) of the Cu(II)complex where M is the molar concentration of the complex, L is the specific conductance. The specific conductance obtained at 25°C is 75 \( \mu \)S .When this value is converted by using the above relation the molar conductance of the complex was 78 Smol⁻¹cm². This value lies within the range of a 1:1 electrolyte in nitromethane. Hence one of the two chlorides per Cu(II) ion is in the ionization sphere, while the other is in coordination or non-ionizable sphere. This is in agreement with proposed formula [CuLCl]Cl.2H₂O.
2.3.5 IR spectral interpretation
IR spectrum of the complex recorded in KBr medium reveals the formation of a 1:2 condensation product between ninhydrin and ethylenediamine. Comparison of the free ninhydrin and ethylene diamine spectra with that of the Cu(II) complex supports this conclusion. The results also suggest the formation of metal complex in which the ligand behaves as a neutral NNONN pentadentate towards Cu(II). The spectral data further support the presence of water in the complex as lattice water.
Free ninhydrin exists in two different forms that is-dihydroxyiketo and triketohydrate forms as shown in fig 12.
It exhibits characteristic IR spectral bands in the regions corresponding to $\nu_{\text{OH}}$ and $\nu_{\text{C=O}}$ functions besides $\nu_{\text{C=C}}$, $\nu_{\text{C-H}}$ and other related bands. A broad band in the region of 3400-3000 cm$^{-1}$ is due to $\nu_{\text{OH}}$ and three characteristic bands in the region 1748-1718 cm$^{-1}$ are due to $\nu_{\text{C=O}}$.
Free ethylenediamine is expected to show stretching and deformation characteristics of primary amine functions and CH$_2$ groups at 3368 and 3284 cm$^{-1}$, 2926 cm$^{-1}$, 1597 cm$^{-1}$, 1461 cm$^{-1}$, 1366 cm$^{-1}$, 1170 cm$^{-1}$ and 1047 cm$^{-1}$.22
The notable features of the IR spectrum of Cu(II) complex are :-
(i) The presence of only one band at 1735 cm$^{-1}$ corresponding to $\nu_{\text{C=O}}$ in comparison with three bands of free ninhydrin.
(ii) The absence of the $\nu_{\text{OH}}$ band corresponding to free ninhydrin.
(iii) The appearance of strong sharp multiple bands in the region 1600-1563 cm$^{-1}$ characteristic of $\nu_{\text{C=N}}$
(iv) The absence of characteristic doublets due to $\nu_{\text{NH}_2}$ asymmetric and $\nu_{\text{NH}_2}$ symmetric corresponding to primary amine function in ethylenediamine. Instead, the presence of $\nu_{\text{NH}_2}$ bands at lower frequency (only one of them well resolved at 3174 cm$^{-1}$) is only noted.
(v) The appearance of a strong characteristic $\nu_{\text{OH}}$ band at 3437 cm$^{-1}$ due to lattice water.
(vi) The appearance of medium to weak intensity band in the region 600-448 cm$^{-1}$ is assignable to Cu-N and Cu-O stretching.25,26,27.
The above mentioned observations can be correlated with a 1:2 mole condensation between ninhydrin and ethylenediamine. The presence of only one C=O band corresponding to position two in ninhydrin which involve in coordination along with two azomethine nitrogen and two amine nitrogen can be proposed. The IR spectral data is presented in table 2.

Table 2– IR spectroscopic result for Cu(II) complex.

<table>
<thead>
<tr>
<th>Chemical group</th>
<th>Stretching band (cm⁻¹)</th>
<th>Bending band (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-of water</td>
<td>3437</td>
<td></td>
</tr>
<tr>
<td>NH₂</td>
<td>3174</td>
<td>1600,1274,772</td>
</tr>
<tr>
<td>C=O(Ar)</td>
<td>3065&amp;3006</td>
<td></td>
</tr>
<tr>
<td>C-H(CH2⁻)</td>
<td>2919</td>
<td></td>
</tr>
<tr>
<td>C=N</td>
<td>1583,1563</td>
<td></td>
</tr>
<tr>
<td>C=N</td>
<td>1047</td>
<td></td>
</tr>
<tr>
<td>M-O, M-N</td>
<td>600-448</td>
<td></td>
</tr>
</tbody>
</table>

The IR spectra of the complex and the ninhydrin for reference are attached in appendix A and D, respectively.

2.3.6 Uv-vis spectrum of the Cu(II)complex.
The major features of the spectrum are explained below. The aromatic band at 255 nm (39216 cm⁻¹) is attributed to ninhydrin π→π* transition, the band around 283 nm (35336 cm⁻¹) is due to the n →π* transition of the C=O, which is consistent with the proposed structure. The band at 320 nm (31250 cm⁻¹) is attributed to n →π* transition of C=N chromophore. This is also an indication for the condensation between ninhydrin and ethylenediamine. The electronic spectrum of Cu(II) complex also shows a broad band in the region 478-736 nm (20920-13587 cm⁻¹) is assignable to d-d transition. This band is assumed to be due to merging of ²B₁→²A₁, ²B₁→²B₂, ²B₁→²E transitions with ²B₁.
ground term suggesting tetragonally distorted octahedral geometry for the complex, with approximately elongated octahedral arrangement. The distortion is accountable in view of the electronic degeneracy of Cu(II) (d⁹) as well as the stereochemistry of the ligand (with three exocyclic double bonds and with terminating N,O,N atoms as binding centers on a five membered fused ring).

The spectrum of the Cu (II) complex is presented in appendix B and C.

2.3.7 The magnetic moment

The magnetic susceptibility of the Cu(II) complex was measured at 21°C (294K). The gram susceptibility (χ₉) was measured to be 2.781 x 10⁻⁶. The result indicates that Cu(II) complex is paramagnetic. The molecular weight of the complex is 415 gm/mol. By using the relation,

\[ \chi_M = \chi_g \cdot M_m \]

diamagnetic correction,

\[ \chi_M^{\text{corr}} = \chi_M - \chi_{\text{dia}} \]

The effective magnetic moment (μ_eff) of the complex was calculated by using the working equation of effective magnetic moment.

\[ \mu_{\text{eff}} = 2.83 [\chi_M T]^{1/2} \]

is 1.75B.M.

This value of room temperature magnetic moment supports the presence of one unpaired electron, which can be correlated with the distorted octahedral geometry.
3. Conclusion

Based on analytical, conductivity, spectral and magnetic data, distorted octahedral geometry is proposed corresponding to the molecular formula [CuLCl]Cl.2H₂O

The proposed structure is shown in figure 18.

Figure 18  Proposed structure of the synthesized complex
References

5. T. Suseela, Structural studies on transition metal complex derived from some Symmetric and Unsymmetric Bis-chelating ligands, Osmania University, (1996).

Appendices

APPENDIX A

![Graph with various data points in cm\(^{-1}\) and %T]

- Alb-01

4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400

3854.18 3437.92 3174.17 3065.99 3006.21 2919.13 1735.14 1601.70 1583.98 1563.06 1533.99 1483.30 1457.78 1387.49 1354.35 1328.01 1177.83 1149.53 1137.88 1047.67 935.83 772.31 679.05 556.95 448.70

35.0 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72 74 76.9

cm\(^{-1}\) %T
APPENDIX B

UV-Vis of the complex
Appendix C

![Absorbance vs. Wavelength Graph](image)

- **Cu(II) conc.**
  - Absorbance values labeled at:
    - 478 nm
    - 736 nm