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## **Multi Dentate Ligands and Metal Complexes Derived from Ninhydrin and Ethylen Diamine**

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### **Abstract**

A new Cu(II) chelate formed by the derivatization of the ninhydrin with ethylenediamine (en) in the presence of CuCl<sub>2</sub> · 2H<sub>2</sub>O, 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 · 2H<sub>2</sub>O with a proposed stereochemistry of distorted/elongated octahedron.

**Keywords:** Ninhydrin, Ethylen Diamine, Multi dentate lignads, Cupper complexes

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### **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 K<sub>4</sub>Fe(CN)<sub>6</sub>. Early workers termed the substance such as Prussian blue "complex compounds" and this name has persisted. Eventoday 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 plant, is a magnesium complex and hemoglobin which carries oxygen to animal cells, is an iron complex<sup>1</sup>.

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.<sup>2</sup> 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 worth wile to examine; in what way Cu<sup>2+</sup> 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 and instrumentation**

#### **2.1. Chemicals and Reagents**

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

#### **2.2. 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  $\text{cm}^{-1}$  was recorded in KBr medium on a PerkinElmer spectrum BX spectrometer.

### 3. 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 macro cyclic ligand. A condensation reaction is a reaction in which a bond is formed between two molecules, and a small molecule-often  $\text{H}_2\text{O}$  -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  $\text{Ni}^{2+}$  .The mixture undergoes condensation to give the 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).<sup>3,4</sup> 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.

#### 3.1. 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  $\text{Mn}^{+2} < \text{Fe}^{+2} < \text{Co}^{+2} < \text{Ni}^{+2} < \text{Cu}^{+2} < \text{Zn}^{+2}$  .<sup>4</sup>

#### 3.2. 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 dn 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.<sup>2</sup> This is a consequence of Jahn-Teller distortion and is electronic in origin. Four coordinate planar complexes are also known .

The Cu (II) ion with its  $d^9$  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  $2T_2$  ground state. Octahedral complex with out any distortion are expected to have only one d-d absorption band corresponding to  $2E_g \rightarrow 2T_2g$  transition. In the axially elongated tetragonal distortion three absorption bands corresponding to the transition  $2B_{1g} \rightarrow 2A_{1g}$ ,  $2B_{1g} \rightarrow 2B_{2g}$ ,  $2B_{1g} \rightarrow 2E_g$  are observed. Tetragonal complexes are expected to give a single broad band corresponding to  $2T_2 \rightarrow 2E$  transition in the near IR region. The ground term in the square planar geometry is  $2B_1$  and three d-d bands corresponding to transition  $2B_{1g} \rightarrow 2B_{2g}$  ,  $2B_{1g} \rightarrow 2A_{1g}$ ,  $2B_{1g} \rightarrow 2E_g$  are observed.<sup>5,6</sup>

#### 3.3. 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 (H<sub>4</sub>L=N,N -bis(2-(1,8-naphthalenediol) methylidene) propylenediamine). One Cu(II) ion is coordinated by a  $\text{N}_2\text{O}_2$  compartment of **L** and the other Cu(II) ion is coordinated by an  $\text{O}_4$  compartment of **L** while they are bridged by two aryloxy functions of **L**.<sup>7</sup>



Figure.1. Dinuclear bis(phenoxy)-bridged Cu(II) complex

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 figure I.

### 3.4. 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<sub>3</sub> 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<sub>3</sub> and was subsequently dissolved in HNO<sub>3</sub>. 1% AgNO<sub>3</sub> 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°C. The conductivity of the Cu(II) complex was measured in freshly prepared solution using nitro methane.

The UV-vis spectrum was recorded by dissolving the Cu(II) complex in the nitromethane. 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  $\chi_M = \chi_g \cdot M_m$

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

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 magneto, Mm 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.

### 3.5. Synthesis of Cu(II) complex using template 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 CuCl<sub>2</sub>.2H<sub>2</sub>O, 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)Cl<sub>2</sub>.2H<sub>2</sub>O 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.

- Color:- Brown
- Melting point: 205°C
- Yield (%) = 28

### 4. Result and discussion

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.

#### 4.1 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 nitro methane.

#### 4.2 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 CuCl<sub>2</sub>.C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>N<sub>4</sub> or CuCl<sub>2</sub>.C<sub>13</sub>H<sub>16</sub>ON<sub>4</sub>.2H<sub>2</sub>O or CuCl<sub>2</sub>L.2H<sub>2</sub>O where C<sub>13</sub>H<sub>16</sub>ON<sub>4</sub> corresponds with a 1:2 condensation product between ninhydrin and ethylenediamine.

### 4.3 Chloride

The percentage of chloride obtained from experimental results (16.87) is also in a close agreement with the calculated value (17.00 %) which matches with the molecular formula  $\text{CuLCl}_2 \cdot 2\text{H}_2\text{O}$ .

### 4.4 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  $\mu\text{S}$ . When this value is converted by using the above relation the molar conductance of the complex was 78  $\text{Smol}^{-1}\text{cm}^2$ . 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  $[\text{CuLCl}] \text{Cl} \cdot 2\text{H}_2\text{O}$ .

### 4.5 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 ethylenediamine 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 dihydroxyketo and tri keto hydrate forms.

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  $\text{cm}^{-1}$  is due to  $\nu_{\text{OH}}$  and three characteristic bands in the region 1748-1718  $\text{cm}^{-1}$  are due to  $\nu_{\text{C=O}}$ .

Free ethylenediamine is expected to show stretching and deformation characteristics of primary amine functions and  $\text{CH}_2$  groups at 3368 and 3284  $\text{cm}^{-1}$ , 2926  $\text{cm}^{-1}$ , 1597  $\text{cm}^{-1}$ , 1461  $\text{cm}^{-1}$ , 1366  $\text{cm}^{-1}$ , 1170  $\text{cm}^{-1}$  and 1047  $\text{cm}^{-1}$ .<sup>22</sup> The notable features of the IR spectrum of Cu(II) complex are :-

- The presence of only one band at 1735  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{C=O}}$  in comparison with three bands of free ninhydrin.
- The absence of the  $\nu_{\text{OH}}$  band corresponding to free ninhydrin.
- The appearance of strong sharp multiple bands in the region 1600-1563  $\text{cm}^{-1}$  characteristic of  $\nu_{\text{C=N}}$
- 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  $\text{cm}^{-1}$ ) is only noted.

(v) The appearance of a strong characteristic  $\nu_{\text{OH}}$  band at 3437  $\text{cm}^{-1}$  due to lattice water.

(vi) The appearance of medium to weak intensity band in the region 600-448  $\text{cm}^{-1}$  is assignable to Cu-N and Cu-O stretching.<sup>25,26,27</sup>

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.

Chemical group	Stretching band ( $\text{cm}^{-1}$ )	Bending band ( $\text{cm}^{-1}$ )
OH-of water	3437	
NH <sub>2</sub>	3174	1600, 1274, 772
C-H(Ar)	3065 & 3006	
C-H(CH <sub>2</sub> -)	2919	
C=O	1735	
C=C	1601, 1483, 1457	
C=N	1583, 1563	
C-N	1047	
M-O, M-N	600-448	

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

### 4.6 Uv-vis spectrum of the Cu(II) complex.

The major features of the spectrum are explained below. The aromatic band at 255 nm (39216  $\text{cm}^{-1}$ ) is attributed to ninhydrin  $\pi \rightarrow \pi^*$  transition, the band around 283 nm (35336  $\text{cm}^{-1}$ ) is due to the  $n \rightarrow \pi^*$  transition of the C=O, which is consistent with the proposed structure. The band at 320 nm (31250  $\text{cm}^{-1}$ ) is attributed to  $n \rightarrow \pi^*$  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  $\text{cm}^{-1}$ ) is assignable to d-d transition. This band is assumed to be due to merging of  ${}^2\text{B}_1 \rightarrow \text{A}_1$ ,  ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$ ,  ${}^2\text{B}_1 \rightarrow {}^2\text{E}$  transitions with  ${}^2\text{B}_1$  ground term suggesting tetragonally distorted octahedral geometry for the complex.<sup>28,29</sup> with approximately elongated octahedral arrangement. The distortion is

accountable in view of the electronic degeneracy of Cu(II) ( $d_9$ ) 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.

#### 4.7 The magnetic moment

The magnetic susceptibility of the Cu(II) complex was measured at 21°C (294K). The gram susceptibility ( $\chi_g$ ) was measured to be  $2.781 \times 10^{-6}$ . The result indicates that Cu(II) complex is paramagnetic. The molecular weight of the complex is 415 gm/mol. By using the relation,

$\chi_M = \chi_g \cdot M$  diamagnetic correction,

$\chi_{M\text{corr}} = \chi_M - \chi_{\text{dia}}$

The effective magnetic moment ( $\mu_{\text{eff}}$ ) of the complex was calculated by using the working equation of effective magnetic moment.

$\mu_{\text{eff}} = 2.83[\chi_M \cdot T]^{1/2}$  is 1.75 B.M.

This value of room temperature magnetic moment supports the presence of one unpaired electron, which can be correlated with the distorted octahedral geometry. 30,31

#### 5. Conclusion

Based on analytical, conductivity, spectral and magnetic data, distorted octahedral geometry is proposed corresponding to the molecular formula  $[\text{CuLCl}]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

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