COPPER(II) COMPLEXES WITH DEPROTONATED
N-(2-HYDROXYETHYL)ETHYLENEDIAMINE

THESIS

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By

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This thesis reports the synthesis and characterization of two new copper(II) halide complexes with deprotonated N-(2-hydroxyethyl)ethylenediamine behaving as a bidentate.

The magnetic properties of the new copper(II) complexes were studied from room temperature to liquid nitrogen temperatures. The magnetic data show that both complexes exhibit antiferromagnetic interactions with a singlet ground state and a thermally accessible triplet excited state. Magnetic data and infrared spectra indicate the complexes are halogen-bridged.

Deprotonation at an amine nitrogen is based on the presence of a hydroxyl stretching band in the infrared spectra. Electronic spectra and infrared spectra indicate the complexes are square planar.

Elemental analyses, infrared spectra, electronic spectra, electron spin resonance spectra, and magnetic data are reported and discussed.
ACKNOWLEDGMENT

The financial support of this investigation by the North Texas State University Faculty Research Fund and the Robert A. Welch Foundation is gratefully acknowledged.
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CHAPTER I

INTRODUCTION

The first copper(II) halide complexes with N-(2-hydroxyethyl)ethylenediamine were reported by Breckenridge.¹ Breckenridge reported the preparation of N-(2-hydroxyethyl)ethylenediamine-copper(II) chloride monohydrate, bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) bromide, and bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) chloride. Since this report, Nasanen et al.² have reported with crystal data that the "bis" copper(II) complexes are tetragonally distorted octahedral structures with the anions in the axial positions. The complete x-ray structure of the bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) chloride has been reported by Pajunen and Nasakkala.³ The two reports agree in the structure of this complex. The primary nitrogen atoms were found to be trans to one another in the radial positions and the hydroxyl groups were not coordinated. The two anions were coordinated in the axial positions. The bromide complex has

a similar structure. Nasanen et al.\textsuperscript{4} have reported crystal data and other properties for the N-(2-hydroxyethyl)ethylenediaminecopper(II) bromide and the chloride monohydrate. Both complexes are reported to consist of approximately coplanar units of Cu(LH)X\textsubscript{2} (LH = N-(2-hydroxyethyl)ethylenediamine and X = a halogen) weakly bridged by the halogen anions.

Although no copper(II) complexes in the solid state are known using N-(2-hydroxyethyl)ethylenediamine in the deprotonated form, there are two reports of this type of complex involving other transition metals. Sarma and Bailar\textsuperscript{5} reported the preparation of a cobalt(III) complex where the hydroxyl group was deprotonated and the diaminealcohol was tridentate. Watt and Thompson\textsuperscript{6} reported the preparation of Pt(IV) complexes where an amine nitrogen was deprotonated and the diaminealcohol was bidentate. Thus, it is apparent that this ligand may behave as a bidentate or a tridentate. The sight of deprotonation seems to be determined by how the ligand coordinates itself to the transition metal.

In these reports no magnetic information was given. It seemed of value to investigate the magnetic properties of


complexes involving this ligand deprotonated. There has been a vast amount of research concerning the magnetic behavior exhibited by transition metal complexes, especially polynuclear complexes. In recent years, research efforts in this field have been greatly advanced, largely due to improved, or new equipment, and to theoretical breakthroughs. With the aid of modern x-ray crystallography, magnetic data can possibly be correlated to the type of atoms, through which magnetic interactions takes place, and the bonding angles of these atoms. Usually, a large amount of magnetic information, concerning the extent of any interactions, can be acquired by obtaining magnetic measurements over a temperature range.

Magnetic properties of complexes are commonly expressed in terms of magnetic moments. However, magnetic moments are obtained indirectly from experimentally determined magnetic susceptibilities. The magnetic susceptibility and the moments are related through the equation

\[ \chi_A = \frac{N\beta^2\mu^2}{3kT} \]  

---

where \( \chi_A \) is the magnetic susceptibility per gram-atom, \( N \) is Avogadro's number, \( \beta \) is the Bohr magneton, \( k \) is Boltzmann's constant, \( T \) is the temperature in absolute degrees, and \( \mu_e \) is the "effective magnetic moment". The value of these constants are given in the Appendix. Upon solving equation (1) for \( \mu_e \), the equation becomes

\[
\mu_e = 2.83(\chi_A T)^{1/2} \text{ B.M.} \tag{2}
\]

where 2.83 results from the constants involved.

In order to obtain more accurate magnetic moments, \( \chi_A \) must be corrected for the susceptibilities of the ligand (\( \chi_L \)), the variation in \( \chi_L \) due to the different environment of the atoms due to the nature of the bonds involved (\( \lambda \)), and the temperature independent paramagnetism (\( Na \)) of the metal ion. This temperature independent paramagnetism is a weak paramagnetism that arises by a coupling of the ground state with the excited states under the influence of a magnetic field. Since this is an induced magnetism when under the influence of a magnetic field, it should be corrected for. For copper(II) ions, \( Na \) is taken to be \( 60 \times 10^{-6} \) c.g.s. units. The corrected molar susceptibility (\( \chi_M^{\text{corr}} \)) is obtained from \( \chi_A \) by the equation\(^\text{11}\)

\[
\chi_M^{\text{corr}} = \chi_A - \Sigma n_L \chi_L - \Sigma \lambda + Na \tag{3}
\]

\(^\text{11}\)Ibid., p. 6.
where \( n_L \) is the number of \( L \) atoms of atomic susceptibility \( \chi_L \) in the ligands with \( \lambda \) and \( Na \) having their above meaning. With the correction of \( \chi_A \) for these factors, equation (2) becomes

\[
\mu_e = 2.83(\chi_M^{corrT})^{1/2} \text{ B.M.} \tag{4}
\]

It is common practice to calculate magnetic moments using equation (4), and call this the "effective magnetic moment". In this manner no possibly unjustified implications are attached to empirically sound facts.\(^{12}\)

Since the complexes in the present work involve copper(II), the central metal ions contain only one unpaired electron. The magnetic moment of unpaired electrons is given by the equation\(^{13}\)

\[
\mu_S = g[S(S+1)]^{1/2} \text{ B.M.} \tag{5}
\]

where \( S \) is the absolute value of the total spin quantum number and \( g \) is the gyromagnetic ratio, which is the ratio of the magnetic moment to the angular momentum. For a free electron, \( g \) has the value of 2.0023 which is usually taken as 2.00. With equation (5) the spin-only magnetic moment of an electron is calculated as

\[
\mu_S = 2[1/2(1/2+1)]^{1/2} = 1.73 \text{ B.M.}
\]


\(^{13}\) Earnshaw, p. 34.
Thus, a totally isolated copper(II) ion will possess a magnetic moment of 1.73 B.M. due to the spin-only value. The actual moments are larger than the spin-only value due to an orbital contribution. If the orbital term makes its full contribution to the magnetic moment, the equation used to calculate the magnetic moment is

$$\mu_{S+L} = \left[4S(S+1) + L(L+1)\right]^{1/2} \text{ B.M.} \quad (6)$$

where \(L\) represents the total orbital angular momentum quantum number for the metal ion. Immediately, it is apparent that metal ions whose ground state are \(S\) states have no orbital momentum to contribute. Hence, the magnetic moments of metal ions with \(S\) ground states should be near the spin-only value. When the ground state is other than an \(S\) state, the moment would be expected to have some orbital angular momentum contribution. The copper(II) ion has a \(D\) ground state. Thus, the magnetic moment, resulting from full contribution of the spin-only value and orbital angular momentum using equation (6) is

$$\mu_{S+L} = \left[4(1/2)(1/2+1) + 2(2+1)\right]^{1/2} = 3.00 \text{ B.M.}$$

The observed values are normally closer to the spin-only value. This is explained by what is referred to as "orbital quenching" by the strong action of crystalline electric

\(^{14}\)Cotton and Wilkinson, p. 538.
fields. That is, the interactions with the electric field of the ligands are so strong that the orbital angular momentum does not respond to the application of a magnetic field.

With the previous arguments, an isolated copper(II) ion in a complex should behave as a normal paramagnetic specie, having a magnetic moment a little larger than the spin-only value of 1.73 B.M., which is independent of temperature. However, if the copper(II) ions are not isolated from the neighboring paramagnetic centers (other copper(II) ions), the observed magnetic moment may be decreased or increased from the moment of a normal paramagnetic substance, depending on what type of interaction is present.

The two main types of magnetic interactions exhibited by polynuclear complexes are ferromagnetism and antiferromagnetism. In ferromagnetic systems, the neighboring paramagnetic centers tend to align their unpaired electrons parallel to each other. Thus, the moments are larger than normal paramagnetic substances. Also, the moments are temperature dependent with an increase in the moments as the temperature decreases. In antiferromagnetic systems, the neighboring paramagnetic centers tend to align their unpaired electrons antiparallel to each other. Thus, the moments are smaller than normal paramagnetic substances. As with

16Cotton and Wilkinson, pp. 542-544.
ferromagnetism, the moments of antiferromagnetic systems are
temperature dependent, but in antiferromagnetic systems the
moments decrease as the temperature decreases.

In both types of interactions, thermal agitation tends
to randomize the orientations of the unpaired electrons.
Thus, this effect will tend to weaken the strength of the
magnetic interactions. There is a characteristic temperature
for each polynuclear complex below which the magnetic inter-
actions becomes the dominant factor in how the unpaired
electrons align with each other. For ferromagnetic systems,
this is known as the Curie temperature, $T_C$. For antiferro-
magnetic systems, this is known as the Néel temperature, $T_N$.
Above these temperatures, both systems behave similar to
normal paramagnetic systems. As with normal paramagnetism,
ferro- and antiferromagnetic systems show an increase in
magnetic susceptibilities as the temperature decreases while
above their $T_C$ or $T_N$. Below these points, both interactions
begin to deviate from simple paramagnetic systems. The
susceptibilities of ferromagnetic material increase at a much
faster rate than paramagnetic. Whereas, the susceptibilities
of antiferromagnetic material decreases sharply until the
extreme of diamagnetism (complete pairing of electrons) is
reached. The three systems\textsuperscript{16} are illustrated in Figure 1.

As stated previously, a variable temperature suscep-
tibility study is necessary to magnetically characterize a
complex properly, since ferromagnetic and antiferromagnetic
complexes may display a room temperature moment similar to normal paramagnetism. In the present work, the newly formed deprotonated complexes have room temperature moments slightly larger than the spin-only value, but the moments decrease as the temperature is lowered. Therefore, a further discussion of antiferromagnetism will be given.

In antiferromagnetic systems, the ground state is a singlet with electrons paired. While at a higher energy, a triplet with the electrons unpaired is an excited state. The singlet-triplet system is shown in Figure 2.
Here \( J \) is the energy separation between the singlet ground state and the triplet excited state. \( J \) is commonly known as the "exchange integral" and is known to involve the interchange of the coordinates of the electrons.\(^1^7\) \( J \) has a negative value for antiferromagnetic systems. Both of the newly formed deprotonated copper(II) complexes possess negative \( J \) values.

The experimentally determined magnetic susceptibility is the net result of the population distribution between the singlet ground state and the triplet excited state. While the \( J \) value remains constant, the distribution changes as the thermal energy is varied. As the distribution varies, the susceptibilities change. Thus, an antiferromagnetic system that has a large \( J \) value compared to \( kT \) will populate the excited state very little. Therefore, the complex will display a very low moment. An antiferromagnetic complex that has a small \( J \) value compared to \( kT \) will have moments only slightly smaller than the spin-only value until extremely low temperatures are reached. The latter case is observed in the complexes of the present study.

Bleaney and Bowers\(^1^8\) have related the \( J \) values of dimeric complexes and the magnetic susceptibilities with the equation

\[
\chi_M^{\text{corr}} = \frac{Ng^2B^2}{3kT} \left[ 1 + \frac{1}{3} \exp\left(\frac{-J}{kT}\right) \right]^{-1} + Na \tag{7}
\]

\(^1^7\) Davis, p. 227.

Thus, after the magnetic susceptibilities have been determined, the $J$ values can be calculated from equation (7). As seen in equation (7), the susceptibility should be temperature dependent.

In recent years, the strength and type of interactions exhibited by bridged systems have been correlated to the angle formed by the atoms composing the bridged system. The majority of these reports deal with oxygen-bridged systems. Bertrand and Kelly\(^8\) have reported the x-ray structures of two complexes, Cu(II)(acac:propanolamine) and Cu(II)(acac:ethanolamine). These structures are illustrated in Figure 3.

![Cu(II)(acac:propanolamine)](image)

![Cu(II)(acac:ethanolamine)](image)

Fig. 3--Schematic representation of the structures of Cu(II)(acac:propanolamine) and Cu(II)(acac:ethanolamine).
Cu(II)(acac:propanolamine) is dimeric with a Cu-0-Cu angle of 106.4° and a room temperature moment of 0.41 B.M. While Cu(II)(acac:ethanolamine) is tetrameric with a Cu-0-Cu angle of 97.8° and a room temperature moment of 1.87 B.M. This variation of the magnetic interaction with a change in the bridging angle is explained by what is known as the "super-exchange pathway". Since the interaction pathway is believed to be determined by the Cu-0-Cu angle, the change in interaction is believed to be due to what extent the "s" orbital or the "p" orbitals of the oxygen atom is used to overlap with the "d" orbitals of the copper(II) ions. If the bridging angle is near 90°, the oxygen is expected to be using the "p" orbitals, and the ground state is a triplet. As the angle increases less "p" orbital is used and the "s" orbital is used to a more extent. As more of the "s" orbital is used, the ground state becomes a singlet state. It has been determined that an angle of 97.6° is the crossover between a singlet and a triplet ground state.\textsuperscript{19}

The success of correlating the structural data of the magnetic properties of oxygen-bridged copper(II) systems has not been as applicable to halogen-bridged systems.\textsuperscript{20} This may be due partly to the presence of low-lying "d" orbitals on the halogens. A larger factor may be due to the lack of

\textsuperscript{19}Lippard, p. 179.

x-ray structures of halogen-bridged complexes. At the present there are six chlorine-bridged and only three bromine-bridged complexes known. This is very few compared to the vast number of oxygen-bridged complexes known.

Although it may be a little soon to be correlating the magnetic properties and structural data of halogen-bridged copper(II) complexes, it is worthwhile to note that (Cu(DMG)-Cl₂)₂ (DMG = dimethylglyoxime) has a Cu-Cl-Cu bridging angle of 88° and a J value of +6.3 cm⁻¹. Whereas, (Cu(pic)₂Cl₂)₂ (pic = 2-methylpyridine) has a Cu-Cl-Cu angle of 101.4° and a J value of -7.4 cm⁻¹. Thus, it is seen with these cases an increase in the bridging angle of halogen-complexes brings about a stronger antiferromagnetic interaction.

This study was initiated to prepare copper(II) halide complexes with deprotonated N-(2-hydroxyethyl)ethylenediamine. The magnetic properties were investigated in order to determine the nature and magnitude of the spin-spin interactions of these complexes. Also, it was of interest to determine if the complex would become oxygen- or chlorine-bridged which would probably be determined if the ligand behaved as a tridentate or a bidentate.
CHAPTER II

COPPER(II) COMPLEXES WITH N-(2-HYDROXYETHYL)ETHYLENEDIAMINE

Experimental and Results

Reagents

Reagent grade 2-(2-aminoethylamino)ethanol (97%) \([N-(2-hydroxyethyl)ethylenediamine, \text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH}]\) was obtained from the Aldrich Chemical Company. Salicylaldehyde, copper(II) chloride dihydrate, copper(II) bromide, copper(II) acetate monohydrate and sodium hydroxide were all obtained from the J. T. Baker Chemical Company. Copper(II) hydroxide was prepared by adding dropwise an aqueous sodium hydroxide solution to a stirring aqueous copper(II) acetate monohydrate solution until no noticeable copper(II) acetate monohydrate remained. The bulky blue precipitate was filtered, washed with distilled water and ethanol, and allowed to air dry. No heat should be applied while drying the copper(II) hydroxide, since this results in decomposition of the hydroxide. All solvents used were at least reagent grade.

Preparation of the Complexes

Bis\((N-(2-hydroxyethyl)ethylenediamine)\)copper(II) chloride was prepared in the following manner. Copper(II) chloride monohydrate (8.50 grams, 0.05 mole) was dissolved in 75 ml of
absolute ethanol. While stirring without heat, N-(2-hydroxy-ethyl)ethylenediamine (11.80 grams, 0.11 mole) was added slowly. A reaction took place immediately upon contact of the reagents with the evolution of heat. After three hours of stirring, a bluish-purple precipitate was filtered from the resulting dark blue solution. The product was washed thoroughly twice with absolute ethanol, once with anhydrous ether, and dried under vacuum at 40 °C overnight. The yield was about 85 per cent. The complex melted at 201-203 °C.

Bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) bromide was prepared in the following manner. Copper(II) bromide (11.17 grams, 0.05 mole) was dissolved in 75 ml of anhydrous methanol. While stirring without heat, N-(2-hydroxyethyl)-ethylenediamine (11.80 grams, 0.11 mole) was added slowly. After three hours of stirring, a purple precipitate was filtered from the resulting dark blue solution. The product was washed thoroughly twice with absolute ethanol, once with anhydrous ether, and dried under vacuum at 40 °C overnight. The yield was about 73 per cent. The complex melted at 182-184 °C.

The copper(II) chloride complex with deprotonated N-(2-hydroxyethyl)ethylenediamine was prepared in the following manner.\textsuperscript{1} Bis(N-(2-hydroxyethyl)ethylenediamine)copper(II)

\textsuperscript{1}Henceforth the expressions "LH" will represent the neutral molecule of N-(2-hydroxyethyl)ethylenediamine and "L" will represent the deprotonated form of this diaminealcohol.
chloride (10.97 grams, 0.032 mole) was added to 100 ml of absolute ethanol. While stirring the mixture, copper(II) hydroxide (2.93 grams, 0.03 mole) was added, and the reaction medium was refluxed for two hours. After refluxing, a blue precipitate was filtered from the resulting dark blue solution. The light blue powdery product was washed twice with absolute ethanol, once with anhydrous ether, and dried under vacuum at 40 °C overnight. The yield was about 68 per cent. The complex decomposed at 180 °C.

The copper(II) bromide complex with deprotonated N-(2-hydroxyethyl)ethylenediamine was prepared in the following manner. Bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) bromide (13.81 grams, 0.032 mole) was added to 100 ml of absolute ethanol. While stirring the mixture, copper(II) hydroxide (2.93 grams, 0.03 mole) was added, and the reaction medium was refluxed for two hours. After refluxing, a blue precipitate was filtered from the resulting dark blue solution. The blue powdery product was washed twice with absolute ethanol, once with anhydrous ether, and dried in a vacuum desicator at 40 °C overnight. The yield was about 57 per cent. The complex decomposed at 169 °C.

Although the following compounds were primarily prepared to aid in interpreting the deprotonated complexes spectra, they were analyzed and studied to some extent.

Sal:N-(2-hydroxyethyl)ethylenediamine was prepared in the following manner. Salicylaldehyde was dissolved in 100 ml
of anhydrous methanol. While stirring the solution, N-(2-
hydroxyethyl)ethylenediamine (10.50 grams, 0.10 mole) was added.
After refluxing for one hour, the reaction medium was chilled
at 10 °C overnight. A large mass of yellow crystals were
produced, and recrystallized from toluene. Then, the Schiff
base was washed with anhydrous ether twice, and dried under
vacuum for several hours. The yield was about 93 per cent.
The Schiff base melted at 84-85 °C.

Cu(II)(sal:N-(2-hydroxyethyl)ethylenediamine)·ethanol
was prepared in the following manner. Copper(II) acetate
monohydrate (7.99 grams, 0.04 mole) was added to 100 ml of
methanol. The Schiff base, sal:N-(2-hydroxyethyl)ethylen-
ediamine (9.17 grams, 0.044 mole), was added to the copper(II)
acetate monohydrate solution. After refluxing for thirty
minutes, sodium hydroxide (3.20 grams, 0.08 mole) in 40 ml of
methanol was added dropwise to the reaction flask. Upon
completion of adding the base, a large mass of a dark blue
precipitate appeared. After recrystallizing in absolute
ethanol, the dark blue product was washed with anhydrous ether
twice and dried under vacuum overnight. The yield was about
78 per cent. The complex decomposed at 145 °C.

Cu(II)(sal:N-(2-hydroxyethyl)ethylenediamine) was pre-
pared in the same manner as the ethanol adduct. Except, after

2The expression "L" will represent the Schiff base,
formed from salicylaldehyde and N-(2-hydroxyethyl)ethylen-
ediamine, with both hydroxyl groups deprotonated.
the recrystallization in absolute ethanol, the ethanol adduct was washed in boiling chloroform. This yielded a green precipitate which was washed with anhydrous ether and dried under vacuum overnight. The yield was about 74 per cent. The complex decomposed at 198 °C.

**TABLE I**

**ANALYTICAL DATA FOR THE COPPER(II) COMPLEXES**

<table>
<thead>
<tr>
<th>Complex</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(LH)$_2$Cl$_2$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>18.54</td>
</tr>
<tr>
<td>Found:</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>18.44</td>
</tr>
<tr>
<td>Cu(LH)$_2$Br$_2$</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>14.72</td>
</tr>
<tr>
<td>Found:</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>14.70</td>
</tr>
<tr>
<td>(CuLCl)$_2$</td>
<td>23.77</td>
<td>5.47</td>
<td>13.86</td>
<td>31.43</td>
</tr>
<tr>
<td>Found:</td>
<td>23.60</td>
<td>5.48</td>
<td>13.85</td>
<td>31.17</td>
</tr>
<tr>
<td>(CuLBr)$_2$</td>
<td>19.48</td>
<td>4.50</td>
<td>11.36</td>
<td>25.77</td>
</tr>
<tr>
<td>Found:</td>
<td>19.33</td>
<td>4.46</td>
<td>11.10</td>
<td>26.01</td>
</tr>
<tr>
<td>CuL'</td>
<td>48.97</td>
<td>5.23</td>
<td>10.38</td>
<td>23.55</td>
</tr>
<tr>
<td>Found:</td>
<td>48.83</td>
<td>5.24</td>
<td>10.22</td>
<td>23.27</td>
</tr>
<tr>
<td>CuL'·EtOH</td>
<td>49.44</td>
<td>6.38</td>
<td>8.87</td>
<td>20.12</td>
</tr>
<tr>
<td>Found:</td>
<td>49.27</td>
<td>6.30</td>
<td>8.82</td>
<td>19.86</td>
</tr>
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**Analyses of the Complexes**

The per cent copper of the complexes were determined using a Sargent-Slomin Electrolytic Analyzer with platinum electrodes. The per cent carbon, hydrogen, and nitrogen of the complexes were determined by the Galbraith Laboratories,
Inc., Knoxville, Tennessee. The analytical data is listed in Table I.

**Infrared Spectra**

Infrared spectra were recorded over the range of 4000 to 200 cm$^{-1}$ on a Perkin-Elmer Model 621. Nujol and fluorolube mulls were obtained using cesium iodide plates. In order to prevent the interference of atmospheric absorptions, due to water or carbon dioxide, in the 400 to 200 cm$^{-1}$ region, the instrument was purged continuously with a steady flow of pressurized dry air. The infrared spectra of the deprotonated complexes are shown in Figure 4 and 5.

**Magnetic Susceptibilities**

Magnetic susceptibility measurements were determined using the Gouy method. Mercuric tetrathiocyanatocobaltate(II), Hg(Co(NCS)$_4$), was used as the calibrant for all measurements. The temperature for measurements between liquid nitrogen and room temperature were monitored with a Leeds-Northrup Model 8691 Millivolt Potentiometer using a copper-constantan thermocouple and an ice solution for the reference temperature. The magnetic susceptibilities were corrected for diamagnetism of the ligands ($\chi_L$) using Pascal's constants$^4$ and the temperature independent paramagnetism ($\chi_T$).


$^4$Ibid., p. 6.
Fig. 4--Infrared spectrum of (CuLCl)_2
Fig. 4 (continued)
Fig. 4 (continued)
Fig. 4 (continued)
Fig. 4 (continued)
Fig. 5--Infrared spectrum of (CuLBr)$_2$
Fig. 5 (continued)
Fig. 5 (continued)
Fig. 5 (continued)

(Frequency, cm$^{-1}$)
Fig. 5 (continued)
The liquid nitrogen and room temperature susceptibilities were determined using the procedure as described in the literature. The magnetic susceptibilities between liquid nitrogen and room temperature were obtained using the set-up illustrated in Figure 6. The desired temperature was obtained by passing nitrogen gas, that had flowed through the liquid nitrogen reservoir, at a specific flow rate through the region containing the sample. The temperature was monitored by a millivolt potentiometer as previously described. A layer of nitrogen gas was maintained above the sample tube to prevent condensation of moisture that might produce an error in the weighing measurements.

**TABLE II**
MAGNETIC SUSCEPTIBILITY DATA FOR THE COPPER(II) COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp.(°K)</th>
<th>$\chi^\text{corr}_M$</th>
<th>$\mu_e$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CulCl)$_2$</td>
<td>294</td>
<td>1312</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>223</td>
<td>1675</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>2452</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>4427</td>
<td>1.66</td>
</tr>
<tr>
<td>(CulBr)$_2$</td>
<td>294</td>
<td>1297</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>223</td>
<td>1612</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>2297</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>4104</td>
<td>1.60</td>
</tr>
<tr>
<td>CuL'</td>
<td>297</td>
<td>1472</td>
<td>1.87</td>
</tr>
<tr>
<td>CuL'·EtOH</td>
<td>296</td>
<td>1430</td>
<td>1.84</td>
</tr>
</tbody>
</table>

* $10^6$ c.g.s. units.
Fig. 6--System used for determining variable temperature magnetic susceptibilities.
The magnetic moments were calculated according to equation (4). The magnetic susceptibilities and moments at the specified temperature are listed in Table II.

**Electronic Spectra**

The electronic spectra of the Schiff base and the deprotonated complexes were obtained on a Cary Model 14 Recording Spectrophotometer using one-centimeter matched quartz cells. Solid state spectra were obtained with nujol mulls of filter paper between 12,500 cm\(^{-1}\) and 33,333 cm\(^{-1}\). The spectra of deprotonated complexes in the region of interest are shown in Figure 7 and 8. The maxima frequencies of the solid state spectra are listed in Table III.

**TABLE III**

**ELECTRONIC BAND MAXIMA OF THE COPPER(II) COMPLEXES**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Band Maxima(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CuLCl)_2</td>
<td>14,660</td>
</tr>
<tr>
<td>(CuLBr)_2</td>
<td>14,680</td>
</tr>
<tr>
<td>CuL'</td>
<td>15,540</td>
</tr>
<tr>
<td>CuL'·EtOH</td>
<td>17,010</td>
</tr>
</tbody>
</table>

**Electron Spin Resonance Spectra**

Electron spin resonance spectra were recorded with a Varian V-4502-12 X-band Spectrometer using 100-kc modulation.
Fig. 7--Electronic spectrum of \((\text{CuLCl})_2\)
Fig. 8—Electronic spectrum of \( \text{(CuLBr)}_2 \)
The spectra were obtained with powdered samples which were packed in cylindrical quartz tubes with diphenylpicrylhydrazyl (DPPH) used as the internal reference. The frequency was monitored with a Hewlett-Packard Model 5340A Automatic Microwave Frequency Counter. Part of the ESR spectra of the chloride deprotonated complex is shown in Figure 9.

Fig. 9--ESR spectrum of (CuLCl)$_2$
Discussion

Infrared Spectra

The infrared spectra of both deprotonated complexes were very similar. Based on the presence of the strong broad absorption at 3390 cm\(^{-1}\) and the elemental analyses of the bromide deprotonated copper(II) complex, it is concluded that the newly formed complexes have retained the hydroxyl group. Therefore, this implies that the sight of deprotonation is at one of the amine groups. This conclusion is supported by the work of Watts and Thompson,\(^5\) who reported that an amine nitrogen was deprotonated in their diaminealcohol which is the same as the one of present concern. The elemental analyses of the chloride deprotonated complex agrees well with the theoretical analyses, although what is believe to be the O-H stretching absorption appears as a shoulder on the N-H stretching bands. The infrared spectra of the chloride and the bromide deprotonated copper(II) complexes in nujol mulls are shown in Figure 4 and 5, respectively.

In the Schiff base complex Cu(II)(sal:N-(2-hydroxyethyl)-ethylenediamine) the elemental analyses and the infrared spectra indicate no hydroxyl groups. Therefore, the absorption at 3199 cm\(^{-1}\) is assigned to the N-H stretching band of secondary amine in this Schiff base, since there is no primary

N-H group. Although the ethanol adduct Schiff base showed no O-H stretching band in the expected region, an absorption at 3176 cm\(^{-1}\) with similar intensity and shape as the other Schiff base complex was assigned to the N-H stretch of its secondary amine group. With these assignments of the Schiff base complexes, the bands at 3206 cm\(^{-1}\) and 3197 cm\(^{-1}\) are assigned to the N-H stretch of the secondary amine in the bromide and chloride deprotonated complexes, respectively. Thus, this implies that deprotonation took place at the primary amine position. Both complexes show another absorption near 3140 cm\(^{-1}\) which is due to the N-H stretch of the hydrogen remaining on the primarily nitrogen group. The bands near 1600 cm\(^{-1}\) are assigned to the N-H bending vibrations.\(^6\)

The large absorptions between 3000 cm\(^{-1}\) and 2850 cm\(^{-1}\) are assigned to C-H stretching mode of the nujol in the mull and in the complexes. The large bands near 1450 cm\(^{-1}\) is assigned to -CH\(_2\)- bending vibrations in the nujol and in the complexes.\(^7\)

If the hydroxyl group becomes coordinated, the ligand could behave as a tridentate. There has been many investigations studying the tendency of hydroxyl groups to coordinate. Watt and Thompson reported that N-(2-hydroxyethyl)ethylene-diamine molecule behaved as a bidentate in all cases that they


\(^7\)Ibid., pp. 78-79.
studied involving Pt(II), Pt(IV), and Pd(II). Zimmerman and Hall\(^8\) have reported in their study the tendency of the hydroxyl group in some diaminealcohols to coordinate in copper(II) complexes. N-(2-hydroxyethyl)ethylenediamine was among the diaminealcohols that they studied. In their work they report that absorptions near 860 to 810 cm\(^{-1}\) offers the greatest correlation with, and evidence for, in assuming the hydroxyl group to be coordinated or not coordinated. They coorelated the presence of a medium to strong band in this region to the noncoordination of hydroxyl oxygen atom. The presence of a weak band or the absence of a band indicated that hydroxyl group was coordinated in the complex. As in Zimmerman and Hall's report, bis(N-(2-hydroxyethyl)ethylenediamine)copper(II) chloride showed a strong band at 842 cm\(^{-1}\). They did not report on the bromide analog, but a strong band at 866 cm\(^{-1}\) was taken as evidence for an uncoordinated hydroxyl group.

In the present study a similar system is involved with the same metal ion, the same type of anions, and the same diaminealcohol. Therefore, Zimmerman and Hall's proposed correlation is taken as being operative here, also. With (CuLCl)_2 displaying an absorption of medium intensity at 837 cm\(^{-1}\), and (CuLBr)_2 displaying an absorption of medium intensity at 834 cm\(^{-1}\), both deprotonated complexes are considered to have uncoordinated hydroxyl groups. Thus, the

Fig. 10--Infrared region showing the band for an uncoordinated hydroxyl group.
diamine alcohol is bidentate in present study. Spectra of the complexes in the 700 to 900 cm\(^{-1}\) region are shown in Figure 10.

In the far-infrared region there are several bands between 700 cm\(^{-1}\) and 400 cm\(^{-1}\) in the complexes. Thus, it is difficult to make a direct assignment to each vibration. However, a weak band at 404 cm\(^{-1}\) in Cu(LH)Cl\(_2\) is in the region for a terminal Cu-Cl stretch band to which it is assigned since it is absent in Cu(LH)\(_2\)Br\(_2\). A strong band at 285 cm\(^{-1}\) is assigned to a Cu-Br stretching band, since it is absent in Cu(LH)\(_2\)Cl\(_2\). These bands are absent in the deprotonated complexes. With the halogens being bridged in these complexes the Cu-Cl and Cu-Br stretching absorptions are probably below 200 cm\(^{-1}\). The region below 400 cm\(^{-1}\) in the deprotonated complexes are virtually absent of bands, except that both complexes show a band of medium intensity near 330 cm\(^{-1}\). These bands are at 332 cm\(^{-1}\) in (CuLCl)\(_2\) and at 329 cm\(^{-1}\) in (CuLBr)\(_2\). These bands are attributed to the Cu-N stretching vibrations using the work reported by Lever and Mantovani.\(^9\) A summary of the assignments for the deprotonated complexes are listed in Table IV.

**Magnetic Susceptibilities**

The parent complexes, Cu(LH)\(_2\)Cl\(_2\) and Cu(LH)\(_2\)Br\(_2\), are known to be monomeric with room-temperature magnetic moments

## TABLE IV
INFRARED ASSIGNMENTS OF THE DEPROTONATED COPPER(II) COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency* cm⁻¹</th>
<th>Intensity**</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CuLCl)₂</td>
<td>3400</td>
<td>w,br</td>
<td>O-H stretching band</td>
</tr>
<tr>
<td></td>
<td>3197</td>
<td>s,br</td>
<td>N-H stretching band of ²° amine</td>
</tr>
<tr>
<td></td>
<td>3145</td>
<td>s,br</td>
<td>N-H stretching band of ¹° amine</td>
</tr>
<tr>
<td></td>
<td>2960</td>
<td>vs,br</td>
<td>Nujol, C-H stretch</td>
</tr>
<tr>
<td></td>
<td>1599</td>
<td>s,sh</td>
<td>N-H bending</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>s,br</td>
<td>Nujol, -CH₂- bend</td>
</tr>
<tr>
<td></td>
<td>837</td>
<td>m,sh</td>
<td>O-H, uncoordinated</td>
</tr>
<tr>
<td></td>
<td>332</td>
<td>m,sh</td>
<td>Cu-N stretching band</td>
</tr>
<tr>
<td>(CuLBr)₂</td>
<td>3390</td>
<td>s,br</td>
<td>O-H stretching band</td>
</tr>
<tr>
<td></td>
<td>3206</td>
<td>s,br</td>
<td>N-H stretching band of ²° amine</td>
</tr>
<tr>
<td></td>
<td>3130</td>
<td>s,br</td>
<td>N-H stretching band of ¹° amine</td>
</tr>
<tr>
<td></td>
<td>2960</td>
<td>vs,br</td>
<td>Nujol, C-H stretch</td>
</tr>
<tr>
<td></td>
<td>1591</td>
<td>s,sh</td>
<td>N-H bending</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>s,br</td>
<td>Nujol, -CH₂- bend</td>
</tr>
<tr>
<td></td>
<td>834</td>
<td>m,sh</td>
<td>O-H, uncoordinated</td>
</tr>
<tr>
<td></td>
<td>329</td>
<td>m,sh</td>
<td>Cu-N stretching band</td>
</tr>
</tbody>
</table>

* cm⁻¹

** vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = sharp.
of 1.86 B.M. and 1.87 B.M., respectively. The deprotonated complexes are believed to be dimeric with both exhibiting antiferromagnetic interactions. As shown in Table II, both deprotonated complexes at room temperatures display moments slightly larger than the spin-only value. However, it is observed that as the temperature is lowered the moments decrease to subnormal values. Using the Bleaney-Bowers equation\textsuperscript{10} for dimeric copper(II) complexes, the average $J$ values were calculated to be $-46.5$ cm$^{-1}$ and $-60.1$ cm$^{-1}$ for the chloride and bromide, respectively. The $J$ values indicate the singlet-triplet splittings. The negative $J$ values further support the assumption of antiferromagnetic interactions being present in the new complexes. Although the moments and $J$ values indicate weak interactions, this sort of interaction is typical of halogen-bridged dimeric systems.\textsuperscript{11} Also, it is to be noted that the deprotonated bromide complex has a stronger interaction than the chloride.

This is generally observed in bromide and chloride analogs where the bridging geometries are very similar. In the work reported by Estes et al.,\textsuperscript{12} the out-of-plane Cu-Br separation in $[\text{Cu(tmen)}\text{Br}_2]_2$ (tmen = tetramethylethlenediamine)


was only 0.05 Å longer than in the chloride analog. Since the covalent radius of bromine is about 0.15 Å larger than that of chlorine, the near-equivalence of the metal-halogen separation permits the bromide orbitals to overlap with the copper(II) "d" orbitals more than the smaller chlorine orbitals.

Fig. 11--Plots of the reciprocal of $\chi_M$ against $T$ in (a) antiferromagnetic, (b) simple paramagnetic and (c) ferromagnetic complexes.

When the plot of the reciprocal of $\chi_M$ against $T$ yields a linear plot intercepting the origin, the complex is said to follow the Curie law\textsuperscript{13} which is usually observed for normal paramagnetic substances. If the plot produces a linear plot which does not intercept at the origin, the complex is said to follow the Curie-Weiss law\textsuperscript{14}. The non-zero intercept is


\textsuperscript{14}Ibid., p. 15.
referred to as the Weiss constant, \( \theta \), of the complex. The sign of the Weiss constant, suggests if ferromagnetism or antiferromagnetism is present. A positive Weiss constant indicates ferromagnetism, whereas a negative Weiss constant indicates antiferromagnetism. The three possible cases are illustrated in Figure 11.

Extrapolation of a least squares fitting for the plots of the reciprocal of \( \chi_M \) against \( T \) for the deprotonated complexes yields \( \theta \) values of -26.1 and -14.7 for the bromide and chloride, respectively. As discussed, the negative Weiss constants imply that antiferromagnetic interactions are operative in these complexes. The plots of the reciprocal of \( \chi_M \) against \( T \) for the deprotonated complexes are shown in Figure 12.

Although a linear plot of the reciprocal of \( \chi_M \) against \( T \) is generally for simple paramagnetic substances, a ferromagnetic or antiferromagnetic substance will closely follow the Curie-Weiss law when at a temperature range above the Curie or Neel temperature. The fact that the deprotonated complexes magnetic measurements were obtained above their Neel temperature is supported by the increase in the magnetic susceptibilities while the moment decreases upon lowering the temperature. Many halogen-bridged dimers have Neel temperatures below liquid nitrogen temperatures.

**Electronic Spectra**

The solid state spectra of both deprotonated copper(II) complexes are very similar, illustrating similar geometry.
Fig. 12--Plots of the reciprocal of $\chi_M$ against $T$ for $(\text{CuLCl})_2$ and $(\text{CuLBr})_2$. 
The deprotonated complexes were insoluble in the usual non-coordinating solvents. As a result, no molar absorptivity values could be obtained. With the aid of the infrared spectra and the crystal data work of Nasanen et al.,\textsuperscript{15} the deprotonated copper(II) complexes are considered to be square planar. The band maxima of the complexes are listed in Table III.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{diagram.png}
\caption{Energy level diagram showing an octahedral complex being distorted to a square planar configuration.}
\end{figure}

An energy level diagram\textsuperscript{16} showing the further splitting of the transition metal "d" orbitals as an octahedral complex is progressively distorted to a square planar complex is illustrated in Figure 13.


As shown in Figure 13, the degeneracy of the \( d_{x^2-y^2} \) and \( d_z^2 \) orbitals is removed by the removal of the ligands on the z-axis. Also, the \( d_{xy} \), \( d_{xz} \), and \( d_{yz} \) orbitals are split with the \( d_{xy} \) orbital being raised to a higher energy, while the \( d_{xz} \) and \( d_{yz} \) orbitals remain degenerate being moved to a lower energy. This splitting is explained by the reasoning that in a square planar complex the "d" orbitals containing any "z" component will be less perturbed than in an octahedral complex. Although the energy level diagram of Figure 13 shows the \( d_z^2 \) orbital slightly above the degenerate \( (d_{xz}, d_{yz}) \) pair, it is suggested that the positions could possibly reverse in some cases.\(^{16}\)

With the energy level diagram of Figure 13, three absorption transitions should be possible for a copper(II) square planar complex. These are \( d_{xy} \rightarrow d_{x^2-y^2} \), \( d_z^2 \rightarrow d_{x^2-y^2} \), and the \( (d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2} \) transitions. The band maxima listed in Table II and shown in Figures 7 and 8 is probably due to the d-d transition of the lowest energy \( (d_{xy} \rightarrow d_{x^2-y^2}) \) with the shoulder being the \( d_z^2 \rightarrow d_{x^2-y^2} \) transition. It is noticed that the transition of highest energy \( (d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}) \) is larger in a square planar complex than in an octahedral complex. Therefore, the \( (d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2} \) transition is expected to be at a much higher energy than the lower two transitions. With this resulting, the \( (d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2} \) transition is probably overlapped by the huge absorption beginning near 23,000 cm\(^{-1}\) which is believed to be due to a charge-transfer transition.
**Electron Spin Resonance**

The technique of electron spin resonance involves the direct measurement of the first order Zeeman effect. The Zeeman effect is the interaction of the angular momentum of the system with an applied magnetic field. The angular momentum of a free electron has two possible orientations under the influence of a magnetic field. The different orientations are known as the "spins" of the electron. In absence of a magnetic field, the "spins" are degenerate with $M_S$ values of $-1/2$ and $+1/2$. Upon applying a magnetic field, the degeneracy is lifted with separation of the states increasing as the strength of the magnetic field, $H$, increases.\(^{17}\) This is illustrated in Figure 14.

Fig. 14—Variation of spin energy levels with magnetic field strength.

When a molecule is radiated with a constant energy, $h\nu$, and the spin states are split by the magnetic field equal to the energy difference between the quantized energy levels of the spin states, a transition of $\Delta M_S = 1$ is observed. This transition is shown in Figure 14.

A molecule in which two unpaired electrons interact with one another is a spin triplet with $M_S$ values of $-1$, $0$, and $+1$. As the single electron case, these spin states are degenerate in unperturbed conditions. Unlike the single electron case, as ligands arrange about a metal ion with triplet spin state, the degeneracy is lifted such that the spin states of different magnitudes are separated. This is known as "zero-field splitting". The "zero-field" refers to the absence of a magnetic field. The introduction of a magnetic field removes the degeneracy further. The removal of the spin triplet state degeneracy is diagrammatically shown in Figure 15.

![Diagram of Figure 15](image)

**Fig. 15**--Removal of the degeneracy of the spin triplet states due to (a) the zero-field splitting and (b) the magnetic field.

---

As seen in Figure 15, three transitions are possible for a triplet spin state. There are two $\Delta M_S = 1$ transitions, and one $\Delta M_S = 2$ transition. There is no $\Delta M_S = 2$ transition in monomeric copper(II) complexes.

Both deprotonated complexes exhibit a spin triplet state. This is strongly supported by the magnetic susceptibility data and the presence of a large "half-field" ($\Delta M_S = 2$) transition.\(^{19}\) The $\Delta M_S = 2$ transition is called the "half-field" because it occurs at about half the average $H$ for the $\Delta M_S = 1$ transitions.\(^{20}\) The "half-field" transition for both deprotonated complexes was near 1550 gauss (1541 gauss for the chloride and 1549 gauss for the bromide at a frequency of 9.150 GHz).

It was stated previously that three transitions are possible in a spin triplet molecule. If the molecule could be oriented with respect to the $x$, $y$ and $z$ axes, the absorptions corresponding to the $\Delta M_S = 1$ transitions could be split into three individual lines. Since the "half-field" transition is isotropic,\(^{21}\) only one $\Delta M_S = 2$ absorption is observed. Thus, seven transitions are possible to detect. If the $x$ and $y$ axes are equal, or almost equal, the number of lines will be reduced to four. In a square planar complex (where the $x$ and $y$ axes

---


are equal) four transitions are expected. In the present work, as with other reports of square planar complexes,\textsuperscript{22} the electron spin resonance spectra of the deprotonated complexes are confusing.

Although no gyromagnetic ratio, $g$, in equation (7) was able to be obtained from the electron spin resonance spectra, the observed absorptions below 3000 gauss are listed in Table V. The resolution of the rest of the spectra was poor with very broad absorptions.

**TABLE V**

**SUMMARY OF ESR TRANSITION ASSIGNMENTS***

<table>
<thead>
<tr>
<th>Complex</th>
<th>Field Strength**</th>
<th>Intensity***</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CuLCl})_2$</td>
<td>2683</td>
<td>$w,sh$</td>
</tr>
<tr>
<td></td>
<td>1951</td>
<td>$m,br$</td>
</tr>
<tr>
<td></td>
<td>1541</td>
<td>$s,sh$</td>
</tr>
<tr>
<td></td>
<td>834</td>
<td>$w,br$</td>
</tr>
<tr>
<td>$(\text{CuLBr})_2$</td>
<td>2395</td>
<td>$s,br$</td>
</tr>
<tr>
<td></td>
<td>1831</td>
<td>$w,sh$</td>
</tr>
<tr>
<td></td>
<td>1549</td>
<td>$s,sh$</td>
</tr>
<tr>
<td></td>
<td>629</td>
<td>$w,br$</td>
</tr>
</tbody>
</table>

* at a frequency of 9.150 GHz.

** gauss.

*** $w$ = weak, $m$ = medium, $s$ = strong, $sh$ = sharp, $br$ = broad.

CHAPTER III

CONCLUSION

It is concluded that both deprotonated copper(II) complexes have antiferromagnetic interactions with a singlet ground state and a thermally accessible triplet excited state. This is supported by a decrease in the magnetic moments with a decrease in temperature, and further supported by the negative J and θ values. The fact that the susceptibilities increase, with a decrease in temperature, indicates that the temperature range studied was above the Neel temperature.

The diaminealcohol behaves as a bidentate, instead of a tridentate, in the parent and deprotonated complexes. This has been confirmed in the parent complexes by crystal data.\(^1\) This is concluded in the deprotonated complexes due to the presence of an O-H stretching band in the infrared spectra and on the presence of a medium to large band near 835 cm\(^{-1}\) which has been reported\(^2\) as indicating an uncoordinated hydroxyl group in diaminealcohols.

Since the hydroxyl group is not coordinated and the elemental analyses show a copper to ligand to halogen ratio


of 1:1:1, it is concluded that the diaminealcohol was deprotonated at an amine nitrogen. Although Watt and Thompson\textsuperscript{3} were not able to distinguish which amine nitrogen was deprotonated in their study, it is believed with the studies of the present work that deprotonation occurred at the primary amine position. Although free hydroxyl groups are well known to be more acidic than most free amine groups, it is possible for the amine group's acidity to be enhanced upon coordination. Also, it is of interest to note that the procedure of preparation clearly shows the weak acidity of the hydroxyl group in N-(2-hydroxyethyl)ethylenediamine compared to some aminealcohols. Uhlig and Staiger\textsuperscript{4} have prepared and studied a number of aminealcohol copper(II) complexes. In their work, the hydroxyl groups were deprotonated, and oxygen was the bridging atom. In their synthesis, the complexes were formed by a metal to aminealcohol ratio of 1:2 where the extra mole of ligand, presumably, behaved as the base in removing the proton from the coordinated hydroxyl group. This does not happen with the diaminealcohol of present interest.

Since both complexes exhibit similar infrared spectra, electronic spectra, electron spin resonance spectra and magnetic properties, the bromide and chloride complexes should


have the same structure. It is believed that the bridging angles are approximately the same in both complexes, since the bromide has a slightly stronger interaction than the chloride. The proposed structure, based on the work of Nasanen et al. with the present work, is illustrated in Figure 16.

\[
\begin{align*}
&\text{H}_2\text{C} & \text{NH} & X & \text{NH} & \text{Cu} & \text{Cu} & \text{H}_2\text{C} \\
&\text{H}_2\text{C} & \text{NH} & X & \text{NH} & \text{CH}_2 & \text{CH}_2 & \text{C}_2\text{H}_4\text{OH} \\
&\text{C}_2\text{H}_4\text{OH} & & & & & & \\
&\text{X} = \text{Cl, Br}
\end{align*}
\]

Fig. 16—Proposed structure of \((\text{CuLX})_2\) complexes

---


## Physical Constants

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
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<tbody>
<tr>
<td>Avogardo's number</td>
<td>N</td>
<td>$6.0225 \times 10^{23}$ mole$^{-1}$</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>$\beta$</td>
<td>$9.2732 \times 10^{-21}$ erg/ gauss</td>
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<tr>
<td>Boltzmann's constant</td>
<td>k</td>
<td>$1.3805 \times 10^{-16}$ erg/ deg</td>
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<td>Gyromagnetic ratio for a free electron</td>
<td>$g_e$</td>
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<tr>
<td>Planck's constant</td>
<td>h</td>
<td>$6.6256 \times 10^{-27}$ erg-sec</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY

Books


Articles


