MAGNETIC PROPERTIES OF COPPER(II) COMPLEXES OF SCHIFF BASES

THESIS

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

By

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The synthesis and characterization of two new Schiff base copper(II) complexes are reported. These are Cu(acac:2-amino-1-phenylethanol) and Cu(acac:2-amino-1-butanol). The ligands, derived from acetylacetone and the appropriate aminoalcohol, are dibasic tridentates with O,N,O donor atoms.

The magnetic properties of the complexes were studied at several temperatures between 78 °K and 296 °K. The magnetic moment of Cu(acac:2-amino-1-phenylethanol) varied little with temperature, and that of Cu(acac:2-amino-1-butanol) increased as the temperature was lowered. This is in contrast to the magnetic moment of Cu(acac:ethanolamine), which decreases as the temperature decreases.

Molecular weight data, infrared spectra, magnetic data, electronic spectra, and electron spin resonance spectra of both complexes 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 magnetic properties of transition metal complexes have been of interest to chemists for sometime, since information can be obtained about the structure and bonding in complexes through studies of these properties. Copper (II), having one unpaired electron, is a $3d^9$ system and often forms polynuclear complexes. Often these complexes exhibit subnormal magnetic moments and are of an antiferromagnetic nature. This means that in a dimeric molecule the unpaired electrons on the copper(II) interact through some mechanism and are paired. When this happens, the electrons are presumed to have available to them a low-energy spin singlet state and a higher energy spin triplet state which is thermally accessible. At room temperature some population of both states will occur. This is shown diagramatically in Figure 1.

\[
\begin{array}{c}
\text{triplet} \\
(S=1; \ 2S+1=3) \\
\text{singlet} \\
(S=0; \ 2S+1=1)
\end{array}
\]

Fig. 1--Singlet-Triplet Splitting of Copper(II) Ions Exhibiting Magnetic Interaction.
Such a molecule is Cu(acac:propanolamine)$^1$, I,

\[
\begin{align*}
\text{H}_3\text{C} & - \text{O} - \text{Cu} - \text{O} - \text{C} - \text{H}_2 \\
\text{H} & - \text{C} - \text{N} & \text{CH}_2 & - \text{CH}_2
\end{align*}
\]

which has a subnormal magnetic moment of 0.41 B.M. at room temperature, and has been shown by x-ray crystallographic studies to be dimeric. The structure of this dimer$^1$ is shown in Figure 2.

Fig. 2--Structure of the Cu(acac:propanolamine) Dimer (from ref. 1).

The copper atoms and all atoms bonded to them lie in a plane with oxygen atoms occupying the bridging positions. The stereochemistry about these oxygen atoms is also planar.

Another complex which has been characterized is Cu(acac:ethanolamine)$^1$, II. Based on x-ray crystallographic studies, it has been shown to be a tetramer which has a room temperature magnetic moment of 1.87 B.M. and has been shown to exhibit both ferromagnetic and antiferromagnetic interactions$^2$.

![Diagram of Cu(acac:ethanolamine) tetramer]

The tetramer may be thought of most easily as being two dimers, one of which has been rotated 90° with respect to the other. The structure of the Cu(acac:ethanolamine) tetramer is shown in Figure 3. In each dimer the atoms about the copper(II) are not in the same plane, and the bridging oxygen atoms do not have planar coordination. The Cu-Cu distance within a dimer is 3.006 ± 0.008 Å, while the Cu-Cu distance between the dimers is 3.259 ± 0.008 Å.

Fig. 3--Structure of the Cu(acac:ethanolamine) Tetramer (from ref. 1).
Analogs of these compounds have been prepared by replacing acetylacetone with salicylaldehyde\textsuperscript{3,4,5} or pyrrole-2-carboxaldehyde\textsuperscript{6} and by placing a substituent on the aminoalcohol portion of the ligand\textsuperscript{6}.

Replacement of acetylacetone with salicylaldehyde yielded Cu(sal:propanolamine), III, which is a dimer with a reported room temperature magnetic moments of 0.39 B.M.\textsuperscript{3} and 0.49 B.M.\textsuperscript{4} and with the proposed structure\textsuperscript{4} shown in Figure 4.

---


Cu(sal:ethanolamine), IV, is a tetramer which is thought to be of similar structure to Cu(acac:ethanolamine)

\[ \text{IV} \]

and has a room temperature magnetic moment of 1.83 B.M.

The proposed structure of Cu(sal:ethanolamine) is shown in Figure 5.

Fig. 5--Proposed Structure of Cu(sal:ethanolamine) tetramer (from ref. 5).

The complexes prepared using pyrrole-2-carboxyl-aldehyde in place of acetylacetone produced two changes in the ligand, but in the reported compounds no great changes in the structure of the complex were apparent. Cu(pyrr:propanolamine)\(^7\), V, and Cu(pyrr:ethanolamine)\(^6\), VI,
yielded a dimer and a tetramer respectively, and these had room temperature magnetic moments of 0.44 B.M. and 1.89 B.M. The structure of Cu(pyrr:propanolamine) is known and is shown in Figure 6.

Fig. 6--Structure of the Cu(pyrr:propanolamine) Dimer (from ref. 7).

In the series of complexes prepared using N-(hydroxy-alkyl)pyrrole-2-aldimines as ligands as substituent was

added to the carbon atom next to the bridging oxygen atom of the complex. This complex, Cu(pyrr:isopropanolamine),\textsuperscript{7} VII, has a room temperature magnetic moment of 1.80 B.M.,

\[ \text{VII} \]

and it, as well as Cu(pyrr:ethanolamine), are proposed to have the tetrameric structure\textsuperscript{6} shown in Figure 7.

\[ \text{Fig. 7--Proposed Structure of the Cu(pyrr:ethanolamine) and Cu(pyrr:isopropanolamine) Tetramers (from ref. 6).} \]

This work reports two new copper(II) Schiff base complexes, Cu(acac:2-amino-1-phenylethanol), VIII, and Cu (acac:2-amino-1-butanol), IX. No x-ray studies are available
for these compounds, but molecular weights indicate that both are tetrameric. The magnetic data indicates structures similar to that of the Cu(acac:ethanolamine) tetramer with Cu(acac:2-amino-1-phenylethanol) having a room temperature magnetic moment of 1.80 B.M. and Cu(acac:2-amino-1-butanol) having a room temperature magnetic moment of 1.86 B.M. The proposed structure of these complexes is presented in Figure 8.

Fig. 8--Proposed Structure of Cu(acac:2-amino-1-phenylethanol) and Cu(acac:2-amino-1-butanol).
This work was undertaken to prepare new tetrameric complexes of copper(II), to investigate the effects that substituents on the aminoalkoxide portion of the Schiff base have on the properties of the complexes, and to consider possible mechanisms for electron exchange between the metal atoms.
CHAPTER II

COPPER(II) COMPLEXES OF SCHIFF BASES FORMED FROM ACETYLACETONE AND VARIOUS ALCOHOLAMINES

Experimental and Results

Reagents

Acetylacetone was obtained from Eastman Organic Chemicals, 2-amino-1-phenylethanol was obtained from the Aldrich Chemical Company, and 2-amino-1-butanol was obtained from Matheson, Coleman and Bell. Copper(II) acetate monohydrate and potassium hydroxide were obtained from the J. T. Baker Chemical Company. All chemicals used were of reagent grade quality.

Preparation of the Complexes

Cu(acac:2-amino-1-phenylethanol) was prepared by refluxing 3.50 grams of acetylacetone and 4.80 grams of 2-amino-1-phenylethanol in 100 ml of anhydrous methanol for one hour. The resulting yellow solution was added dropwise to 6.29 grams of copper acetate monohydrate in 150 ml of refluxing anhydrous methanol. After refluxing for 18 hours, the mixture was filtered, yielding a blue powder which was recrystallized from chloroform to give blue microcrystals. The yield was about 75%
Cu(acac:2-amino-1-phenylethanol) with a melting point of 219 - 219.5° C.

Cu(acac:2-amino-1-butanol) was prepared as above using 3.50 grams of acetylacetone, 3.12 grams of 2-amino-1-butanol, and 6.29 grams of copper acetate monohydrate. 3.93 grams of potassium hydroxide was also added. Recrystallization from acetone gave blue microcrystals. The yield was about 75%

Cu(acac:2-amino-1-butanol) with a melting point of 216 - 217° C.

**Elemental Analysis**

The per cent carbon, hydrogen, and nitrogen were determined by PCR, Inc. of Gainsville, Florida. The percentage copper was determined by electrodeposition of copper metal on a platinum electrode using a Sargent-Slomin Electrolytic Analyzer. The analytical data are presented in Table I.

<table>
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<th>TABLE I</th>
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<td>ANALYTICAL DATA FOR COPPER COMPLEXES</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Complex</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(acac:2-amino-1-phenylethanol)</td>
<td>Calcd 55.60</td>
<td>5.38</td>
<td>4.98</td>
<td>22.63</td>
</tr>
<tr>
<td></td>
<td>Found 54.79</td>
<td>5.43</td>
<td>4.75</td>
<td>22.34</td>
</tr>
<tr>
<td>Cu(acac:2-amino-1-butanol)</td>
<td>Calcd 46.44</td>
<td>6.50</td>
<td>6.02</td>
<td>27.34</td>
</tr>
<tr>
<td></td>
<td>Found 46.38</td>
<td>6.75</td>
<td>5.89</td>
<td>26.72</td>
</tr>
</tbody>
</table>
Molecular Weight Determinations

The molecular weights of the complexes were determined in benzene solution on a Mechrolab Model 310A Vapor Pressure Osmometer using Benzil as the calibrant. The molecular weight of Cu(acac:2-amino-1-phenylethanol) was found to be 1069 and that of Cu(acac:2-amino-1-butanol) was found to be 903, compared to theoretical values of 1123 and 931, respectively.

Infrared Spectra

Infrared spectra were obtained using a Perkin-Elmer Model 621 instrument scanning the range of 200 cm$^{-1}$ to 4000 cm$^{-1}$. Nujol- and fluorlube-mull techniques and cesium iodide plates were employed. The spectra of Cu(acac:2-amino-1-phenylethanol) and Cu(acac:2-amino-1-butanol) are shown in Figure 9 and 10, respectively.

Electronic Spectra

The electronic spectra were obtained on a Cary 14 Recording Spectrophotometer in benzene solutions. Matched quartz sample cells were employed, and the region from 3846 cm$^{-1}$ to 50,000 cm$^{-1}$ was scanned. The absorption maximum for Cu(acac:2-amino-1-phenylethanol) is 16,000 cm$^{-1}$ ($\varepsilon = 105$ l. mole$^{-1}$ cm$^{-1}$) and that of Cu(acac:2-amino-1-butanol) is 16,529 cm$^{-1}$ ($\varepsilon = 107$ l. mole$^{-1}$ cm$^{-1}$). The spectra of this region of Cu(acac:2-amino-1-phenylethanol) and Cu(acac:2-amino-1-butanol) are shown in Figures 11 and 12, respectively.
Figure 9--Infrared Spectrum of Cu(acac:2-amino-1-phenylethanol).

% Transmittance

Frequency (cm⁻¹)

3200 3000 2800
Fig. 9 (continued)
Fig. 9 (continued)
Fig. 9 (continued)
Figure 10--Infrared Spectrum of Cu(acac:2-amino-1-butanol).
Fig. 10 (continued)

% Transmittance

Frequency (cm$^{-1}$)

2600 2400 2200
Fig. 10 (continued)
Fig. 10 (continued)
Figure 11--Electronic Spectrum of Cu(acac:24amino-1-phenylethanol).
Figure 12--Electronic Spectrum of Cu(acac:2-amino-1-butanol).
Magnetic Data

The magnetic susceptibilities were obtained employing an Alpha Model 7500 Electromagnet and Regulated Power Supply System. The Guoy method\(^1\) of determination was used with mercury tetrathiocyanatocobaltate(II)\(^2\), Hg[Co(CNS)_4], as the calibrant, and the standard corrections were made for the diaganetism of the ligands and temperature independent paramagnetism, T.I.P., was taken to be $60 \times 10^{-6}$ c.g.s. units. The magnetic moments were calculated using the equation

$$\mu_{\text{eff}} = 2.83 \chi_M^\text{corr} \text{ T B.M.}$$

and experimental data.

The magnetic susceptibilities were measured at several temperatures between 296° K and 78° K. The room temperature and liquid nitrogen temperature measurements were obtained using published methods\(^1\). For other temperatures the apparatus shown in Figure 13 was used.

The tube containing the sample was suspended inside a cylindrical copper tube which was encased in an insulated glass jacket. Nitrogen gas which was cooled by being passed through a liquid nitrogen reservoir was passed through the glass jacket with the temperature being regulated by adjusting the flow rate of the nitrogen gas through the liquid nitrogen

---


Figure 13--Apparatus used at temperatures other than 296° and 78° K to determine susceptibilities.
reservoir. The temperature was measured using a copper-constantan thermocouple placed near the sample and connected to a Leeds and Northrup Model 8691 Millivolt Potentiometer with an ice-water bath as the reference temperature. An atmosphere of nitrogen gas was maintained around the sample to retard frost formation.

The average of four susceptibilities taken at 2, 4, 6, and 8 amps is given in Table II. The graphs of $(x_M^{corr})^{-1}$ vs. T for Cu(acac:2-amino-1-phenylethanol) is shown in Figure 14, and that for Cu(acac:2-amino-1-butanol) in Figure 15.

TABLE II
MAGNETIC DATA FOR COPPER COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp.(°K)</th>
<th>$x_M^{corr}$</th>
<th>$\mu_{eff}$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(acac:2-amino-1-phenylethanol)</td>
<td>296</td>
<td>1371</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>1592</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>223</td>
<td>1831</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>184</td>
<td>2182</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>2720</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>117</td>
<td>3537</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>5177</td>
<td>1.80</td>
</tr>
</tbody>
</table>

| Cu(acac:2-amino-1-butanol)       | 296       | 1467         | 1.86              |
|                                  | 261       | 1768         | 1.92              |
|                                  | 223       | 2080         | 1.93              |
|                                  | 184       | 2774         | 2.02              |
|                                  | 148       | 3443         | 2.02              |
|                                  | 117       | 4523         | 2.06              |
|                                  | 78        | 7584         | 2.18              |

$x \times 10^{-6}$ c.g.s. units.
Figure 14--Graph of $(\chi_M^{corr})^{-1}$ vs $T$ for Cu(acac:2-amino-1-phenylethanol).
Figure 15--Graph of $(\chi M^\text{corr})^{-1}$ vs $T$ for Cu(acac:2-amino-1-butanol).
Figure 16--Electron Spin Resonance Spectrum of Cu(acac: 2-amino-1-phenylethanol).
Figure 17--Electron Spin Resonance Spectrum of Cu(acac: 2-amino-1-butanol).
Electron Spin Resonance Spectra

The electron spin resonance spectra for the complexes were obtained employing powdered samples in quartz tubes with a small quantity of finely ground 2,2-Diphenyl-1-picryl-hydrazil as an internal standard. The instrument used was a Varian Model V-4502 ESR Spectrophotometer using a cylindrical cavity and a nine-inch electromagnet. The frequency of the microwave radiation was determined with a Hewlett-Packard Model 5340A Automatic Microwave Frequency Counter. The spectra of Cu(acac:2-amino-l-phenylethanol) and of Cu(acac:2-amino-l-butanol) are shown in Figures 16 and 17, respectively.

Discussion

Molecular Weight Determinations

Based on these investigations, both complexes were shown to be tetrameric in benzene solution.

Infrared Spectra

The major features of spectra for both complexes are similar. The Nujol mull spectra of Cu(acac:2-amino-l-phenylethanol) and of Cu(acac:2-amino-l-butanol) are shown in Figure 9 and 10, respectively.

The absence of a broad band of strong intensity in the region between 3100 cm\(^{-1}\) and 3700 cm\(^{-1}\) indicates that there is no water or solvent coordinated to the metal ion. A group
of very strong bands between \(2760\ \text{cm}^{-1}\) and \(3100\ \text{cm}^{-1}\) are assigned to the C-H stretching vibrations of the Nujol mulling agent, as well as the C-H stretching vibrations of the ligand. The strong band between \(1540\ \text{cm}^{-1}\) and \(1630\ \text{cm}^{-1}\) is attributed to the C=N stretch. The strong absorption between \(1415\ \text{cm}^{-1}\) and \(1470\ \text{cm}^{-1}\) and the medium to strong band between \(1335\ \text{cm}^{-1}\) and \(1380\ \text{cm}^{-1}\) are attributed to \(-\text{CH}_2-\) bending and \(-\text{CH}_2\text{-CH}_3\) bending vibrations from the Nujol mulling agent. Between \(1240\ \text{cm}^{-1}\) and \(1265\ \text{cm}^{-1}\) is a band of medium to strong intensity due to the C-N stretching vibration. A band, which is assigned to the C-O stretching vibration, appears between \(1035\ \text{cm}^{-1}\) and \(1060\ \text{cm}^{-1}\) with medium to strong intensity. Between \(720\ \text{cm}^{-1}\) and \(775\ \text{cm}^{-1}\) a band of medium to strong intensity due to the \(-\text{(CH}_2\text{)}_n-\) bending vibration of the aminoalkoxide portion of the ligand appears. This discussion can be applied to one or both of the complexes. The Cu(acac:2-amino-1-phenylethanol) complex has an additional absorption which appears as a shoulder at \(1600\ \text{cm}^{-1}\) on the C=N absorption. Table III summarizes the band assignments of the infrared spectra.
TABLE III
ASSIGNMENTS OF INFRARED ABSORPTION BANDS
FOR COPPER COMPLEXES

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity*</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>2760-3100</td>
<td>vs</td>
<td>C-H stretching vibration from Nujol</td>
</tr>
<tr>
<td>1540-1630</td>
<td>s</td>
<td>C=N stretching vibration</td>
</tr>
<tr>
<td>1600**</td>
<td>sh</td>
<td>C-C multiple bond stretching vibration</td>
</tr>
<tr>
<td>1415-1470</td>
<td>s</td>
<td>(-\text{CH}_2)- bending vibration from Nujol</td>
</tr>
<tr>
<td>1335-1380</td>
<td>m,s</td>
<td>C-CH(_3) bending vibration from Nujol</td>
</tr>
<tr>
<td>1240-1265</td>
<td>m,s</td>
<td>C-N stretching vibration</td>
</tr>
<tr>
<td>1035-1065</td>
<td>m,s</td>
<td>C-O stretching vibration</td>
</tr>
<tr>
<td>720-755</td>
<td>m,s</td>
<td>(-(\text{CH}(_2))_n)- bending vibration from ligand</td>
</tr>
</tbody>
</table>

*vs = very strong, s = strong, m = medium, sh = shoulder.

**Present only in Cu(II)(acac:2-amino-1-phenylethanol).

Electronic Spectra

In previously reported cube-like tetramers of copper(II) complexes, the coordination about the metal ion has been reported to be trigonal bipyramidal\(^3\). In this environment

the d-orbitals of the metal ion split into the energy
levels\textsuperscript{4} shown in Figure 18.

\begin{align*}
&\text{\underline{\hspace{1em} d}_{z^2}} \\
&\text{\underline{\hspace{1em} d}_{xy, d_{x^2-y^2}}} \\
&\text{\underline{\hspace{1em} d}_{xz, d_{yz}}} \\
\end{align*}

Figure 18--Splitting of the d-orbitals in a Trigonal Bipyramidal Environment (from ref. 4).

In this instance the nine d-electrons of copper(II) would fill the orbitals in such a way that the unpaired electron would reside in the orbital of highest energy, the \text{d}_{z^2} orbital. The electronic spectra of both complexes are presented in Figures 11 and 12, and Table III on page gives a summary of the frequencies of the maximum absorption bands and the molar absorptivities of these bands. These properties compare favorably with the band maximum, 15,748 \text{cm}^{-1} (\epsilon = 106 \text{ l. mole}^{-1} \text{ cm}^{-1}) of Cu(acac:ethanolamine) and are also similar to the values reported for the salicylaldehyde and pyrrole-2-carboxaldehyde analogs\textsuperscript{5,6}.


Magnetic Susceptibilities

The graphs of the inverse susceptibility versus temperature on pages give values for $\Theta$ of +2.1 K for Cu(acac:2-amino-1-phenylethanol) and +30.8 K for Cu(acac:2-amino-1-butanol). The positive values indicate that both complexes have ferromagnetic interactions\(^7\). In the cube-like structure formed by the four copper ions and the four bridging oxygen atoms the copper ions are in a trigonal bipyramidal environment\(^3\). In these complexes the possibility for both ferromagnetic and antiferromagnetic coupling is present\(^8\).

The super-exchange pathway for ferromagnetic coupling is shown in Figure 19. The $d_z^2$ orbitals of the copper ions, each containing one electron, overlap with two p-orbitals, each containing two electrons of the oxygen atoms. According to Anderson's theory\(^9,10,11,12\) this super-exchange pathway allows the electrons to align with their spins parallel and reinforce each other, resulting in ferromagnetic coupling.

Another super-exchange pathway is shown in Figure 20. This involves the $d_{z^2}$ orbitals of the metal ions and the oxygen atom's s-orbital containing two electrons. The result of exchange through this pathway is the electron spins aligning antiparallel due to orbital symmetry considerations. In this pathway the electron spins cancel one another out, giving antiferromagnetic coupling. The ferromagnetic coupling is apparently stronger than the antiferromagnetic coupling and the complexes exhibit an overall ferromagnetic interaction.
**Electron Spin Resonance Spectra**

The spectra do not show the resolution of the salicyl-dehydimine and the pyrroleimine analogs; thus, it is difficult to evaluate the parameters associated with the complexes. However, the lack of an absorption near 3200 gauss indicates that the complexes are free from monomeric impurities.
CHAPTER III

CONCLUSION

In this study two new Schiff base complexes with copper(II) have been synthesized and characterized. They are obtained free of solvent or water molecules in the coordination sphere of the metal ion. They are tetrameric in benzene solution and show no evidence of monomeric behavior in polycrystalline solid samples.

The stereochemistry which has previously been reported\(^1,2,3\) for the aliphatic aminoalkoxide chains seems to be continued with these complexes. That is, a three-carbon chain length gives a dimeric structure, while a two-carbon atom chain length gives a cube-like tetrameric structure. Ginsberg has stated that both ferromagnetic and antiferromagnetic couplings are present in this tetrameric structure\(^4\).


The addition of substituents to the aminoalkoxide linkage have produced a striking change in the magnetic properties of Cu(acac:2-amino-1-phenylethanol) and Cu(acac:2-amino-1-butanol) compared to the same properties of Cu(acac:ethanol-amine). The magnetic moment of Cu(acac:2-amino-1-phenylethanol) shows little variation as the temperature is lowered, but that of Cu(acac:2-amino-1-butanol) exhibits a definite increase under the same conditions as seen in Table II on page 26, while the magnetic moment of Cu(acac:ethanol-amine) decreases as the temperature is lowered.

This may be attributed to a steric hindrance imposed in the one complex which is not present in the other. This steric hindrance affects the Cu-O-Cu bond angles, and in doing so, will alter the magnetic properties by changing the ability of the $d_{z^2}$ orbitals of the copper ions to overlap with the s and p orbitals of the bridging oxygen atoms. Cu-O-Cu bond angles of 90° give best orbital overlap for ferromagnetic coupling, and Cu-O-Cu bond angles of 180° give best orbital overlap for antiferromagnetic coupling.

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The addition of substituents to the aminoalkoxide linkage have produced a marked change in the magnetic properties of Cu(acac:2-amino-l-phenylethanol) and Cu(acac:2-amino-1-butanol) compared to the same properties of Cu(acac:ethanolamine). The complexes with substituents are both ferromagnetically coupled, while (Cu(acac:ethanolamine) is coupled in an antiferromagnetic manner.

There is a striking difference in the magnetic properties of Cu(acac:2-amino-l-phenylethanol) and those of Cu(acac:2-amino-1-butanol) in that the magnetic moment of Cu(acac:2-amino-l-phenylethanol) remains essentially unchanged as the temperature is lowered, but that of Cu(acac:2-amino-1-butanol) exhibits a definite increase under the same conditions as seen in Table II on page 26. This may be attributed to a steric hindrance imposed in the one complex which is not present by the other. This steric hindrance affects the Cu-O-Cu bond angles, and in doing so, will alter the magnetic properties by changing the ability of the d_{z^2} orbitals of the copper ions to overlap with the s and p orbitals of the bridging oxygen atoms. Cu-O-Cu bond angles of 90° give best orbital overlap for ferromagnetic coupling, and Cu-O-Cu bond angles of 180° give best orbital overlap for antiferromagnetic coupling.

APPENDIX

BASIC MAGNETIC PRINCIPLES

The magnetic moment of a substance is not measured directly; however, the magnetic susceptibility is, and the two properties can be related by the equation

\[
\chi_M^{\text{corr}} = \frac{N\mu^2}{3kT} \tag{1}
\]

where \( \chi_M^{\text{corr}} \) is the corrected molar susceptibility,

\( N \) is Avagadro's number,

\( \mu \) is the effective magnetic moment,

\( k \) is Boltzman's constant,

and \( T \) is the temperature at which the measurement was taken.

Solving for the magnetic moment gives

\[
\mu_{\text{eff}} = \sqrt{\frac{3k}{N}} \sqrt[3]{\chi_M^{\text{corr}}} \tag{2}
\]

and inserting the values for the expression \( \sqrt{3k/N} \) yields

\[
\mu_{\text{eff}} = 2.83 \sqrt[3]{\chi_M^{\text{corr}}} \tag{2}
\]

For a single electron it can be shown that the magnetic moment \( \mu_s \), in Bohr Magnetons, is

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\(^2\) Cotton and Wilkinson, p. 537.
\[ \mu_s = g \sqrt{s(s+1)} \] (3)

where \( s \) is the absolute value of the spin quantum number of the electron, and \( g \) is the gyromagnetic ratio, the ratio of the magnetic moment to the angular momentum of the electron. The value of \( g \) for a free electron is 2.0023, which may be taken to be 2.00 as a good approximation. From equation (3) the moment for an electron may be calculated

\[ \mu_s = 2 \sqrt{\frac{1}{2}(\frac{1}{2}+1)} = \sqrt{3} = 1.73 \text{ B.M.} \]

Thus, any atom, ion, or molecule having one unpaired electron such as \( \text{H}, \text{Cu}^{++}, \text{or ClO}_2 \) should have a magnetic moment of 1.73 B.M. from the electron spin.

In transition metal ions there are up to seven unpaired electrons with a spin quantum number \( S \) which is the sum of the electron spin quantum numbers and equation (3) becomes \(^3\)

\[ \mu_s = 2 \sqrt{S(S+1)}. \] (4)

Also, the angular momentum of the electrons will make a contribution to the overall magnetic moment. The equation for a magnetic moment using the spin quantum number and the angular momentum quantum number of a particle is \(^4\)

\[ \mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \] (5)

\(^3\)Cotton and Wilkinson, p. 537.

\(^4\)Cotton and Wilkinson, p. 541.
For most transition metal ions the experimentally-found magnetic moment is usually between $\mu_S$ and the $\mu_{S+L}$ values.

In equations (1) and (2) $\chi_M^{corr} = \chi_A - \chi_L - T.I.P.$, where $\chi_A$ is the measured susceptibility, $\chi_L$ is the susceptibility of the ligand, and T.I.P. is the temperature independent paramagnetism of the metal ions in the substance. This temperature independent paramagnetism is a weak paramagnetism which arises from the coupling of the ground state of the system with one or more excited states, while under the influence of a magnetic field and is independent of the temperature of the system. Temperature independent paramagnetism is usually small, being from zero to five-hundred c.g.s. units per mole in value.

One method for determining the magnetic susceptibility is the Gouy method, in which a uniform rod of sample is placed in a nonuniform magnetic field and then the force on the sample is measured. When the field gradient over a given volume, $\delta V$, of the sample is $\delta H/\delta l$, where $\delta H$ is magnetic field strength, and $\delta l$ is the length of the sample, then the force, $\delta F$, which is exerted, is\(^5\)

$$\delta F = (k_1 - k_2)\delta VH^2/\delta l$$  \hspace{1cm} (6)

where $k_1$ and $k_2$ are the susceptibilities per unit volume.

of the specimen and the displaced medium, respectively.
Integrating over the length of the sample from $H = H_1$ at zero length to $H = H_0$ at length $l$ yields

$$F = (k_1 - k_2)V(H_1^2 - H_0^2)/2l.$$  \hspace{1cm} (7)

When $F$, in dynes, is replaced by $wg$, where $w$ is in grams and $(H_1^2 - H_0^2)$ by $H^2$ and rearranged, then

$$k_1 = k_2 + 2lgw/VH^2$$  \hspace{1cm} (8)

however\(^6\), $k = \chi \rho = \chi W/V$, where $W$ is the total sample weight and $\rho$ is its density. Substituting and rearranging

$$\chi_g = (k_2V + 2glw/H^2)/W$$  \hspace{1cm} (9)

where $\chi_g$ is the gram susceptibility of the compound. When the experiment is carried out in a nitrogen atmosphere, the $k_2V$ term may be taken to be zero, since $V$ is small and $k$ for nitrogen gas $= 0.0004 \times 10^{-6}$ c.g.s. units\(^7\). Thus, equation (9) reduces to

$$\chi_g = (2gl/H^2)(w/W)$$  \hspace{1cm} (10)

\(^6\)Earnshaw, p. 85.

\(^7\)Earnshaw, p. 92.
By using a compound of well known susceptibility, the susceptibility of an unknown compound may be obtained as is seen when equation (9) is rearranged

\[ \frac{\chi_k W_k}{W_k} = \frac{2g_1}{H^2} \]

for the standard compound, and

\[ \frac{\chi_s W_s}{W_s} = \frac{2g_1}{H^2} \]

for the unknown compound, and thus

\[ \frac{\chi_k W_k}{W_k} = \frac{\chi_s W_s}{W_s} \]  \hspace{1cm} (11)

Two compounds which make quite good standards are mercury tetrathiocyanatocobaltate(II), \( \text{Hg}[\text{Co(CNS)}_4] \), and trisethylenediaminennickel(II) thiosulfate, \( \text{Ni(en)}_3 \text{S}_2 \text{O}_3 \), whose \( \chi_g \) values at 20° C are \( 16.44 \times 10^{-6} \) c.g.s. units and \( 11.03 \times 10^{-6} \) c.g.s. units, respectively. These compounds have respective \( \theta \) values of \( 10^\circ \text{K} \) and \( 0^\circ \text{K} \). By using the Curie-Weiss relationship, \( \chi_k \) at any temperature may be calculated using

\[ \chi_1(T_1-\theta) = \frac{C}{T_1-\theta} = \chi_2(T_2-\theta) \]

or

\[ \chi_1 = \frac{\chi_2(T_2-\theta)}{(T_1-\theta)}. \]  \hspace{1cm} (12)

The value of \( \theta \) in the Curie-Weiss law

\[ \chi = \frac{C}{(T-\theta)} \]  \hspace{1cm} (13)

may be determined by finding the molar susceptibility at a large range of temperatures, then plotting the inverse susceptibility vs the temperature at which the measurement

\^8 Earnshaw, p. 87.
was taken and extrapolating the best straight line through these points. The point where this line crosses the temperature axis is equal to $\theta$. Figure 21 shows how this intercept indicates (a) simple paramagnetism, (b) ferromagnetism, and (c) antiferromagnetism. In other words, if $\theta$ is zero, simple paramagnetism is present; if $\theta$ is positive, the compound is ferromagnetic; and if $\theta$ is negative, the compound is antiferromagnetic$^9$.

\[ (\chi_M^{corr})^{-1} \]

\[ \text{Temperature} \]

Figure 21--Graphs of the inverse susceptibility vs temperature showing (a) simple paramagnetism, (b) ferromagnetism, and (c) antiferromagnetism.

In Figure 22 the relationships of (a) simple paramagnetism, (b) ferromagnetism, and (c) antiferromagnetism with temperature are shown$^{10}$. The curves (b) and (c) have

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distinct discontinuities. At temperatures above these points of discontinuity, $T_C$ and $T_N$, the compounds behave as simple paramagnets, but below the Curie temperature, $T_C$, or the Néel temperature, $T_N$, interatomic interactions have magnitudes comparable to the thermal energies at the Curie and Néel temperatures, and these become even greater as the temperature is further reduced.

For a ferromagnetic system, the moments of the individual ions align themselves parallel, and thus reinforce each other. However, above the Curie temperature, the thermal energy is sufficient to randomize the orientations.

In an antiferromagnetic system, the moments align antiparallel and thus cancel out one another. Above the Néel
temperature thermal energy is great enough to randomize orientations. This type of magnetism has long been the most interesting for inorganic chemists, because it can be taken as a measure of the bonding characteristics in a compound containing two or more paramagnetic centers.
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