MAGNETIC PROPERTIES OF METAL(II)
SCHIFF BASE COMPLEXES

THESIS

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

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MASTER OF SCIENCE

By

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Ligands prepared from various combinations of aldehydes and ketones with the appropriate aminealcohol were complexed with cupric acetate monohydrate. The complexes with O,N,O or N,N,O donor atoms were synthesized to study the influences of the ligand on molecular structure, spin-spin interaction, and on the value of the exchange integral.

The magnetic data indicated that of the eight Cu(II) complexes discussed, two behaved differently from known analogous compounds. Cu(benzoylacetone:ethanolamine) was compared to Cu(acac:ethanolamine), and Cu(pyrr:o-aminophenol) was compared to Cu(acac:o-aminophenol). Each pair of complexes was postulated to have the same molecular structure.

The synthesis and characterization of Mn(pyrr:o-aminophenol)$_2$H$_2$ is also discussed. The following physical data were collected and discussed: elemental analysis, melting point, molecular weight, infrared spectra, electronic spectra, and magnetic susceptibility.
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CHAPTER I

INTRODUCTION

In recent years there has been considerable interest in spin-spin coupling of polynuclear metal (II) complexes (6, 12, 16). Many of the investigations began nearly twenty years ago, but the interest has not waned. In fact, as recently as 1976, Sinn (24, 25) reported the crystal structures of three substituted (salicylaldehyde:propanolamine) tridentate Cu(II) Schiff base complexes. Many questions remain unanswered; and with the advent of automatic diffractometers, x-ray studies are providing experimental data for the theoreticians.

One of the major studies being conducted involves the ligand and the structural modifications it may produce on the environments of the metal atoms and the bridging oxygens. In particular, where binuclear complexes are formed with tridentate ligands, there is usually a bridging oxygen between the central copper ions. Studies have been reported (12, 22) that correlate the strength of antiferromagnetic interactions with this bridging Cu-O-Cu angle. The subsequent hypotheses were made after interpreting experimental evidence provided by workers over several years. Some of the results supporting the theoreticians shall be discussed.
Around 1957, Kishita and coworkers (18-20) reported the synthesis and room temperature magnetic moments of three cupric Schiff base complexes. The effective magnetic moments at 287°K were reported as follows: Cu(acac:o-aminophenol), I, 1.37 BM; Cu(benzoylacetone:o-aminophenol), II, 1.11 BM; and Cu(sal:o-aminophenol), III, 1.34 BM.

Since these were bivalent tridentate ligands, it was presumed that copper (II) might have the unusual coordination number of three. If that had been the case, the unpaired electron on copper would have given an observed moment close to 1.73 BM per copper ion. Since all the moments were in fact subnormal, a dimer formulation leading to spin-spin coupling between the copper atoms was strongly considered. At that time, however, superexchange via oxygen had not been considered as a mode for this coupling (1-4). In 1961, Barclay, Harris, and coworkers (5) published the x-ray crystal structure of Cu(acac:o-aminophenol), and concurrently performed the variable temperature susceptibility only to discover
that the magnetic behavior was similar to that of copper acetate monohydrate (9). The molecular structure, Fig. 1,

![Molecular Structure of Cu(acac:o-aminophenol)](from ref. 5).

answered the questions raised by Kishita, et al., because the Cu-Cu bond length of 3.00 Å was too long to afford direct interaction as in \([\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}]_2\). Fig. 2 illustrates the "stacked dimer" relationship between the two copper dimers in the crystalline molecule. The peculiarity is that Cu(1) has a square pyramidal environment, while Cu(3) has a square planar coordination. Complex I was believed to be the first complex reported to behave
magnetically like copper acetate monohydrate without having the same structure. Hatfield and Inman (11), in 1969, also reported the variable temperature measurements and discussed the value of the exchange integral (21, pp. 176-183) relative to a tetramer rather than a dimer. Ison and Kokot (13) reported the variable temperature susceptibility measurements for Cu(sal:o-aminophenol). Even though the salicylaldehyde moiety introduced rigidity into the system, their results indicated that the magnetic behavior was similar to complex I. For that reason, the structure was postulated to be that shown in Fig. 2.
Later, another complex was introduced that also had a 6-membered imine ring and a 5-membered aminealcohol ring system. This particular complex, Cu(acac:ethanol-amine) was synthesized first by Jäger (14).

This complex differs from Cu(acac:o-aminophenol) in that it introduces flexibility into the aminealcoholportion of the ring system. Jäger reported the room temperature magnetic moment to be 1.84 BM. Bertrand and Kelly (7) resumed the study of the complex and reported the moment to be 1.87 BM at 298°K, in good agreement with Jäger. These moments were obviously unlike that of complex I even though the ring size was the same. In fact, the room temperature moments actually appear to be close to normal. Bertrand and Kelly, in the same paper, elucidated the structure of complex IV as shown in Fig. 3a. The diagram, Fig. 3b, illustrates that one dimer is rotated 90° with respect to the other resulting in a cubane structure. The coordination about copper is distorted
but is essentially trigonal bipyramidal. The Cu-O-Cu bond angle was determined to be 97.8°, and the Cu-Cu bond length within each dimer is 3.01 Å and between dimers is 3.26 Å. Helm, et al., (15) have determined the variable temperature magnetic susceptibility for Cu(acac:ethanolamine) and have observed that as the temperature is lowered, the moment decreases. The effective magnetic moments per copper ion ranged from 1.84 BM at 295.3°K to 1.35 BM at 28.3°K. This supports Ginsberg's (10) conclusion that

![Diagram](image)

**Fig. 3--a)** The Molecular Structure of Cu(acac:ethanolamine); **b)** Schematic Representation of the Cubane (from ref. 7).

both antiferromagnetic and ferromagnetic interactions are involved, and that the molecule has a singlet ground state (21, pp. 170-183). In this respect, complex IV behaves magnetically like Cu(acac:o-aminophenol) even though the structure is different.
The salicyladehyde analog of complex IV was synthesized by Syamal and Theriot (26), and the reported effective magnetic moments ranged from 1.83 BM at 294°K to 1.89 BM at 78°K. The room temperature moment is very close to that of Cu(acac:ethanolamine), but the moment appears to increase slightly with decreasing temperature. No x-ray studies have been reported on Cu(sal:ethanolamine), but molecular weight studies indicate a tetramer in chloroform. Based on the physical data provided, it was postulated that the structure is the cubane tetramer form shown in Fig. 3b. The increase in magnetic moment as the temperature is lowered suggests ferromagnetic coupling, and this behavior is different from that of Cu(acac:ethanolamine) in the temperature range studied.

Since the aminealcohol portion of the molecule created large effect on the magnetic behavior and the crystal structure, it seemed of interest to investigate the effect of ring size and donor atoms on these complexes. Pauley and Theriot (23), in 1974, prepared Cu(pyrr:ethanolamine) for this study. The effective magnetic moment

![Diagram of molecule V]
at $293^0K$ was 1.89 BM and at $78^0K$ was 2.08 BM. The molecular weight data indicated a tetramer in chloroform, so the structure was postulated to be the cubane in Fig. 3b. The variable temperature data clearly indicated that lowering the temperature resulted in an increase in the magnetic susceptibility. In all probability, Cu(sal:ethanolamine) is behaving in a similar manner, but values at still lower temperatures for both compounds would be informative. Cu(pyrr:ethanolamine) still has a magnetic behavior very different from Cu(acac:ethanolamine), complex IV.

At the same time that complex IV was being studied, Bertrand and Kelly (7) synthesized and reported the molecular structure of Cu(acac:propanolamine) as shown in Fig. 4a. The room temperature moment was reported at $298^0K$ to be 0.41 BM, which is subnormal. This 6/6 chelate ring system has a planar coordination around copper, and the complex is dimeric. The bridging oxygen is from the aminealcohol portion; the Cu-Cu bond distance is 3.03 Å; and the Cu-O-Cu bond angle is $106.4^0$. Bertrand and Kelly stated that the main difference between the "2-carbon" ethanolamine and the "3-carbon" propanolamine, is the coordination of the bridging oxygen and not of copper as might be suspected. In Cu(acac:propanolamine), the coordination about oxygen is planar, while on Cu(acac:ethanolamine), it is tetrahedral.
Fig. 4--a) The Molecular Structure of Cu(acac:propanolamine); b) Schematic Representation (from ref. 7).

The longer chelate ring can maintain planarity without steric strain. To relieve the strain that would be experienced by the smaller ring, a change to sp$^3$ hybridization is observed. For some reason, out-of-plane interactions are possible in this system, and a tetrameric cubane-like structure results as shown in Fig. 3.

Yamada and coworkers (27) had earlier synthesized Cu(sal:propanolamine). They reported the room temperature magnetic moment to be 0.39 BM. This complex was re-synthesized and studied with a series of analogous substituted compounds by Kato, Jonassen, et al. (16), and the moment at 298$^0$K was found to be 0.49 BM. The magnetic data of this complex is similar to Cu(acac:propanolamine) and is, therefore, presumed to have a similar square planar dimeric configuration.
Bertrand and Kirkwood (8) prepared Cu(pyrr:propanol-amine) for the express purpose of evaluating the structural analysis. They reported the room temperature moment at 299.50 K to be 0.54 BM. Pauley and Theriot (23) independently synthesized complex VI and reported the variable temperature susceptibility. The effective magnetic moments ranged from 0.44 BM at 2930 K to 0.11 BM at 1200 K. Even though this is a NNO donor system and has a smaller ring size than either the salicyaldehyde or the acetylacetone analogs, the magnetic behavior is similar. From the x-ray data, Fig. 5, the bridging oxygen is from the aminealcohol portion of the ligand as has been the case exclusively thus far. The Cu-O-Cu bond angle is 103.9° and the Cu-Cu bond distance is 3.001 Å. The coordination about the copper as well as the bridging oxygen is planar. The magnetic data indicate a singlet ground state with a thermally accessible triplet excited state.

It has become evident after examining the differences and similarities in the above cited complexes, that no
clear-cut pattern of structural influences has been established. It is therefore suggested that further studies into the steric influences, substituent effects, geometric requirements, and donor atoms be conducted.

Fig. 5--a) The Molecular Structure of Cu(pyrr:propanolamine); b) Schematic Representation (from ref. 8).

It is hoped that after the synthetic work, physical data, and magnetic studies have been done on new complexes that some important contributions can be made to the already existing data. It is hoped that these investigations will provide the stimulus for further x-ray work in this area. New crystal structures would reveal the geometric requirements, such as bond angle and bond length; and how these relate to the mechanisms of superexchange, and the subsequent value of the exchange integral.


CHAPTER II

SCHIFF BASE COMPLEXES OF COPPER(II)

The complexes to be discussed in this chapter were synthesized and characterized for the purpose of further investigating the correlation between structural features, their influence on the magnetic behavior and on the magnitude of the exchange integral. The following compounds will be discussed: Cu(benzoylacetonе:ethanolamine), Cu(benzoylacetonе:propanolamine), Cu(pyrr:o-aminophenol), Cu(acac:m-aminophenol), Cu(sal:m-aminophenol), and [Cu(pyrr:m-aminophenol)H] OH. Cu(benzoylacetonе:ethanolamine) was synthesized by Jäger (24) for the purpose of continuing the work he had conducted (25) on some metal chelates that had a formal coordination number of three. Unfortunately for Jäger, Cu(benzoylacetonе:ethanolamine) did not behave as he had predicted based on his previous work. He chose to discontinue the study after having reported only the room temperature moment which appeared normal. In view of the work mentioned in Chapter I, it was felt that this complex deserved further investigation into its magnetic properties, and how they relate to the new structural evidence presented. Cu(benzoylacetonе:propanolamine) had not been reported in the literature, as
might have been expected. The preparation of the complexes appear at the end of the chapter.

\[ \text{Cu(benzoylacetone:ethanolamine)} \]

**Results**

The sea-green microcrystals obtained from toluene had a melting point range of 255-256°C, and gave the following elemental analysis: calcd. for \( \text{CuC}_{12}\text{H}_{13}\text{NO}_{2} \), C, 54.02; H, 4.87; N, 5.25; Cu, 23.81. Found: C, 54.18; H, 4.80; N, 5.29; Cu, 23.70. Molecular weight determinations in spectral grade chloroform solutions indicated that the complex was tetrameric (calcd. for \( \text{[Cu(benzoylacetone:ethanol-amine)]}_4 \), 1066. Found: 1050). The infrared spectrum is shown in Fig. 6 and a summary of the band assignments is given in Table X. The electronic spectra are shown in Fig. 7 and Fig. 8. The complex exhibits a broad absorption band in toluene with the \( \lambda_{\text{max}} \) around 15,680 cm\(^{-1} \) (\( \varepsilon = 121.1 \text{ mole}^{-1} \text{ cm}^{-1} \)). The complex absorbs around 16,390 cm\(^{-1} \) with a side band at 15,500 cm\(^{-1} \) for the nujol solid phase.
Fig. 6--Nujol Mull Infrared Spectrum of Cu(benzoylacetonate:ethanolamine)
Fig. 7--Electronic Spectrum of Cu(benzoylacetoné:ethanol-amine) in Toluene, [0.0052 M].
Fig. 8--Nujol Mull Electronic Spectrum of Cu(benzoylacetone:ethanolamine).
The magnetic susceptibility and magnetic moment data as the temperature varies from $78^\circ$K to $296^\circ$K are given in Table I. These values are for per copper ion.

**TABLE I**

MAGNETIC DATA FOR Cu(bza:eth)

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>$\chi_M^{corr} \times 10^6$, cgs</th>
<th>$\mu_{eff}$, BM</th>
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<tr>
<td>296</td>
<td>1470</td>
<td>1.86</td>
</tr>
<tr>
<td>261</td>
<td>1679</td>
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<td>223</td>
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<td>1.92</td>
</tr>
<tr>
<td>117</td>
<td>3993</td>
<td>1.93</td>
</tr>
<tr>
<td>78</td>
<td>6559</td>
<td>2.02</td>
</tr>
</tbody>
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**Discussion**

The absence of a broad band of strong-to-medium intensity in the region 3500 cm$^{-1}$ to 3000 cm$^{-1}$ in the infrared indicates that no water or solvent exists in the coordination sphere of the metal. This is confirmed by the analytical data. Of importance also is the very intense band of 1595 cm$^{-1}$ which is attributed to the C=N stretching vibration (31, p. 79).

In the visible region, the position and molar absorptivity of these bands are close to that reported by Bertrand and Kelly (9) for the Cu(acac:ethanolamine) complex which absorbs at 15,748 cm$^{-1}$ ($\epsilon = 106$ l. mole$^{-1}$ cm$^{-1}$).
The electronic spectra give evidence for a distorted trigonal bipyramidal arrangement around copper based on the cubane crystal structure reported by Bertrand and Kelly (9) as shown in Fig. 3. An energy level diagram (22, pp. 282-83) for the d orbitals in a trigonal bipyramidal environment is presented in Fig. 9. For this particular complex there was an advantage to having both a solid state

\[ \begin{array}{c}
\downarrow \\
E \\
\downarrow \\
d_{xy, dx-y^2} \\
\downarrow \\
d_{xz, dy} \\
\downarrow \\
d_{y^2} \\
\end{array} \]

Fig. 9--Energy Level Diagram for the d Orbitals in a Trigonal Bipyramidal Environment (from ref. 22).

and a solution state visible spectrum. The nujol spectrum revealed two absorptions, whereas the solution spectrum revealed a broad absorption enveloping both transitions of the mull phase. It would appear from Fig. 9 that there are two possible d-d transitions which is in agreement with that observed for the mull, Fig. 8. Cotton and Wilkinson (13, pp. 914-16) have mentioned that without polarized spectra of single crystals, the definite resolution of the proper number of sub-bands and their location is difficult.
The solution spectrum has demonstrated that without single crystal spectra, several overlapping transitions can reside under unsymmetrical envelopes. Exact assignments of the d-d transitions can, therefore, not be made.

The magnetic susceptibility reported was determined experimentally by the Gouy method (17). The quantity of importance is the molar susceptibility, $\chi_M$, which is corrected for the diamagnetism of the ligand, $\chi_L$, and for the temperature-independent paramagnetism (TIP) of the central ion. The following equation exemplifies this relationship:

$$\chi_M^{\text{corr}} = \chi_M - \chi_L - \text{TIP}$$

The effective magnetic moment is related to the susceptibility by the following equation:

$$\mu_{\text{eff}}(\text{BM}) = 2.83 \sqrt{\chi_M^{\text{corr}} T}$$

where $T$ is in degrees Kelvin (13, pp. 541-42; 16, p. 394; 17, p. 4). A graph of the susceptibility and magnetic moment versus temperature is given in Fig. 10. An expression known as the Curie law states that the magnetic susceptibility varies inversely with the temperature. However, this is not always the case. In this event, the Curie-Weiss law is used which introduces the Weiss constant, $\theta$. This law is represented as follows:

$$\chi_M^{\text{corr}} = C/T - \theta$$
Fig. 10--Magnetic Susceptibility $\cdot$ and Magnetic Moment $\ast$ of Cu(benzoylacetone:ethanolamine) as a Function of Temp.
where \( C \) is the Curie constant. The value \( \theta \) is the temperature at which the plot of \( (\chi_M^{\text{corr}})^{-1} \) vs. \( T \) intercepts the temperature axis. If the value of \( \theta \) is positive, the material exhibits ferromagnetic behavior; while a negative value of \( \theta \) would correspond to antiferromagnetic behavior (16, p. 396). A plot of the reciprocal of \( \chi_M^{\text{corr}} \) vs. \( T \) appears in Fig. 11. The value of \( \theta \) taken from a linear least squares evaluation for \( \text{Cu(benzoylacetone:ethanol-amine)} \) is \(+14^\circ K\), indicating a ferromagnetic behavior (21, pp. 175-176).

Another important value is \( J \), the exchange integral, which corresponds to the separation between a singlet and a triplet state. The sign and magnitude of \( J \) are important terms. If \( J \) is negative, then antiferromagnetism predominates. This negative sign indicates that the triplet state lies above the singlet ground state. If, however, \( J \) is positive, then ferromagnetism predominates (27, pp. 178-183). The value of \( J \) for a \( d^9 \) system can be calculated from the experimentally determined susceptibility by utilizing the Bleaney-Bowers (11) equation as follows:

\[
\chi_M^{\text{corr}} = \frac{g^2 N B^2}{3kT} \{1 + \frac{1}{3} \exp(-J/kT)\}^{-1}
\]

for which the terms and their numerical values are given in the Appendix. This particular complex gives an average \( J \) value of \(+65 \text{ cm}^{-1}\). This clearly indicates a ferromagnetic behavior as did the Weiss constant, \( \theta \).
Fig. 11—Reciprocal of the Corrected Magnetic Susceptibility Vs. Temperature for Cu(benzoylacetone:ethanolamine).
If Cu(benzoylacetone:ethanolamine) has the tetrameric cubane structure illustrated in Fig. 3b, then it is possible for both antiferromagnetic as well as ferromagnetic coupling to exist. Ginsberg (18) calculated two exchange integrals for Cu(acac:ethanolamine). For the exchange integral between dimers, Ginsberg denoted this as $J_{\text{Long}}$ and obtained $+4 \text{ cm}^{-1}$. For the exchange integral operative within each dimer, he denoted this as $J_{\text{short}}$ and obtained $-15 \text{ cm}^{-1}$. Ginsberg therefore concluded that the antiferromagnetic character dominates over the ferromagnetic behavior, and assigned a singlet ground state. However, in the Cu(bza:eth) complex, it appears that the ferromagnetic interaction predominates.

McGregor, Hodgson, Hatfield and coworkers (28) have examined relevant structural and magnetic data and have observed a decrease arithmetically in the value of $J$ as the value of the Cu-O-Cu angle, $\phi$, increases. If the interaction between the copper ions is through the bridging ligand, then perhaps an explanation based on the principles of superexchange (1-4) could provide a foundation for the above observations. If the orbitals used by the bridging oxygen atoms are purely $p$ orbitals, the bond angle is expected to be $90^\circ$ and the ground state is predicted to be a triplet (i.e., $J>0$); if the orbitals are purely $s$, the ground state is predicted to be a singlet (i.e., $J<0$).
Hence, since an increased value of the bridging angle implies greater s character in the bridging orbitals, a decrease in $J$ would be expected as the angle $\phi$ is increased from $90^\circ$ (21, pp. 176-179).

Ginsberg (18) pointed out that in Cu(acac:ethanolamine) it was the s orbital on the bridging oxygens that was involved with the $d_{z^2}$ orbital on the copper ion. If it is assumed that in both of these complexes the copper is in a trigonal bipyramidal environment, then the unpaired electron occupies the $d_{z^2}$ orbital. Based on the studies of McGregor, Hatfield, et al. (28) and on superexchange, it is the orbital on oxygen which allows the spins to align antiparallel in Cu(acac:ethanolamine) and parallel in Cu(benzoylacetone:ethanolamine). It should be noted that this slight modification in the aldehyde moiety has resulted in dramatic changes in the observed magnetic properties. It is therefore believed that the Cu-O-Cu-O ring is very sensitive to structural properties of the ligand.

\[ \text{Cu(benzoylacetone:propanolamine)} \]

**Results**

The brown microcrystals obtained from toluene had a melting point range of 256-258°C and gave the following elemental analysis: calcd. for CuCl$_3$H$_{15}$NO$_2$, C, 55.54%; H, 5.34%; N, 4.98%; Cu, 22.62. Found: C, 55.12%; H, 5.37%;
N, 4.84; Cu, 22.50. Molecular weight determinations in spectral grade chloroform solutions indicate that the complex was dimeric (calcd. for $\left[ \text{Cu(benzoylacetone:propanol-amine)} \right]_2$, 562. Found: 552). The infrared spectrum appears in Fig. 12 and a summary of the band assignments is given in Table X. The electronic spectrum is shown in Fig. 13. The absorption spectrum in toluene show as $\lambda_{\text{max}}$ around 17,760 cm$^{-1}$ ($\varepsilon = 91 \text{ l. mole}^{-1} \text{ cm}^{-1}$) with a shoulder around 16,000 cm$^{-1}$. The solid state nujol spectrum resolves the same band and position. The magnetic susceptibility and magnetic moment data are given in Table II.

TABLE II
Magnetic data for Cu(bza:prop)

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>$\chi_M^{\text{corr}} \times 10^6$, cgs</th>
<th>$\mu_{\text{eff}}$, BM</th>
</tr>
</thead>
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<td>42</td>
<td>0.31</td>
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<tr>
<td>261</td>
<td>33</td>
<td>0.36</td>
</tr>
<tr>
<td>117</td>
<td>15</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Fig. 12--Nujol Mull Infrared Spectrum of Cu(benzoylacetone:propanolamine)
Fig. 13--Electronic Spectrum of Cu(benzoylacatone:propanolamine) in Tolune, [0.0081 M].
Discussion

The absence of a broad band of strong-to-medium intensity in the region 3500 cm\(^{-1}\) to 3000 cm\(^{-1}\) in the infrared indicates that no water or solvent is coordinated to the metal. This is confirmed by the analytical data. The very intense band seen in the region of 1580 cm\(^{-1}\) is attributed to the C-N stretching vibration (31, p. 79).

In the visible region, the position and molar absorptivity of this band is close to that reported by Pauley and Theriot (29) for Cu(pyrr:propanolamine) which absorbs around 17, 900 cm\(^{-1}\) (\(\varepsilon = 129\) l. mole\(^{-1}\) cm\(^{-1}\)). The structure (Fig. 5) was reported by Bertrand and Kirkwood (10) and the coordination around each copper is essentially square planar. An energy level diagram (6, p. 69) for the d orbitals in a square planar environment is presented in Fig. 14. The unpaired electron occupies the orbital of highest energy, the dx\(^2\)-y\(^2\) orbital.

![Energy Level Diagram for the d Orbitals in a Square Planar Environment](from ref. 6).

Fig. 14--Energy Level Diagram for the d Orbitals in a Square Planar Environment (from ref. 6).
A graph of the susceptibility and magnetic moment versus temperature is given in Fig 15. The room temperature magnetic moment is subnormal, and as the temperature is lowered the moment decreases. At temperatures other than those reported, the magnetic susceptibilities were negative, indicating diamagnetism. The average \( J \) value as calculated from the Bleaney-Bowers equation 4 is \(-978\) cm\(^{-1}\). The value of the exchange integral as well as the variance of the moment with temperature indicates a singlet ground state. The large negative \( J \) value shows that antiferromagnetism predominates. According to McGregor, Hodgson, Hatfield and coworkers (28), the exchange integral is a function of the Cu-O-Cu bond angle. The larger the angle is than \( 90^\circ \), the greater the s character. The structure of Cu(pyrr:propanolamine) (10) revealed the Cu-O-Cu angle to be \( 103.9^\circ \), and the \( J \) value was reported to be \(-750\) cm\(^{-1}\) (29). It is probable that the bond angle in Cu(benzoylacetone:propanolamine) is greater than \( 103.9^\circ \). The only difference between Cu(benzoylacetone:ethanolamine) and Cu(benzoylacetone:propanolamine) is one -CH\(_2\)-group, and yet their structures and magnetic behaviors are radically different.

\[ \text{Cu(pyrr:o-aminophenol)} \]

**Results**

This Schiff base condenses with Cu(OAc)\(_2\)·H\(_2\)O to form two types of complexes: CuL\(_2\)H\(_2\) and CuL. The Cu(pyrr:o-aminophenol-
Fig. 15--Magnetic Susceptibility • and Magnetic Moment * of Cu(benzoylacetone:propanolamine) as a Function of Temperature.
phenol)\textsubscript{2}H\textsubscript{2} complex forms lime-green needles from chloroform having a melting point of 255°C. The Cu(pyrr:o-aminophenol) complex forms dark-green microcrystals from chloroform and has a melting point range of 230-232°C. The elemental analysis of both compounds is given in Table III.

**TABLE III**

ANALYTICAL DATA FOR Pyrr:o-aminophenol 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(pyrr:o-aminophenol)\textsubscript{2}H\textsubscript{2}</td>
<td>Calcd</td>
<td>60.89</td>
<td>4.15</td>
<td>12.91</td>
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<td>Found</td>
<td>60.83</td>
<td>4.27</td>
<td>------</td>
</tr>
<tr>
<td>Cu(pyrr:o-aminophenol)</td>
<td>Calcd</td>
<td>53.32</td>
<td>3.23</td>
<td>11.31</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>53.29</td>
<td>3.19</td>
<td>11.21</td>
</tr>
</tbody>
</table>

The molecular weight measurements in spectral grade chloroform solutions indicated that the CuL complex was tetrameric (calcd for [Cu(pyrr:o-aminophenol)]\textsubscript{4}, 990. Found: 983). The CuL\textsubscript{2}H\textsubscript{2} complex is believed to be a monomer. The infrared spectra of the CuL\textsubscript{2}H\textsubscript{2} complex and the CuL complex are shown in Fig. 16 and Fig. 17, respectively.
Fig. 16—Nujol Mull Infrared Spectrum of Cu(pyrroloaminophenol)2H2
Fig. 17—Nujol Mull Infrared Spectrum of Cu(pyrrlo-o-aminophenol)
The visible spectrum for CuL$_2$H$_2$ (Fig. 18) shows two absorptions in toluene: 16, 260 cm$^{-1}$ ($\varepsilon = 407$ l. mole$^{-1}$ cm$^{-1}$) and 17,540 cm$^{-1}$ ($\varepsilon = 460$ l. mole$^{-1}$ cm$^{-1}$). The spectrum of CuL (Fig. 19) shows a broad absorption centering around 15,500 cm$^{-1}$ in a chloroform solution ($\varepsilon = 138$ l. mole$^{-1}$ cm$^{-1}$). The mull spectra of both complexes were comparable to the solution spectra. The magnetic susceptibility data for Cu(pyrr:o-aminophenol) is given in Table IV. Since the CuL$_2$H$_2$ complex was believed to be monomeric, only the room temperature and liquid nitrogen magnetic moments were measured: 1.77 BM and 1.80 BM, respectively.

**TABLE IV**

MAGNETIC DATA FOR Cu(pyrr:ortho)

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>$\chi_M^{corr} \times 10^6$, cgs</th>
<th>$\mu_{eff}$, BM</th>
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<td>223</td>
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<td>1.56</td>
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<td>184</td>
<td>1580</td>
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<td>148</td>
<td>2018</td>
<td>1.55</td>
</tr>
<tr>
<td>117</td>
<td>2472</td>
<td>1.52</td>
</tr>
<tr>
<td>78</td>
<td>3624</td>
<td>1.50</td>
</tr>
</tbody>
</table>

**Discussion**

Since the ligand has both an N-H and an O-H, there is a question as to which proton is removed during the complexation of Cu(pyrr:o-aminophenol)$_2$H$_2$. The nujol
Fig. 18--Electronic Spectrum of Cu(pyrr:o-aminophenol)$_2$H$_2$ in Tolune, [0.0011 M].
Fig. 19—Electronic Spectra of Cu(pyrr:o-aminophenol) in Chloroform, [0.0038 M] Upper; Nujol Mull, Lower.
infrared spectrum is not diagnostic in this respect. It reveals that considerable hydrogen bonding occurs in the solid resulting in not only a shift in the band but a complete removal \(^{(8, 14)}\). In the corresponding manganese Schiff base complex it was determined that the hydroxyl proton was removed based on the infrared spectrum, Chapter 3, Fig. 47. It is assumed that the hydroxyl proton is likewise removed in this copper complex thereby leaving the amine proton. The infrared spectrum of Cu(pyrr:o-aminophenol) reveals an absence of the characteristic \(\tilde{\nu}(OH)\) thereby indicating that neither water nor a solvent molecule is coordinated to the metal. The band assignments are given in Table X. The analytical data supports the observations made on both of the pyrr:o-aminophenol copper(II) complexes.

It was observed that in the visible region, the CuL\(_2\)H\(_2\) complex had two d-d transitions in toluene: 16,260 cm\(^{-1}\) and 17,540 cm\(^{-1}\). The higher energy absorption is assigned to a square planar geometry, and has a position similar to Cu(pyrr:propanolamine) which is known by structure \((10)\) to be square planar. This position is also similar to Cu(benzoylacetone:propanolamine) which absorbs at 17,760 cm\(^{-1}\) with a shoulder at 16,000 cm\(^{-1}\) and is believed to be square planar also. This square planar geometry indicates that the tridentate pyrr:o-aminophenol Schiff base acts as a bidentate ligand as
The energy level diagram for the d orbitals in both square pyramidal and square planar environments is given in Fig. 20.

Fig. 20--Crystal Field Splitting of the d orbitals of a Central Ion: A (Tetrahedral), B (Free ion), C (Octahedral), D (Square Pyramidal), and E (Square planar) (from ref. 6).

The Cu(pyrr:o-aminophenol) complex, on the other hand, has a broad absorption around 16,000 cm\(^{-1}\). Since the
molecular weight indicates a tetramer and the $\lambda_{\text{max}}$ is of fairly low energy for a d-d transition, a square pyramidal geometry is assigned. Figure 20 illustrates the crystal field splitting for the d orbitals in that environment. This assignment is based on the fact that the structure of Cu(acac:o-aminophenol) was reported by Barclay, Harris and coworkers (5) to be a stacked dimer as illustrated in Figs. 1 and 2 of Chapter I. Since the Schiff base in question, pyrr:o-aminophenol, has similar rigidity as that of acac:o-aminophenol, it is assumed that a similar coordination around copper could result. As the schematic, Fig. 2, illustrates, the central copper ion experiences both a square planar and a square pyramidal environment. It would not be unheard of, therefore, to see a predominance of one geometry over another as (1) the ligand is altered, or (2) as the concentration is changed from a mull to a solution. The visible spectra of Cu(acac:o-aminophenol) in both nujol mull and toluene solution are given in Figs. 21 and 22. The absorptivity is 120 l. mole$^{-1}$ cm$^{-1}$. The band in the solid state has a position around 16,000 cm$^{-1}$, and in solution has a position around 15,740 cm$^{-1}$.

The magnetic data for the CuL$_2$H$_2$ complex indicate a slight increase in the moment as the temperature is lowered from room temperature to that of liquid nitrogen. Since it has been proposed that a square planar configuration
Fig. 22 -- Electronic Spectrum of Cu(acac:o-aminophenol) in Tolune, [0.0042 M].
exists, it is possible that individual monomers could have slight interaction with each other. Certainly, this cannot be ruled out. It has been demonstrated that in a solid mull, there is considerable hydrogen bonding as evidenced by the infrared spectrum. Therefore, it might be possible that in a powdered sample, as one used for the Gauy method, some interaction between monomers could take place even though it is weak.

The graph of the magnetic data as a function of temperature is shown in Fig. 23 for the CuL complex. The magnetic moment per copper ion is subnormal at room temperature and decreases as the temperature is lowered. This indicates an antiferromagnetic interaction. However, the susceptibility curve looks very much like that of Cu(benzoylacetone:ethanolamine) in Fig. 10, which exhibited a ferromagnetic interaction. The average J value as calculated from the Bleaney-Bowers equation is \(-126 \text{ cm}^{-1}\). The Weiss constant, \(\theta\), as determined from the plot of \((\chi_M^{\text{corr}})^{-1}\) vs. temperature, Fig. 24, is very close to zero. The linear least squares evaluation calculates \(\theta\) to be \(+0.66^0\text{K}\). This intercept is so close to zero that the complex seems to be following the Curie law fairly closely. The large negative exchange integral and the subnormal moment indicate that overall antiferromagnetism predominates. It is believed, therefore,
Fig. 23--Magnetic Susceptibility • and Magnetic Moment * of Cu(pyrr:o-aminophenol) as a Function of Temp.
Fig. 24--Reciprocal of the Corrected Magnetic Susceptibility Vs. Temperature for Cu(pyrr:o-aminophenol).
that within the temperature range studied, a normal paramagnetic behavior occurs. It is anticipated that as the temperature is measured below 78^0K, the Néel point will occur and the susceptibility will drop. Hatfield and Inman (20) evaluated the exchange integral for Cu(acac:o-aminophenol) as a tetramer instead of a dimer. The evaluation found the J value within each dimer to be different (-140 cm⁻¹) from the J value between dimers (-48 cm⁻¹). There essentially is no difference in that the sign and magnitude of J indicate that antiferromagnetism predominates. Perhaps in the new complex, Cu(pyrr:o-aminophenol), the influence of each J value may vary as the temperature changes. Perhaps there is a "crossover" temperature at which point both J values are of equal influence. Based on the data collected so far, the ground state of the complex cannot be assigned.

Schiff Bases of Meta-aminophenol

Results

Meta-aminophenol was condensed with acetylacetone and salicylaldehyde to form two different Schiff bases. These Schiff bases were complexed with Cu(OAc)₂·H₂O to form three compounds: Cu(sal:m-aminophenol)₂H₂, Cu(sal:m-aminophenol), and Cu(acac:m-aminophenol). The Cu(sal:m-
aminophenol)₂H₂ forms dark brown microcrystals from ethanol having a melting point range of 233-235°C.

The Cu(sal:m-aminophenol) was a very dark brown powder that could not be recrystallized due to poor solubility. Its melting point is greater than 255°C. The Cu(acac:m-aminophenol) complex forms a reddish-brown powder from toluene. This complex also has a poor degree of solubility and so was not recrystallized. This complex decomposed between 245-255°C. The elemental analysis of these compounds is presented in Table V. The molecular weight measurements were not taken on these complexes because the two CuL compounds were insoluble and the CuL₂H₂ compound was believed to be a monomer. The infrared spectra of Cu(sal:m-aminophenol)₂H₂, Cu(sal:m-aminophenol), Cu:acac:m-aminophenol), and the Schiff bases are
### TABLE V

**ANALYTICAL DATA FOR M-AMINOPHENOL COMPLEXES**

<table>
<thead>
<tr>
<th>Complex</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Cu</th>
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<tbody>
<tr>
<td>Cu(sal:m-aminophenol)$_2$H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>Found</td>
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<td>Cu(sal:m-aminophenol)</td>
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<td></td>
<td></td>
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<td>Calcd</td>
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<td>Found</td>
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<td>3.18</td>
<td>5.02</td>
<td>22.99</td>
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<tr>
<td>Cu(acac:m-aminophenol)</td>
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<td>52.48</td>
<td>4.10</td>
<td>5.64</td>
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Presented in Figs. 25, 26, 27, 28, and 29. The electronic spectra of the CuL$_2$H$_2$ complex and the Cu(sal:meta) complex is shown in Figs. 30 and 31, respectively. The CuL$_2$H$_2$ has an absorption band around 15,380 cm$^{-1}$ ($\varepsilon = 335$ l. mole$^{-1}$ cm$^{-1}$) in ethanol and nujol mull. The Cu(sal:m-aminophenol) complex has a d-d transition around 16,660 cm$^{-1}$. Fig. 31 indicates the mull spectra taken at two different concentrations with the more concentrated demonstrating the band clearly. The Cu(acac:meta), Fig. 32, has a broad band centering around 17,090 cm$^{-1}$ from a mull. The magnetic data for the CuL$_2$H$_2$ monomer was measured at room temperature and liquid nitrogen only: 1.75 BM and 1.73 BM, respectively. The magnetic data for Cu(sal:m-aminophenol) is given in Table VI, and for Cu(acac:m-aminophenol) is given in Table VII.
Fig. 26--Nujol Mull Infrared Spectrum of Cu(sal:m-aminophenol)$_2$H$_2$
Fig. 26--Continued
Fig. 27—Nujol Mull Infrared Spectrum of Cu(sal·m·aminophenol)
Fig. 28--Nujol Mull Infrared Spectrum of Acac:m-aminophenol Ligand
Fig. 29—Nujol Mull Infrared Spectrum of Cu(acac:m-aminophenol)
Fig. 30--Electronic Spectra of Cu(sal:m-aminophenol)$_2$H$_2$ in Ethanol, [0.0021 M] Upper; Nujol Mull, Lower.
Fig. 31--Electronic Spectra of Cu(sal:m-aminophenol) in Nujol Mull, More Concentrated Upper; Less Concentrated, Lower.
Fig. 32--Electronic Spectrum of Cu(acac:m-aminophenol) in Nujol.
These magnetic moments are per Cu ion and calculated from equation 2.

**TABLE VI**

**MAGNETIC DATA FOR Cu(sal:meta)**

<table>
<thead>
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<th>$\chi_M^{corr} \times 10^6$ cgs</th>
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<td>78</td>
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**TABLE VII**

**MAGNETIC DATA FOR Cu(acac:meta)**

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>$\chi_M^{corr} \times 10^6$ cgs</th>
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<tr>
<td>78</td>
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<td>0.37</td>
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**Discussion**

The infrared spectrum of each Schiff base indicates the presence of a hydroxyl band but shifted from 3600-
3500 cm$^{-1}$ to 3300-3150 cm$^{-1}$ by hydrogen bonding. The position of the $\nu$(OH) is very clear in the mull spectrum of the sal:m-aminophenol ligand. Since the protons in these complexes are hydroxyl protons only, any band in the characteristic region can only be attributed to an OH stretch. This situation is very different from that of the pyrr:o-aminophenol ligand. The Cu(sal:m-aminophenol)$_2$H$_2$ has lost only one proton so the shifted band around 3150 cm$^{-1}$ can only be attributed to the remaining hydroxyl group. The Cu(sal:m-aminophenol) complex does not show the characteristic $\nu$(OH) but does have the C=N band at 1600 cm$^{-1}$. The analytical data confirms the observations on all three complexes.

The CuL$_2$H$_2$ complex showed one d-d transition around 15,380 cm$^{-1}$ in both solution and nujol. Since this is of rather low energy, a square pyramidal geometry has been assigned. The energy level diagram for the d orbitals is shown in Fig. 20. This would indicate that one ligand acts as a tridentate and one acts as a bidentate as shown:
The position of the band at 16,660 cm\(^{-1}\) for Cu(sal:m-aminophenol) is midway between square planar and square pyramidal, but closer to square pyramidal. The broadness of the band for Cu(acac:m-aminophenol), however, indicates a strong presence of both geometries since 17,090 cm\(^{-1}\) is of higher energy than that observed for Cu(sal:m-aminophenol). Considering the crystal structure reported for Cu(acac:o-aminophenol), Fig. 1, which indicated that one of the central coppers had a square planar geometry and that the other copper had a square pyramidal environment, these electronic spectra give evidence that both Cu(acac:m-aminophenol) and Cu(sal:m-aminophenol) probably have similar crystal structures to that of Cu(acac:o-aminophenol).

The magnetic moment for the CuL\(_2\)H\(_2\) did not vary significantly when the temperature was lowered, and this confirms that it is probably an isolated monomer. The room temperature magnetic moment for both Cu(sal:m-aminophenol) and Cu(acac:m-aminophenol) is subnormal. A graph of the magnetic susceptibility vs. temperature is shown in Fig. 33 and Fig. 34. Both graphs have the data from the respective ortho-aminophenol complexes superimposed on the new data. This is to illustrate that the meta-aminophenol complexes behave similarly but exhibit a stronger degree of antiferromagnetism. The average J value for sal-ortho as reported by Ison and Kokot (23) is
Fig. 33--Magnetic Susceptibility as a Function of Temperature for Cu(sal:o-aminophenol) • and Cu(sal:m-aminophenol) *, Values for Cu(sal:o-aminophenol) are from ref. 23.
Fig. 34--Magnetic Susceptibility as a Function of Temperature for Cu(acac:o-aminophenol) • (from ref. 20), and Cu(acac:m-aminophenol) *.
-293 cm$^{-1}$, whereas the $J$ value as calculated by the Bleaney-Bowers equation 4 for the Cu(sal:m-aminophenol) is -433 cm$^{-1}$. The average $J$ value for Cu(acac:o-aminophenol) as reported by Barclay, Harris, and Hoskins (5) is -298 cm$^{-1}$. The average $J$ value for Cu(acac:m-aminophenol) as calculated by the Bleaney-Bowers equation 4 is -531 cm$^{-1}$.

A closer examination of the graphs of $\chi_M^{corr}$ vs. Temp. reveals that both new meta-aminophenol complexes have an increase in the susceptibility as the temperature is lowered beyond a certain temperature. According to Ginsberg (18) this behavior can probably be attributed to the presence of some paramagnetic impurity. This could possibly result since neither complex could be recrystallized. The graphs also indicate that both new complexes have a higher Neel point than their corresponding ortho-aminophenol complex. It has been discussed before that there is a correlation between the value of the exchange integral, $J$, and the Cu-O-Cu bond angle (28). Since the meta complexes have larger negative $J$ values, then it is safe to assume that the corresponding Cu-O-Cu bond angles are greater than those in the ortho complexes.

$$\left[\text{Cu(pyrr:m-aminophenol)}\right]_2\text{OH}$$

**Results**

This Schiff base condenses with Cu(OAc)$_2$·H$_2$O to form, in this case, a bridging hydroxide dimer. The
conditions for preparation allowed this formation even though the intended product was of a CuL coordination with a divalent tridentate ligand similar to both (sal:m-aminophenol) and (acac:m-aminophenol). The complex which was prepared was a very dark grey-black powder with a melting point greater than 255°C. The following elemental analysis was reported for the complex with a formulation (CuLH)OH:

calcd. C_{11}C_{10}N_{2}O_{2}Cu; C, 49.71; H, 3.76; N, 10.54; Cu, 23.92.

Found: C, 49.28; H, 3.66; N, 10.40; Cu, 23.97. The molecular weight determination could not be measured because the complex is insoluble in most organic solvents. Its high melting point also ruled out a mass spectrum.

The infrared spectra of the complex and its precursor, Cu(OH)(OAc), are shown in Figs. 35 and 36. Two electronic spectra of the Cu(pyrr:m-aminophenol)H OH are shown in Figs. 37 and 38 to demonstrate that a mull spectrum is not always reproducible and two different spectra may reveal the presence of different bands. Fig. 37 shows a low energy band around 14,810 cm\(^{-1}\) and another band at 16,800 cm\(^{-1}\). The second spectrum, Fig. 38, shows a broad absorption around 16,260 cm\(^{-1}\) which seems to be centered in
Fig. 36--Nujol Mull Infrared Spectrum for \([\text{Cu(pyrr:}m\text{-aminophenol)}\text{H}]\text{OH}\)
Fig. 37--Electronic Spectrum of [Cu(pyrr:m-aminophenol)H]OH in Nujol.
Fig. 38—Electronic Spectrum of [Cu(pyrr:m-aminophenol)H]OH in Nujol.
between the bands of the first spectrum. The band around 21,970 cm$^{-1}$ is attributed to charge transfer, inner-
ligand, or ligand-metal interaction rather than to a d-d transition. The magnetic susceptibility and magnetic
moment data as the temperature varies from 78$^0$K to 296$^0$K are given in Table VIII. These data are presented on a

<table>
<thead>
<tr>
<th>Temp., $^0$K</th>
<th>$\chi_M^{corr} \times 10^6$, cgs</th>
<th>$\mu_{eff}$, BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>566</td>
<td>1.16</td>
</tr>
<tr>
<td>261</td>
<td>618</td>
<td>1.14</td>
</tr>
<tr>
<td>223</td>
<td>675</td>
<td>1.10</td>
</tr>
<tr>
<td>184</td>
<td>799</td>
<td>1.08</td>
</tr>
<tr>
<td>148</td>
<td>1043</td>
<td>1.11</td>
</tr>
<tr>
<td>117</td>
<td>1233</td>
<td>1.08</td>
</tr>
<tr>
<td>78</td>
<td>1831</td>
<td>1.07</td>
</tr>
</tbody>
</table>

per copper ion basis. The near-infrared spectrum from 3840 cm$^{-1}$ to 5000 cm$^{-1}$ are shown in Fig. 39. The band
maximum is around 4250 cm$^{-1}$. A graph of the frequency vs. absorbance for this near-infrared spectrum is shown in
Fig. 40 to clarify the position of the band taken from the original spectrum. The thermogravimetric analysis
and differential scanning calorimetry data provided for by Texas Instruments did not reveal any change in weight
due to water content.
Fig. 39--Near-Infrared Spectrum as a Nujol Mull of [Cu(pyrr:m-aminophenol)H]OH.
Fig. 39--Continued
Discussion

The ligand was not isolated due to decomposition, so its infrared spectrum is not shown. However, the spectra for both the (CuLH)OH complex and its precursor, Cu(OH)(OAc) are presented. Close examination of the (CuLH)OH complex reveals an absence of the characteristic v(OH) in the region $3650-3584 \text{ cm}^{-1}$ for a non-hydrogen bonded hydroxyl. This occurrence would perhaps indicate that the elemental analysis resulted from an impurity. But if the complex were that of a bridging hydroxide, then the ligand acts as a bidentate with only one proton removed. As in the case of Mn(pyrr:o-aminophenol)$_2$H$_2$, it is believed that the amine proton is not removed, thereby permitting strong hydrogen bonding to occur between the amine proton and the bridging hydroxyl. This entire formulation could not occur unless the central copper already had a hydroxyl coordinated to it prior to complexation with the ligand. The blue powder which is formed prior to the formation of the dark complex has been analyzed to be

$$\text{H}_3\text{C} - \text{C} - \text{Cu} - \text{O} - \text{Cu} - \text{C} - \text{CH}_3$$

$$[\text{Cu(OH)(OAc)}]_2.$$ The infrared spectrum of this intermediate has the following bands not present in the (CuLH)OH
complex: 3580 cm\(^{-1}\) (sharp), 3480 cm\(^{-1}\) (medium), 3100 cm\(^{-1}\) (weak), 1970 cm\(^{-1}\) (weak), 1570 cm\(^{-1}\) (strong), and 1530 cm\(^{-1}\) (strong). According to Silverstein and Bassler (31, p. 84), the three bands in the region 3580 cm\(^{-1}\) to 3100 cm\(^{-1}\) are attributed to the bridging O-H. This bonded O-H behaves slightly different from the free, uncoordinated hydroxyl. The band at 1970 cm\(^{-1}\) can probably be attributed to the metal-carbonyl-like bond of the carboxylate anion with the central copper. Conley (12, p. 183) states that metal carbonyl compounds have characteristic absorptions in the 2050-1750 cm\(^{-1}\) region. The properties of these bands may vary depending on the complexity of the metal-carbonyl compound. Certainly this acid salt complex with copper(II) is not an ordinary metal-carbonyl complex, so it is possible that the band position and intensity would be of an intermediate type. Conley (12, p. 183) states that terminal carbonyls give rise to bands near the high-frequency end of the 2050-1750 cm\(^{-1}\) regions; and the bridged carbonyl groups absorb near 1800 cm\(^{-1}\). The bands at 1570 cm\(^{-1}\) and 1530 cm\(^{-1}\) are attributed to the asymmetrical and symmetrical stretching frequencies of the carboxylate anion. Some overlap with the \(-\text{CH}_{2}-\) bending vibration of nujol is likely (12, pp. 140-160; 31, p. 91). This infrared spectrum gives further evidence as to the identity of the blue powder, thereby providing a means to form the (CuLH)OH complex.
The infrared spectrum of the \([\text{Cu(pyrr:m-aminophenol)H}]\)OH complex does have the band at 1515 cm\(^{-1}\) which is attributed to the C=\(\text{N}\) stretching vibration, also the band at 1270 cm\(^{-1}\), which is attributed to the C-N stretching vibration. Both bands are absent in the Cu(OH)(OAc) spectrum. The elemental analysis indicates the presence of an H-OH moiety which could be explained as a coordinated water molecule or as a bridging hydroxyl with a protonated nitrogen remaining on the Schiff base moiety. If this had been a coordinated water molecule, the infrared would have, in most cases, revealed a very broad band. Also the thermogravimetric analysis and differential scanning calorimetry would have indicated a loss of weight at a given temperature corresponding to a water molecule. These results were negative. It has been reported (8, 14, 30) that strong hydrogen bonding cannot only shift the position of the \(\text{v(OH)}\), but in very strong bonding completely remove the band. Even in the mull of Cu(OH)(OAc) the bands are slightly shifted to lower energy. The electronic spectra of \([\text{Cu(pyrr:m-aminophenol)H}]\)OH shows a \(\lambda_{\text{max}}\) around 16,260 cm\(^{-1}\) which is in the range for a square pyramidal geometry as shown. This conformation would
indeed permit hydrogen bonding to the extent that both the N-H stretch and the O-H stretch are removed. This would explain the presence of only the C-H stretch for nujol for the complex. In 1963, Goldstein and Penner (19) reported the near-infrared absorption for liquid water as a function of temperature. Free water gives an enormous band between 3600 cm\(^{-1}\) and 3000 cm\(^{-1}\), as previously mentioned. They also reported an absorption between 7600 cm\(^{-1}\) and 4600 cm\(^{-1}\). Therefore if a complex had a true coordinated water molecule, not only would it have a broad band in the infrared region (3600-3000 cm\(^{-1}\)), but it would also have two more bands in the near-infrared. Figure 39 and Fig. 40 show the near-infrared spectrum for the bridging hydroxide complex. Figure 40 graphically illustrates the original spectrum and shows the maximum at 4250 cm\(^{-1}\) which is of lower energy than either of the near-infrared bands for water. Conley (12, pp. 231-237) has a chapter dedicated to the study of near-infrared spectra. He states that this particular region can provide evidence for molecular interactions of the hydroxyl group with other functional groups within the same molecule (i.e., intramolecular hydrogen bonding). The near-infrared absorption band with a \(\lambda_{\text{max}}\) of 4250 cm\(^{-1}\) is attributed to the bridging hydroxide. The position of this band and its intensity is different from an alcohol or water, and this is understandable.
Fig. 40--Absorbance vs. Frequency in the Near-Infrared Region for \([\text{Cu(pyrr:m-aminophenol)H}]\text{OH}\).
This bridging hydroxyl is also expected to have intramolecular hydrogen bonding with the amine group from the Schiff base which would also influence its absorption. The evidence presented thus far—elemental analysis, TGA, DSC, IR, near-IR—all indicate the presence of a bridging hydroxide.

The magnetic data indicates a subnormal moment of 1.16 BM at room temperature which is characteristic of the bridging oxygen molecules studied in the past (28). The graph of the magnetic susceptibilities as a function of temperature is given in Fig. 41. The magnetic moment decreases with temperature while the susceptibilities continues to increase. This behavior is very similar to that of Cu(pyrr:o-aminophenol), Fig. 23. The average J value was calculated from the Bleaney-Bowers Eq. 4 to be -338 cm⁻¹. This also indicates a strong antiferromagnetic interaction. A plot of the reciprocal of $\chi_M^{\text{corr}}$ vs. Temp. is shown in Fig. 42 and indicates that the behavior follows the Curie law very closely as did Cu(pyrr:o-aminophenol).

Based on the magnetic data, it is presumed that within the temperature range studied, normal paramagnetism occurs; but that at lower temperatures, strong antiferromagnetism predominates, leading to a very low Neel point.

Experimental

Reagents

Reagent grade salicylaldehyde, cupric acetate monohydrate, and potassium hydroxide were obtained from the
Fig. 41--Magnetic Susceptibility as a Function of Temperature for \([\text{Cu(pyrr:m-aminophenol)H}]\text{OH}\).
Fig. 42--Reciprocal of the Magnetic Susceptibility vs. Temperature for [Cu(pyrr:m-aminophenol)H]OH.
Ortho-aminophenol (99%), meta-aminophenol (95%), ethanol-amine (95%), propanolamine, pyrrole-2-carboxaldehyde (99%), and benzoylacetone (i.e., 1-phenyl-1, 3-butanedione), were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. Acetylacetone (i.e., 2, 4-pentanedione) was obtained from Eastman Organic Chemical, Rochester, New York. All solvents were reagent and/or absolute where indicated.

Preparation of the Complexes

A Schiff base is the condensation product of a carbonyl compound (usually an aldehyde or ketone) with a primary amine, and contains the azomethine (-RC=N-) linkage. These bases can be effective chelating agents if either the carbonyl compound or the amine (or both) contain potentially coordinating functional groups (e.g., OH) near the site of condensation (21, pp. 199-200). For example, the reaction of benzoylacetone with ethanolamine gives a potentially dibasic tridentate ligand. A summary of the Schiff bases isolated during this work is presented in Table IX.
TABLE IX
PROPERTIES OF ISOLATED SCHIFF BASES

<table>
<thead>
<tr>
<th>Schiff Base</th>
<th>Stoichiometry</th>
<th>MP, °C</th>
<th>Color: Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>sal:o-ap</td>
<td>C_{13}H_{11}NO_2</td>
<td>185</td>
<td>red-orange: micro</td>
</tr>
<tr>
<td>sal:m-ap</td>
<td>C_{13}H_{11}NO_2</td>
<td>90-91</td>
<td>yellow-orange: porous</td>
</tr>
<tr>
<td>acac:o-ap</td>
<td>C_{11}H_{13}NO_2</td>
<td>184-185</td>
<td>yellow: small needles</td>
</tr>
<tr>
<td>acac:m-ap</td>
<td>C_{11}H_{13}NO_2</td>
<td>130-132</td>
<td>white: rectangular</td>
</tr>
<tr>
<td>pyrr:o-ap</td>
<td>C_{11}H_{10}N_2O</td>
<td>120-121</td>
<td>red-orange: needles</td>
</tr>
<tr>
<td>acac:eth</td>
<td>C_{12}H_{15}NO_2</td>
<td>83-86</td>
<td>white: rectangular</td>
</tr>
</tbody>
</table>

Cu(benzoylacetone:ethanolamine) was prepared in the following manner:

\[ \text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} + \text{SB} \rightarrow \text{CuL} \]

where SB stands for "Schiff base" and L represents "ligand."

Reagent grade benzoylacetone (8.11 g; 0.05 mole) was dissolved in 75 ml of anhydrous methanol. Ethanolamine (3.05 g; 0.05 mole) was added dropwise. A clear yellow solution resulted which was allowed to stir at reflux for one hour, after which time the solution turned a darker yellow. In 250 ml of anhydrous methanol, Cu(OAc)_2 \cdot \text{H}_2\text{O} (9.6 g; 0.048 g) was dissolved. To this, the yellow Schiff base solution was added dropwise. Immediately afterwards, 0.1 mole of potassium hydroxide, which had been dissolved in methanol, was added. The volume of solvent was increased...
by 100 ml to accommodate the precipitate which formed after refluxing overnight. A green powder was isolated and washed with methanol and ether. The sea-green microcrystals were isolated from hot toluene giving a final yield of 63%.

*Cu(benzoylaceton:propanolamine)* was prepared in the same manner as *Cu(benzoylaceton:ethanolamine)* only propanolamine (3.75 g; 0.05 mole) was used. A brownish green shiny powder was collected during suction filtration, and the powder was later washed with methanol and ether. The compound was recrystallized from toluene and brown microcrystals were recovered. The final yield was 45%.

*Cu(pyrr:o-aminophenol)* was synthesized by the insertion technique (13, pp. 777-779),

\[
\begin{align*}
\text{Cu(OAC)}_2\text{H}_2\text{O} + \text{LH}_2 & \rightarrow \text{CuL}_2\text{H}_2 \quad \text{(Step 1)} \\
\text{CuL}_2\text{H}_2 + \text{Cu(OAc)}_2\text{H}_2\text{O} & \rightarrow 2 \text{CuL} \quad \text{(Step 2)}
\end{align*}
\]

where LH2 represents a dibasic ligand emphasizing that two protons can be removed; and CuL2H2 indicates that only one proton was removed from the ligand, thereby forming a bis compound with copper(II). Ortho-aminophenol was purified with decolourizing charcoal from absolute ethanol to form white crystals. Pyrrole-2-carboxaldehyde (4.75 g; 0.05 mole) was dissolved with purified ortho-aminophenol (5.45 g; 0.05 mole) in 100 ml of ethanol and refluxed for one hour. The volume of the Schiff base solution was reduced and large orange needle-like crystals resulted. The
Soxhlet apparatus with Al₂O₃ in the basket was used in the remaining synthesis. Cupric acetate monohydrate was powdered and dissolved in 300 ml of absolute ethanol, and the solvent was allowed to reflux and siphon over the drying agent several times. The crystalline Schiff base was then added slowly to the Cu(OAc)₂·H₂O solution and allowed to reflux overnight. A very rich yellow-green precipitate formed which required that the volume of the solvent be increased to about 800 ml. The yellow-green powder was recrystallized from chloroform giving lime-green fibrous needle-like crystals. Depending on the choice of the solvent and on the choice of either isolating the Schiff base or synthesizing it in situ, the color of the crude powder from Step 1 may vary in shades of green. A shiny forest green powder may form which closely resembles the product from Step 2. In any event, the recrystallized product will positively identify the complex as that of CuL₂H₂ (Step 1) or of CuL (Step 2) coordination. The yield for Step 1 after purification is 65%. In this particular system, the preferential complex formed by the Schiff base method of preparation using a 1:1 ratio of ligand to copper(II) is that of CuL₂H₂ and not CuL, as is usually the case.

The formation of the CuL complex requires that one mole of cupric acetate monohydrate be reacted with one mole of the CuL₂H₂ crystals. The Soxhlet apparatus
containing aluminum oxide in the basket was used in this procedure. In about 300 ml of absolute ethanol, the Cu(pyrr:o-aminophenol)$_2$H$_2$ complex was powdered and added slowly as the solvent heated and stirred. The solvent was allowed to reflux and siphon over the basket before the Cu(OAc)$_2$·H$_2$O was added. The Cu(OAc)$_2$·H$_2$O was crushed and added slowly to the mixture. After refluxing overnight, the solution turned dark and a small dark precipitate was observed on the sides of the flask, indicating that a reaction had taken place. A shiny greenish-black powder was collected during filtration. The dark powder was dried at 70°C under vacuum overnight, giving an 80% yield. The complex was recrystallized from chloroform giving dark green microcrystals. The yield of crystals was very low compared to the initial amount. The elemental analysis indicated fairly pure crystals of the CuL coordination (Step 2).

Cu(acac:m-aminophenol) was prepared by reacting the Schiff base with cupric acetate monohydrate.

\[
\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} + \text{SB} \rightarrow \text{CuL}
\]

The reagents, acetylacetone (4.0 g; 0.04 mole) and meta-aminophenol (4.36 g; 0.04 mole), were refluxed in absolute ethanol two hours. The solution was purified with decolorizing charcoal and then the volume was reduced. White plate-like crystals were isolated from ethanol
with approximately a 70% yield. A Soxhlet apparatus with 
Al₂O₃ in the basket was used in the remaining synthesis. 
The cupric acetate monohydrate was crushed and put in 300 ml 
of toluene. The solvent was allowed to reflux and siphon 
over the drying agent twice. The crystalline Schiff base 
was added a little at a time to avoid bumping. The 
solution turned brown, and then was allowed to reflux 
overnight. A large amount of an unusual reddish-brown 
powder was isolated. It should be noted that if this 
procedure is not followed as specified, various unidentified 
products will result. Even if this is prepared in an 
alcohol medium, the desired product will not be formed. 
In fact, the composition of this reddish-brown product 
was questionable until the elemental analysis revealed 
that the CuL complex had been formed with an 80% yield. 
This complex is insoluble in most organic solvents and, so, 
was studied as a powder.

\[
\text{Cu(sal:m-aminophenol)} \text{ was synthesized by the insertion} \\
\text{method (13, pp. 777-779),} \\
\text{Cu(sal)}_2 + \text{m-ap} \rightarrow \text{Cu(sal:m-ap)}_2\text{H}_2 \hspace{1cm} \text{(Step 1)} \\
\text{Cu(sal:m-ap)}_2\text{H}_2 + \text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \rightarrow 2 \text{CuL} \hspace{1cm} \text{(Step 2)}
\]

It was learned through the synthesis of the known system, 
Cu(sal:o-aminophenol) (23) that substitution of o-ap in 
Step 1 produced the CuL complex instead of CuL₂H₂. This 
proved that one mole of the ligand could be abstracted
from the central metal. That fact was the basis for attempting Step 2, because the meta-aminophenol system did not behave identical to its isomer, ortho-aminophenol. In this case, the preferential product was CuL₂H₂. By use of the Soxhlet apparatus and the Al₂O₃ dehydrating agent, anhydrous Cu(sal)₂ was isolated. The insoluble anhydrous Cu(sal)₂ was put into 400 ml of absolute ethanol, and the solvent was allowed to reflux as described before. Afterwards, solid meta-aminophenol (6.54 g; 0.06 mole) was added a little at a time to avoid bumping. After one hour of refluxing, the solution turned dark brown-black and the solubility of the substance increased. After another hour, the solution was filtered and no solid material was collected on a medium porosity frit. The volume of the filtrate was reduced to 250 ml, cooled and refrigerated overnight. Shiny black-brown microcrystals were recovered from the absolute ethanol. These crystals analyzed to be the anhydrous CuL₂H₂ complex (Step 1) with a 78% yield.

Obtaining the CuL complex was similar to that of the Cu(pyrr:o-aminophenol) system. The Soxhlet apparatus was used in the same manner as before. The black-brown soluble microcrystals of the Cu(sal:m-aminophenol)₂H₂ (11.3 g; 0.023 mole) were dissolved in 400 ml of absolute ethanol and the solution was allowed to reflux. Cupric acetate monohydrate (4.0 g; 0.02 mole) was powdered and added as a
solid a little at a time to prevent bumping. Refluxing overnight using the Soxhlet resulted in a black-brown precipitate which indicated that a reaction had taken place. The powder was washed with ethanol and dried under vacuum at 70°C overnight. The elemental analysis was comparable to its isomer Cu(sal: o-aminophenol) indicating that the desired CuL product (Step 2) had been formed. The yield was approximately 63%. This product was insoluble in most common organic solvents, therefore it was not recrystallized. This compound also did not sublime under 0.20 mm Hg vacuum at a 260°C oil bath. No other means of purification were successful, therefore the complex was studied as a powder. If the above procedures are not followed as specified, the reaction products are not reproducible. Likewise, the Schiff base method of utilizing a crystalline Schiff base with Cu(OAc)₂·H₂O does not yield remotely the desired product.

\[
\left[\text{Cu(pyrr: m-aminophenol)H}\right] \text{OH was prepared in the following proposed manner:}
\]

\[
\begin{align*}
\text{Cu(OAC)₂·H₂O} & + 2 \text{ pyrr} & \rightarrow & \text{Cu(OH)(OAc) + ETOH Blue} & \quad (\text{Step 1}) \\
2 \text{ pyrr} + 2 \text{ m-ap} & & & & \\
\text{Cu(OH)(OAc) + 2LH₂} & & & \text{CuLH(OH) + HAc + LH₂} & \quad (\text{Step 2})
\end{align*}
\]

This reaction was unexpected. The intended product of Cu(pyrr)₂ was to be reacted with meta-aminophenol to yield CuL₂H₂ as had been the case in Cu(pyrr:o-aminophenol).
However, the solid blue intermediate, Cu(OH)(OAc), was isolated and the elemental analysis indicated its composition. Apparently, Cu(OH)(OAc) reacted with the Schiff base that had been formed in the interim, producing the hydroxide-bridged complex where only one proton had been removed from the ligand. The elemental analysis for the copper complex of Step 2 gave the same formulation as CuL(HOH), but no water band was present in the infrared. Based on the composition of the blue intermediate, the bridging hydroxide complex was proposed. Further investigation proved that Cu(pyrr)₂ can be prepared by using basic copper carbonate, and is more difficult to prepare than Cu(sal)₂. Attempts to prepare the Schiff base, pyrr:m-amino-phenol, from an alcoholic medium resulted in a black tar-like product upon exposure to the atmosphere overnight. Apparently, there was decomposition.

Physical Measurements-Instrumentation

Analysis of the Complexes.—Percent carbon, hydrogen, and nitrogen were determined by PCR, Inc., P. O. Box 1466, Gainesville, Florida and Galbraith Laboratories, Inc., P. O. Box 4187, Knoxville, Tennessee. Percent copper was determined by electrodeposition of copper metal onto a platinum electrode using a Sargent-Slomin Electrolytic Analyzer.
Molecular Weight Determination.--The molecular weights of the soluble complexes were determined in spectral-grade chloroform at 37°C on a Mechrolab Model 310A Vapor Pressure Osmosmeter using benzil as the calibrant. Several concentrations were used in the measurements.

Melting Point.--Micro-melting points were measured on a Thomas Hoover Capillary Melting Point apparatus. The oil bath had a limiting temperature of 260°C.

Infrared Spectra.--The infrared spectrum of each complex was obtained using a Perkin-Elmer Model 621 Recording Spectrophotometer. Nujol and flurolube mull techniques were both used for diagnostic purposes for some of the complexes. The scanning range was 4000 cm⁻¹ to 600 cm⁻¹ using sodium chloride discs. Band assignments for the complexes are given in Table X and the information was provided by Conley (12, pp. 87-194), Silverstein and Bassler (31, pp. 64-109), and Bellamy (7, pp. 69-83).

Electronic Spectra.--The electronic spectrum of each complex was obtained on a Cary 14 Recording Spectrophotometer. Solution spectra were obtained on soluble complexes using the appropriate solvent in matched one-centimeter quartz sample cells. The molar absorptivities and frequencies of corresponding band maxima were then determined. Solid state spectra were obtained on nujol mulls. The scanning
TABLE X
SUMMARY OF ASSIGNMENTS FOR INFRARED ABSORPTION BANDS

<table>
<thead>
<tr>
<th>Frequency, cm(^{-1})</th>
<th>Intensity*</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650-3584</td>
<td>s, sh</td>
<td>O-H stretching vibration, &quot;free&quot;</td>
</tr>
<tr>
<td>2960-2840</td>
<td>vs, br</td>
<td>C-H stretching vibration from Nujol</td>
</tr>
<tr>
<td>1605-1580</td>
<td>vs, sh</td>
<td>C-N stretching vibration</td>
</tr>
<tr>
<td>1570-1440</td>
<td>s, m</td>
<td>(3-4 bands) C=C benzene ring vibration</td>
</tr>
<tr>
<td>1470-1450</td>
<td>s, m</td>
<td>-CH(_2)- bending vibration from Nujol</td>
</tr>
<tr>
<td>1390-1350</td>
<td>s, m</td>
<td>-C-CH(_3)- bending vibration from Nujol</td>
</tr>
<tr>
<td>1310-1280</td>
<td>s, m</td>
<td>C-N stretching vibration</td>
</tr>
<tr>
<td>1060-1010</td>
<td>s</td>
<td>C-O stretching vibration</td>
</tr>
<tr>
<td>900-700</td>
<td>s</td>
<td>out-of-plane C-H deformation of benzene ring</td>
</tr>
<tr>
<td>755-720</td>
<td>s, m</td>
<td>-(CH(_2))(_n)- bending vibration of chelate</td>
</tr>
<tr>
<td>700-500</td>
<td>s, m</td>
<td>metal chelate ring vibration</td>
</tr>
</tbody>
</table>

*vs = very strong; s = strong; w = weak; m = medium; sh = sharp; br = broad.
range was that of the visible region 7000 Å (14,280 cm$^{-1}$) to 300 Å (33,330 cm$^{-1}$) for the purpose of observing d-d transitions for the Cu(II) ion.

Magnetic Data.--The magnetic susceptibilities were measured by using an Alpha Model 7500 Electromagnet and a Regulated Power Supply System. The Gouy method of determination was used with mercury tetrathiocyanatocobaltate(II), $\text{Hg}[\text{Co(NCS)}_4]$, as the calibrant (17, pp. 84-94). The apparatus is schematically represented in Fig. 43. The diamagnetic corrections for the ligand were computed using Pascal's constants (17, p. 6); and the magnetic susceptibilities were corrected for TIP using a value of $60 \times 10^{-6}$ cgs units for Cu(II), and zero for Mn(II). The magnetic moments were calculated using equation 2.

The magnetic susceptibilities were measured over the temperature range of 296 K to 78 K. The room temperature and liquid nitrogen temperature measurements were obtained by using methods described in Earnshaw (17). The measurements determined at intermediate temperatures were obtained from the method to be described by using the apparatus illustrated in Fig. 44. A tube containing the sample was suspended in a cylindrical copper tube encased in an insulated glass jacket. Nitrogen gas, cooled by passing through a liquid nitrogen reservoir, was passed through the glass jacket.
Fig. 43—Apparatus Used to Determine Magnetic Data by the Gouy Method.
Fig. 44—Apparatus Used to Determine Variable Temperature Magnetic Susceptibilities.
around the copper tube containing the sample. The various temperatures were obtained by regulating the flow rate of the nitrogen gas through the liquid nitrogen reservoir. Figure 43 represents the overall set-up of the instruments as described. The temperatures were determined by using a copper-constantan thermocouple placed near the sample and connected to a Leeds and Northrup Model 8691 Milivolt Potentiometer with an ice-water bath as the reference temperature. A nitrogen atmosphere was maintained around the tube containing the sample to prevent the formation of frost. Linear least squares treatment of \( (X_{M}^{corr})^{-1} \) vs. Temperature was performed on a Compucorp Model 325 Scientist Desk Calculator (15).

Conclusion

Several general observations can be made with regard to the complexes discussed in this chapter. Historically, the main interest has centered around the differences and similarities of the so-called "2- and 3-carbon" amine-alcohol chain, as they effect the properties of the Cu(II) Schiff base complexes. Generalities should not be issued irresponsibly. The length of the carbon chain as an independent factor is not solely responsible for the observed results. It has been pointed out that when the length of the aminealcohol chain within two different complexes is equal, factors such as unsaturation, steric hindrance, and
flexibility are also influential. For example: Cu(acac:ethanolamine) has a cubane tetrameric form, whereas Cu(acac:o-aminophenol) has a stacked tetrameric structure. Likewise, where all facets of the ligand are equal except for a lone substituent, the results are interesting. For example Cu(acac:ethanolamine) exhibits overall antiferromagnetic behavior, where Cu(benzoylacetone:ethanolamine) exhibits ferromagnetic behavior; and both are postulated to have the same structure. Let it be mentioned also that changing the ring size and donor atoms has profound consequences as will be discussed later. For example: the plot of $\chi_m$ vs. Temp. for Cu(pyrr:o-aminophenol) has a lower Neel point than Cu(acac:o-aminophenol).

Other observations shall be classified together. All of the 2-carbon systems, regardless of the structure, had crystals that were shades of green. All of the 3-carbon systems, irrespective of the structure, were very dark brown to black. All of the meta-aminophenol complexes had extremely poor degrees of solubility. Both of the meta ligands whose infrared spectra are shown, Fig. 25 and Fig. 28, had few bands in the fingerprint region, excluding nujol, and the bands were slightly broad. The $[\text{Cu(pyrr:m-aminophenol)}\text{H}]\text{OH}$ complex had the same characteristics, Fig. 36. The melting points of all of the meta compounds of CuL coordination were greater than 255°C and Cu(acac:m-aminophenol) decomposed. Many of the methods of preparation
presented in the experimental section required several steps, some which required the purification of the products of each step. This was quite unexpected considering most complexes can be made by reacting the Schiff base with Cu(OAc)$_2$·H$_2$O in a straightforward manner in alcohol. Two of the ligands, pyrr:o-aminophenol and sal:m-amino-phenol, formed monomers as the preferred product of the abovementioned Schiff base method. Some of the electronic spectra taken as nujol mulls showed an entire band around 25,000 cm$^{-1}$. However, when a spectrum was repeated in solution, the molar absorptivity of the band indicated that some metal-ligand interaction was responsible and not a d-d transition.

Interpretation of magnetic data is of primary concern here. The major issue, of recent, has been the correlation between structural and magnetic features. A summary of the data of past and present complexes has been collected in Table XI. In conjunction with Table XI is Fig. 45, which is a graph of the exchange integral, J, with the Cu-O-Cu angle, $\phi$. McGregor, et al. (28) state that as the angle increases, the value of J correspondingly decreases. Hodgson (21, pp. 178-79) states that purely p orbitals require 90$^\circ$ orientations and give rise to values of J>0 corresponding to a triplet ground state. Purely s orbitals require >90 orientations leading to more "s"
TABLE XI
SUMMARY OF STRUCTURAL AND MAGNETIC PROPERTIES

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\mu$Temp, BM</th>
<th>$J, \text{cm}^{-1}^*$</th>
<th>Cu-O-Cu, $\phi$, deg.</th>
<th>$\chi_\text{M} \times 10^6 \text{ cgs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sal:eth$^a$</td>
<td>$\mu 294 = 1.83$</td>
<td>+22</td>
<td>-----</td>
<td>1422</td>
</tr>
<tr>
<td>acac:eth</td>
<td>$\mu 295.3 = 1.84$</td>
<td>+22</td>
<td>97.8$^0$</td>
<td>1417</td>
</tr>
<tr>
<td>$\phi$acac:eth$^b$</td>
<td>$\mu 296 = 1.87$</td>
<td>+46</td>
<td>-----</td>
<td>1470</td>
</tr>
<tr>
<td>pyrr:eth</td>
<td>$\mu 293 = 1.89$</td>
<td>+72</td>
<td>-----</td>
<td>1521</td>
</tr>
<tr>
<td>pyrr:prop$^c$</td>
<td>$\mu 299.5 = 0.54$</td>
<td>-750</td>
<td>103.9$^0$</td>
<td>78</td>
</tr>
<tr>
<td>sal:prop</td>
<td>$\mu_{RT} = 0.44$</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>acac:prop</td>
<td>$\mu 298 = 0.41$</td>
<td>-901</td>
<td>106.4$^0$</td>
<td>69</td>
</tr>
<tr>
<td>$\phi$acac:prop</td>
<td>$\mu 296 = 0.31$</td>
<td>-978</td>
<td>-----</td>
<td>42</td>
</tr>
<tr>
<td>acac:ortho$^a$</td>
<td>$\mu 270 = 1.32$</td>
<td>-298</td>
<td>100.7$^0$</td>
<td>-800</td>
</tr>
<tr>
<td>sal:ortho</td>
<td>$\mu 265 = 1.28$</td>
<td>-293</td>
<td>-----</td>
<td>-826</td>
</tr>
<tr>
<td>pyrr:ortho</td>
<td>$\mu 296 = 1.60$</td>
<td>-153</td>
<td>-----</td>
<td>1083</td>
</tr>
<tr>
<td>acac:meta$^e$</td>
<td>$\mu 296 = 0.86$</td>
<td>-556</td>
<td>-----</td>
<td>311</td>
</tr>
<tr>
<td>sal:meta</td>
<td>$\mu 296 = 1.11$</td>
<td>-424</td>
<td>-----</td>
<td>526</td>
</tr>
<tr>
<td>pyrr:meta H(OH)</td>
<td>$\mu 296 = 1.16$</td>
<td>-404</td>
<td>-----</td>
<td>566</td>
</tr>
</tbody>
</table>

$^*$Calculated from Bleaney-Bowers eq. 4;
$^a$eth = ethanolamine;
$^b$acac = benzoylacetone;
$^c$prop = propanolamine;
$^d$ortho = ortho-aminophenol;
$^e$meta = meta-aminophenol.
Fig. 45—The Cu-O-Cu Bridging Angle, $\phi$ vs. The Singlet-Triplet Exchange Integral, $J$. The original graph with $+$ are from ref. 28. 1) Cu(acac:m-aminophenol); 2) Cu(sal:m-aminophenol); 3) Cu(acac:o-aminophenol); 4) Cu(sal:o-aminophenol); 5) Cu(pyrr:o-aminophenol).
character and values of $J<0$ which correspond to a singlet ground state. Figure 45 indicates that at the "crossover" angle of $97.8^0$, the value of $J$ should be zero.

None of the propanolamine complexes have been included on the graph in Fig. 45, even though the Bleaney-Bowers equation 4 is specifically designed for dimers, because most were very diamagnetic at room temperature. Sinn (32) has very recently reported the crystal structures of three additional propanolamine compounds. He clearly states that because there is no maximum for the $\chi_M$ vs. $T$ curves, the values of $J$ cannot be determined accurately. He therefore selects $-800$ cm$^{-1}$ as a lower limit.

All of the ethanolamine complexes reported thus far, with the exception of Cu(acac:ethanolamine), have exhibited overall ferromagnetism. The structure of the other ethanolamine compounds was proposed to be the same as Cu(acac:ethanolamine), (i.e., cubane) and yet their magnetic behavior was very different. This would seem to indicate that the peculiarity lies within the Cu(acac:ethanolamine) complex and not with the others. This peculiar behavior might very well be a consequence of the Cu-O-Cu bond angle of $97.8^0$, which is near the "crossover" in Fig. 45.

Table XII is the magnetic data obtained by Helm (26), and shows that as the temperature is lowered, the moments decrease and this is opposite to the other proposed cubane tetramers. Another compound that shows unusual magnetic
behavior relative to compounds of similar structure is Cu(pyrr:o-aminophenol). Examination of Table IV shows that the magnetic behavior is very similar to that of Cu(acac:ethanolamine) in Table XII and yet the structures are different. Another viewpoint would be that a comparison of the data on Cu(acac:o-aminophenol), Fig. 33, reveals that Cu(pyrr:o-aminophenol) may have the structure of a stacked dimer but exhibits a magnetic behavior inconsistent with that proposed structure. Taking the value of $J$ at $-153$ cm$^{-1}$ and estimating the bond angle from Fig. 45, would indicate that the probable angle is between $98.5^\circ$ and $99^\circ$, which is also close to the "crossover" angle.

Sinn (32) has also mentioned that the strength of antiferromagnetic interaction is determined by the efficiency

**TABLE XII**

MAGNETIC DATA FOR Cu(ACAC:ETHANOLAMINE)*

<table>
<thead>
<tr>
<th>Temp., °K</th>
<th>$\chi_M \times 10^6$, cgs</th>
<th>$\mu_{\text{eff}}$, BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.3</td>
<td>1417</td>
<td>1.84</td>
</tr>
<tr>
<td>227.0</td>
<td>1847</td>
<td>1.84</td>
</tr>
<tr>
<td>176.1</td>
<td>2336</td>
<td>1.82</td>
</tr>
<tr>
<td>116.2</td>
<td>3365</td>
<td>1.78</td>
</tr>
<tr>
<td>88.9</td>
<td>4236</td>
<td>1.74</td>
</tr>
<tr>
<td>28.3</td>
<td>8022</td>
<td>1.35</td>
</tr>
</tbody>
</table>

*Ref. 26.
of the Cu-O-Cu superexchange overlap. The Cu(sal:m-aminophenol) and Cu(acac:m-aminophenol) complexes seem to have more antiferromagnetic character than their corresponding ortho-aminophenol analogs. According to their $J$ values and Fig. 45, the bond angles appear to be greater than the ortho complexes, and this would imply greater s character and greater orbital overlap. This observation is consistent with the data produced for the 3-carbon systems relative to the 2-carbon systems, in that the 3-carbon systems were more antiferromagnetic. For example: Cu(benzoylacetone:propanolamine) was diamagnetic and Cu(benzoylacetone:ethanolamine) was ferromagnetic.

Of the three propanolamine complexes with substituents on the salicylaldehyde functionality that Sinn (32) reported, he noticed that the substituents had no inductive effect. The modification of the ligand is only as good as it influences the immediate geometry of the metal—in his case, square planar. That is, the dependence on the metal environment outweighs the effect of varying the nature of the ligand. For example, Cu(benzoylacetone:ethanolamine) has essentially the same ring systems and donor atoms as Cu(acac:ethanolamine); and yet the substituent, the phenyl ring, introduced enough hindrance to slightly alter the immediate environment of the metal. This slight modification revised the Cu-O-Cu bond angle enough to
force the p orbitals to be used on the oxygen to produce ferromagnetism, instead of the s orbitals that had been used in Cu(acac:ethanolamine) (18). In spite of this substituent, the molecular packing was not influenced and the complex retained the tetrameric structure.

All of the new data presented in the chapter are consistent with the concept that magnetic behavior is determined largely by structural character. The length of the aminealcohol chain is important but only if it is considered carefully. A straight chain which is flexible provides a very different geometry for the copper environment than an unsaturated rigid ring system, even if the length of the chain is the same. Substituents are relatively unimportant except for any structural modifications they produce on the Cu-O-Cu bridging angle, or on the molecular packing. That is, a very bulky substituent might break up a tetramer and force it into a dimeric structure. The effect of the Cu-O-Cu angle on the J value has been documented for a wide range of complexes, but it cannot be taken in isolation. The copper geometry is also important in determining the superexchange overlap along the Cu-O-Cu bonds. As a result of the investigations conducted, two of the complexes, Cu(benzoylacetone:ethanolamine) and Cu(pyrr:o-aminophenol) have been considered for x-ray determinations. It is believed that the results will be significant contributions to the already existing data.
CHAPTER BIBLIOGRAPHY


CHAPTER III

SCHIFF BASE COMPLEXES OF MANGANESE(II)

Introduction

Schiff base complexes of copper(II) have attracted the interest of researchers for years, especially in the study of spin-spin interactions. However, manganese(II) has not been of equal interest. The most detracting feature is the air sensitivity to oxidation when the complex is moist (7, 10). The complexes are air stable when dry, so precautions must be taken during synthesis and isolation to maintain an inert atmosphere. Manganese(II) Schiff base complexes are usually shades of yellow, and upon oxidation turn dark to shades of brown which is characteristic of manganese(III).

Most of the studies of manganese(II) complexes have been with ligands that have been previously investigated with various central metal ions. Lewis and coworkers (10) reported a study of the Mn(salen) complex, and a comparison of its x-ray powder pattern with that of Cu(salen). Cu (salen) is a dimeric complex having an antiferromagnetic behavior. The similarity of these powder patterns allowed these researchers to conclude that Mn(salen) had a binuclear structure in which there was antiferromagnetic exchange.
Earnshaw and coworkers (7) reported Mn(II) complexes of tetradentate ligands. Yarino, et al. (17) studied the oxidation products of manganese(II). Little or no work with tridentate ligands of Schiff bases had been done until Butler and West (3) synthesized and characterized the manganese(II) analog of Cu(sal: o-aminophenol) and similar complexes. Extensive data was collected on variable temperature magnetic susceptibility as well as characterization of the complexes and interpretation of data. The magnetic moment for Mn(sal: o-aminophenol) ranged from 5.76 BM at 295\(^{0}\)K to 5.44 BM at 99.5\(^{0}\)K. The decrease in moment is slight, but nevertheless could result from an antiferromagnetic interaction of the manganese ions. Since that time, much work has been done with Mn(III) and Mn(IV) either as oxidation products of Mn(II), or as complexes with tetradentate ligands (2, 6, 7, 11, 13, 17, 18). Other work involves halides (16). Even a most recent study by Sinn (16) is of the crystal structure of a manganese(II) dimer with bridging chlorides. In view of the publications mentioned, no further work with tridentate ligands of manganese(II) has been done since Butler and West (3). Since it is these tridentate Schiff base ligands that form copper(II) dimers and tetramers of recent interest, it would seem appropriate to continue this type of work with manganese(II). For that reason, the complex of manganese(II) with pyrr: o-aminophenol as the ligand is discussed in this chapter.
Experimental and Results

Preparation of the Complex

Manganese(II) acetate tetrahydrate was obtained from the J. T. Baker Chemical Co., Phillipsburg, New Jersey. Mn(pyrr:o-aminophenol)$_2$H$_2$ was prepared in the following manner:

\[ \text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O} + \text{(pyrr:o-ap)}\text{H} \rightarrow \text{MnL}_2\text{H}_2 \]

Purified ortho-aminophenol (0.33 mole; 3.27 g) was dissolved with pyrrole-2-carboxaldehyde (0.03 mole; 2.85 g) in absolute methanol and refluxed for one hour. Since manganese(II) is sensitive to air oxidation, an inert nitrogen atmosphere was maintained. A reflux apparatus similar to that illustrated in Fig. 46 was used to keep the system purged with nitrogen gas. Mn(OAc)$_2 \cdot 4$H$_2$O (0.02 mole; 4.90 g) was dissolved in about 300 ml of absolute methanol. The Schiff base solution was independently purged and then put into the side arm funnel. The clear yellow Schiff base solution was then added dropwise to the metal solution. A rich canary yellow precipitate formed, and the mixture was allowed to reflux overnight. The precipitate was isolated in a dry bag, and the yield was approximately 80% MnL$_2$H$_2$.

Unlike Cu(pyrr:o-aminophenol), the MnL complex could not be formed by reacting one mole of Mn(OAc)$_2 \cdot 4$H$_2$O.
Fig. 46--Apparatus Used for the Preparation of Manganese(II) Complexes Under an Inert Atmosphere.
with the $\text{MnL}_2\text{H}_2$ complex. The $\text{MnL}_2\text{H}_2$ complex was recovered. The yellow compound could not be recrystallized due to its tendency to oxidize when wet, and was therefore studied as a powder.

**Analysis of the Complex**

The percent carbon, hydrogen, and nitrogen were determined by PCR, Inc., P. O. Box 1466, Gainesville, Florida. The manganese analysis was determined with a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer with a manganese lamp set at a wavelength of 279 nm in the ultraviolet region. The melting point of the yellow powder was greater than $255^\circ\text{C}$, and the elemental analysis was as follows: calcd. for $\text{MnC}_{22}\text{H}_{18}\text{N}_2\text{O}$; C, 62.57; H, 4.23; N, 13.16; Mn, 12.91. Found: C, 62.09; H, 4.37; N, 13.03; Mn, 12.45.

**Infrared Spectra**

The infrared spectra were obtained on a Perkin Elmer Model 631 Recording Spectrophotometer. The nujol mull spectrum of the pyrr:o-aminophenol ligand in the region $4000 \text{ cm}^{-1}$ to $400 \text{ cm}^{-1}$ on cesium iodide discs is shown in Fig. 47. The nujol mull spectrum of $\text{Mn(pyrr:o-aminophenol)}_2\text{H}_2$ in the region $4000 \text{ cm}^{-1}$ to $600 \text{ cm}^{-1}$ on sodium chloride plates is shown in Fig. 48. The flurolube mull spectrum of the $\text{MnL}_2\text{H}_2$ complex in the region $4000 \text{ cm}^{-1}$ to $300 \text{ cm}^{-1}$ on cesium iodide discs is shown in Fig. 49.
Fig. 47--Nujol Mull Infrared Spectrum of Pyrr:o-aminophenol Ligand
Fig. 48—Nujol Mull Infrared Spectrum of Mn(II) (Pyridine-4-aminophenol)\(_2\)H\(_2\)
Magnetic Susceptibility

The magnetic data were determined by the Gouy method, and the liquid nitrogen determination was measured in the manner described in Chapter II. Since the analytical data indicate a bis complex, it was assumed that the compound was a monomer. Previous experience with copper(II) complexes proved that the magnetic moments did not vary with temperature for a monomer. For that reason, only the room temperature and liquid nitrogen measurements were taken. The following results were obtained: RT $\mu_{\text{eff}} = 5.89$ BM; LN $\mu_{\text{eff}} = 6.01$ BM.

Electronic Spectra

The electronic spectrum was obtained on a Cary 14 Recording Spectrophotometer. The nujol mull spectrum for the MnL$_2$H$_2$ complex in the range 14,280 cm$^{-1}$ to 33,300 cm$^{-1}$ is shown in Fig. 50. The following is a summary of the band position and intensity: 16,000 cm$^{-1}$ (weak, broad, shoulder); 17,540 cm$^{-1}$ (weak, shoulder); quintet--20,830, 21,180, 21,270, 21,500; 21,640 cm$^{-1}$ (sharp bands); 22,220-27,770 cm$^{-1}$ (broad envelope, may be more than one band); 29,850 cm$^{-1}$ (maximum).

Discussion

Several attempts were made to synthesize tridentate dibasic Schiff base complexes of magnesium(II). The results
Fig. 50--Nujol Mull Electronic Spectrum of Mn(pyrr:o-aminophenol)₂H₂
varied from oxidized species to incomplete reactions. After the extensive work with copper(II), it has become evident that even the air-stable copper(II) can have complicated and unpredictable synthetic pathways. The Mn(pyrr:o-aminophenol)₂H₂ complex represents new work in this area, and hopefully represents a foundation for continued effort.

**Infrared Spectra**

The infrared spectrum of the ligand is shown in Fig. 47. A closer examination of the spectrum is required to properly identify the bands corresponding to both the N-H stretch and the O-H stretch. This is necessary because in the formation of the metal complex of MnL₂H₂ coordination, only one proton is removed from the ligand. A comparison of the spectra of the ligand and the complex should reveal which element was deprotonated.

Examination of Fig. 47, the ligand, reveals two bands, 3330 cm⁻¹ and 3270 cm⁻¹, in the region of interest. In a dilute solution the "free" unbonded hydroxyl group of alcohols and phenols absorbs strongly in the 3650-3584 cm⁻¹ region. The "free" N-H stretching vibration is observed
in dilute solutions near 3500-3400 cm\(^{-1}\). Since the spectra discussed here are of the solid phase instead of solution phase, the differences in the band positions must be considered. Intermolecular hydrogen bonding (15, p. 84) increases as the concentration increases, and bands start to appear at lower frequencies, 3550-3200 cm\(^{-1}\), at the expense of the "free" hydroxyl band. A band at 3623 cm\(^{-1}\) would result from a "monomer," whereas a broader absorption near 3333 cm\(^{-1}\) would be attributed to a "polymeric" structure (15, p. 84). When the ligand in question here was diluted in carbon tetrachloride to decrease the effect of hydrogen bonding, the band at 3330 cm\(^{-1}\) shifted to 3460 cm\(^{-1}\). If solubility permitted further dilution, it is anticipated that the band would shift to still higher frequency. If the band were to persist even after dilution, then according to Bergmann, et al. (1), the hydroxyl bands observed in the 3450-3380 cm\(^{-1}\) region are due to \textit{intramolecular} hydrogen bonding. Daasch and Hanninen (5) reported structure elucidation of Schiff bases, where there had been discrepancy, and had observed the same effects of hydrogen bonding on the shift in the position of the O-H band. Silverstein and Bassler (15, p. 93) state that overlapping occurs in the observed position of the N-H and O-H stretching frequencies so that an unequivocal differentiation in the structure is sometimes impossible.
In view of this, it is concluded that the band at 3330 cm\(^{-1}\) is attributed to the hydroxyl stretching vibration of the phenol, and that the absorption at 3270 cm\(^{-1}\) is due to the secondary amine N-H stretch of the ligand. The remaining band assignments are in Table X.

The nujol mull infrared spectrum for the MnL\(_2\)H\(_2\) complex is shown in Fig. 48 which reveals two absorptions, 3130 cm\(^{-1}\) and 3050 cm\(^{-1}\). The flurolube mull spectrum, Fig. 49, has exactly the same bands. The only difference between the spectra is the characteristic bands of flurolube marked by "F" in the spectrum. It has been stated that the secondary amines show a single weak band in the 3350-3310 cm\(^{-1}\) region. In more concentrated solutions or in solid samples, the free N-H band is replaced by multiple bands in the 3330-3060 cm\(^{-1}\) region. Multiple bands are observed since the amine group can bond to produce a cis configuration, or produce a polymer with a trans structure (15, p. 94). The schematic is represented as

![Schematic Diagram](image)

CIS

square planar because the visible spectrum of the Cu(II) analog gives evidence of this type of structure. The
diagram merely shows that hydrogen bonding could be inter-
molecular or intramolecular depending on the relationship
of the ligand to the metal. The actual molecular geometry
has not yet been confirmed.

Based on the information obtained, it has been
concluded that the hydroxyl proton was removed during
complexation, leaving the N-H of the pyrrole ring to
hydrogen bond. It is the N-H proton and its interactions
that result in the two bands at 3130 cm\(^{-1}\) and 3050 cm\(^{-1}\).
It is also believed that in a neutral medium, the phenolic
proton is more acidic and therefore more likely to be
removed than the amine proton (8, pp. 303-309). The
remaining band assignments are in Table X.

Electronic Spectrum

The electronic spectrum for Mn(pyrr:o-aminophenol)\(_2\)H\(_2\)
in the region 14,280-33,330 cm\(^{-1}\) is shown in Fig. 50. At
first glance it appears rather unusual compared to the
spectra for the Cu(II) complexes. The electronic con-
figuration for Cu(II) is d\(^9\), and for Mn(II) is d\(^5\). In
order to interpret the spectra of complexes in which the
metal ion has more than one but less than nine d electrons,
Cotton and Wilkinson (4, p. 573) discuss the use of the
energy level diagram based upon the Russell-Saunders states
of the relevant d\(^n\) configuration in the free (uncomplexed)
ion. In this case, the Tanabe-Sugano diagram for the d\(^5\)
configuration would be used (4, p. 1116) to interpret the spectrum in Fig. 50.

Table XIII gives the band assignments for both octahedral (Oh) and tetrahedral (Td) complexes of Mn(II), and the references in which the data was cited. Several important differences between the two possible configurations should be discussed.

1. The transitions from a sextet ground state (6[^A]_1) to a quartet excited state are spin-forbidden by the rules of quantum mechanics. However, weak spin-orbit interactions permit very weak absorption bands.

2. The molar absorbance of an octahedral Mn(II) complex is approximately 100 times weaker than those for similar but spin-allowed transitions.

3. Because of these weak d-d transitions, the color of the Oh Mn(II) complex is a very pale pink, or may even appear to be white. An example is Mn(OAc)₂·4H₂O.

4. The color of a tetrahedral Mn(II) complex is yellow-green, more intense than the octahedral complex.

5. The molar absorbance values for the Td complexes are in the range 1.0-4.0, whereas for the Oh Mn(II) complexes are in the range 0.01-0.04.

6. A very important difference is the position of the bands. Table XIII indicates that for ref. 4, each geometry has six absorption bands in two groups of three,
### TABLE XIII

**ELECTRONIC DATA FOR Td AND Oh Mn(II) COMPLEXES**

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency, cm(^{-1})</th>
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<tbody>
<tr>
<td>Assignment</td>
<td>Td (^a)</td>
</tr>
<tr>
<td>(\lambda_1) (^\text{&quot;T}_1) (^\text{&quot;G})</td>
<td>------</td>
</tr>
<tr>
<td>(\lambda_2) (^\text{&quot;T}_2) (^\text{&quot;G})</td>
<td>21,200</td>
</tr>
<tr>
<td>(\lambda_3) (^\text{&quot;E}) (^\text{&quot;G})</td>
<td>21,900</td>
</tr>
<tr>
<td>(\lambda_4) (^\text{&quot;E}) (^\text{&quot;G})</td>
<td>21,900</td>
</tr>
<tr>
<td>(\lambda_5) (^\text{&quot;E}) (^\text{&quot;G})</td>
<td>21,900</td>
</tr>
<tr>
<td>(\lambda_6) (^\text{&quot;A}_1) (^\text{&quot;G})</td>
<td>22,800</td>
</tr>
<tr>
<td>(\lambda_7) (^\text{&quot;T}_2) (^\text{&quot;D})</td>
<td>25,500</td>
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<tr>
<td>(\lambda_8) (^\text{&quot;E}) (^\text{&quot;D})</td>
<td>26,800</td>
</tr>
<tr>
<td>(\lambda_9) (^\text{&quot;T}_1) (^\text{&quot;P})</td>
<td>27,300</td>
</tr>
<tr>
<td>(\lambda_{10}) (^\text{&quot;T}_4) (^\text{&quot;P})</td>
<td>------</td>
</tr>
</tbody>
</table>

\(^a\)ref. 4: \(\text{[MnBr}_4\text{]}^{2-}\), Td; \(\text{[Mn(H}_2\text{O)}_6]^{2+}\), Oh

\(^b\)ref. 14: \(\text{Mn(SPPh}_2\text{NNPh}_2\text{S)}_2\), Td

\(^c\)ref. Thesis: \(\text{Mn(pyrr:o-aminophenol)}_2\text{H}_2\)
but in the Td complex, the bands are much closer together. This is expected since the $\Delta$ value for the tetrahedral complex should be less than that for the octahedral complex.

The data from ref. 14 show that for the same complex three spectra were taken: solution phase, pressed pellet, and single crystal. The position of the bands is comparable to that reported by Cotton and Wilkinson (4, pp. 578-581) for the tetrahedral geometry. However, an important distinguishing characteristic is that there are a total of nine possible sextet-quartet transitions, and it is only the single-crystal spectrum that was able to resolve most of the bands. It is interesting to note that the spectrum obtained on the MnL$_2$H$_2$ complex remarkably resembles the spectrum of the single crystal Td complex reported by Siiman and Gray (14). The $^4A_1(^4G)$ and $^4E(^4G)$ are degenerate and have been assigned the same energy. Siiman and Gray (14) have assigned the quartet beginning with 21,139-21,346 cm$^{-1}$ as the vibrationally sharp, structured bands for these $^6A_1\rightarrow^4E(^4G)$ and $^6A_1\rightarrow^4A_1(^4G)$ transitions. Siiman and Gray observed that the broad band at 23,700 cm$^{-1}$ assigned to the $^6A_1\rightarrow^4T_2(^4D)$ transition was not observed for the [MnBr$_4$]$^{2-}$ complex. The bands at 28,011 cm$^{-1}$ and 28,329 cm$^{-1}$ were assigned as components of the $^6A_1\rightarrow^4T_4(^4P)$ transition. The position of the bands are shifted from one complex to another and this is understandable considering
that the Mn(SPPh$_2$NPPh$_2$S)$_2$ complex has a bidentate ligand whereas the [MnBr$_4$]$^{2-}$ complex has what could be considered as single point charge ligands.

All of the above data has been collected for the express purpose of interpreting the spectrum of the MnL$_2$H$_2$ complex of Fig. 50. The yellow color of the powder could be evidence for a Td coordination. However, Siiman and Gray (14) have most recently reported the crystal structure of the tetrahedral Mn(II) complex, used here for comparison, which forms pink crystals. Therefore, the color of the compound is not an absolute diagnostic tool. Also, the spectrum is that of a solid state mull; and therefore, the magnitude of the molar absorbance cannot be used to determine the geometry. A similar study of a tridentate ligand (XIV) which complexed with manganese acetate tetrahydrate to form an MnL$_2$H$_2$ complex was studied by Mehta and Singhi (12). They reported the room temperature magnetic moment to be 5.83 BM. Their molecular weight data indicated a monomer. They proceeded to conclude, with no supportive evidence given, that the O-H from the ligand
was actually coordinated to the central metal, thereby
giving a hexacoordinated complex. The complex that Mehta
and Singhi (12) reported had a brown color, according to
their table of data. This is very suspicious because the
Mn(II) Schiff base complexes of tridentate ligands usually
render yellow colors, and the Mn(III) has a characteristic
dark color. The report mentioned no precautions concerning
air sensitivity, so the oxidation state of their metal is
questionable. At any rate, they reported an octahedral
coordination.

Another series of studies were conducted on five-
coordinated Mn(II) complexes by Boucher (2), in which
the complexes were of MnLCl coordination where L is a
tetradentate ligand. The electronic studies conducted
were of a slightly different nature than that reported
above, because the geometry is a square pyramidal type which
is different than octahedral or tetrahedral. According
to the crystal field diagram of Fig. 20, Boucher (2)
reported three allowed d-d transitions and their positions:
14-15,000 cm$^{-1}$ ($d_z^2$→$d_x^2$−$y^2$); 16-17,000 cm$^{-1}$ ($d_{xy}$→$d_x^2$−$d_y^2$);
21,000 cm$^{-1}$ ($d_{xz}$, $d_{yz}$+$d_x^2$−$y^2$) from lower energy→higher
energy. Other higher energy bands were attributed to
metal-ligand interactions.

Based on the data collected, the exact geometry of
the complex is not easily discernible. The electronic
spectrum gives strong indication of a Td arrangement.
The only question left is to decide if the nature of the ligand; i.e., ring size, rigidity, etc., would lend itself better to an Oh or Td conformation as indicated by Mehta and Singhi (12). It seems unusual that the pyrrole ring would be left uncoordinated in space to form a Td arrangement; but without a molecular structure, the issue is open-ended and unresolved.

**Magnetic Susceptibility**

An octahedral or tetrahedral spin-free mononuclear manganese(II) complex has a room temperature magnetic moment of 5.92 BM. Ordinarily, the moment of a monomer is independent of temperature, but in this case a slight elevation occurred as the temperature was lowered by liquid nitrogen to 780K. The exact explanation for this increase is unknown, but perhaps the weak spin-orbit interactions are responsible. Theoretically, the orbital angular moment is zero and would not contribute to the moment. Butler and West (3) reported room temperature moments as high as 6.08 BM, so the observed values here are of the same order.

**Conclusion**

Many tridentate ligands were used in an effort to synthesize MnL complexes that would be similar to the CuL complexes reported. However, complications developed either during isolation in the dry bag, or during the
synthetic procedure itself. It should be noted that most of the copper complexes introduced in Chapter II had unusual synthetic pathways. So, hopefully, through the work with copper, new techniques for the preparation of these MnL complexes will be developed.

The initial goal in this study was to arrive at a suitable ligand that would pair the d electrons on the Mn(II) central ion. However, all attempts failed. The work with copper(II) in conjunction with Butler and West (3) has added new interest in the formation of Mn(II) dimers and maybe tetramers with tridentate ligands. Two highly successful ligands with Cu(II) have been benzoylacetone:ethanolamine and benzoylacetone:propanolamine. The three-carbon system might form a dimer with large antiferromagnetic interaction with manganese(II). This has yet to be done. Even though most d-d transitions are weak, the electronic spectra of new MnL complexes might still be used, as Boucher (2) has done.

Since these Mn(II) Schiff base complexes are non-crystalline, it is anticipated that future synthesis will be coupled with x-ray powder data from the corresponding CuL complex. The possibility for future work with manganese(II) is virtually unlimited at this point.
CHAPTER BIBLIOGRAPHY


APPENDIX

Physical Constants

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<th>Name</th>
<th>Symbol</th>
<th>Value</th>
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<tr>
<td>Avogadro number</td>
<td>N</td>
<td>$6.0225 \times 10^{23}$ mole$^{-1}$</td>
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<tr>
<td>Bohr magneton</td>
<td>B</td>
<td>$9.2731 \times 10^{-21}$ erg gauss$^{-1}$</td>
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<tr>
<td>Boltzmann constant</td>
<td>k</td>
<td>$1.3805 \times 10^{-16}$ erg °K$^{-1}$</td>
</tr>
<tr>
<td>Planck constant</td>
<td>h</td>
<td>$6.6256 \times 10^{-27}$ erg-sec</td>
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</table>

Abbreviations

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<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>acac</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>bza</td>
<td>benzoylaceton</td>
</tr>
<tr>
<td>pyrr</td>
<td>pyrrole-2-carboxaldehyde</td>
</tr>
<tr>
<td>sal</td>
<td>salicylaldehyde</td>
</tr>
<tr>
<td>salen</td>
<td>salicylaldehyde:ethylenediamine</td>
</tr>
<tr>
<td>BM</td>
<td>Bohr magneton</td>
</tr>
<tr>
<td>J</td>
<td>Exchange integral</td>
</tr>
<tr>
<td>Nα</td>
<td>Temperature independent paramagnetism</td>
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<tr>
<td></td>
<td>$60.0 \times 10^{-6}$ cgs for Cu$^{2+}$;</td>
</tr>
<tr>
<td></td>
<td>0.00 for Mn$^{2+}$</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
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<tr>
<td>$\mu_{\text{eff}}$</td>
<td>Effective magnetic moment</td>
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<tr>
<td>$\chi_{\text{M, corr}}$</td>
<td>Corrected magnetic susceptibility</td>
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Abbreviations (contd.)

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<thead>
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<tbody>
<tr>
<td>θ</td>
<td>Weiss constant</td>
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<tr>
<td>ϕ</td>
<td>Cu-O-Cu bond angle</td>
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<tr>
<td>λ_max</td>
<td>Maximum wavelength of an absorption band</td>
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<tr>
<td>ε</td>
<td>Molar absorptivity</td>
</tr>
<tr>
<td>ω</td>
<td>Frequency</td>
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BIBLIOGRAPHY

Books

Anderson, P. W., "Theory of Magnetic Exchange Inter-
actions: Exchange in Insulators and Semiconductors," 
Vol. XIV of Solid State Physics, edited by Fredrich 
Seitz and David Turnbull, New York, Academic Press, 
1963.

_______, "Exchange in Insulators: Superexchange, 
Direct Exchange and Double Exchange," Vol. I of 
Magnetism, edited by George T. Rado and Harry Suhl, 

Basolo, F. and R. G. Pearson, Mechanisms of Inorganic 
Reactions, 2nd edition, New York, John Wiley and 

Bellamy, L. J., The Infrared Spectra of Complex Molecules 

Bertrand, J. A. and P. G. Eller, "Polynuclear Complexes 
with Aminoalcohols and Iminoalcohols as Ligands: 
Oxygen-Bridged and Hydrogen-Bonded Species," 
Vol. XXI of Progress in Inorganic Chemistry, edited 
by S. J. Lippard, New York, Interscience Publishers, 
1976.

Conley, R. T., Infrared Spectroscopy, Boston, Allyn and 

Cotton, F. A. and G. Wilkinson, Advanced Inorganic 
Chemistry, 3rd edition, New York, Interscience 

Drago, R. S., Physical Methods in Inorganic Chemistry, 

Earnshaw, A., Introduction to Magnetochemistry, New York, 

Hendrickson, J. B., D. J. Cram, and G. S. Hammond, 
Organic Chemistry, 3rd edition, New York, McGraw-


Articles


Unpublished Materials

Desiderato, R., North Texas State University, Privately Circulated Computer Program, 1975.