MAGNETIC, ELECTRONIC, AND THERMAL PROPERTIES OF 2: 1 COPPER(II) COMPLEXES OF A SERIES OF AMINOCARBOXYLIC ACIDS

NINA FRANCES ALBANESE
University of New Hampshire, Durham

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MAGNETIC, ELECTRONIC, AND THERMAL PROPERTIES
OF 2:1 COPPER(II) COMPLEXES OF A
SERIES OF AMINOCARBOXYLIC ACIDS

BY

NINA FRANCES ALBANESE
B.S., SUNY College of Environmental Science
and Forestry/Syracuse University, 1975

A DISSERTATION

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This thesis has been examined and approved.

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Date
November 16, 1979
For John Porter.
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ABSTRACT

MAGNETIC, ELECTRONIC, AND THERMAL PROPERTIES
OF 2:1 COPPER(II) COMPLEXES OF A
SERIES OF AMINOCARBOXYLIC ACIDS

by

NINA FRANCES ALBANESE

University of New Hampshire, December, 1979

Copper(II) complexes of the carboxylate anions of L-(−)-proline, pipecolinic acid, picolinic acid, anthranilic acid, 4-chloro-anthranilic acid, 3,5-dichloro-anthranilic acid, N-phenyl-anthranilic acid, and flufenamic acid were prepared and characterized by thermal gravimetric analysis, differential scanning calorimetry, X-ray diffraction, infrared and visible spectroscopy, magnetic susceptibility, and electron paramagnetic resonance spectroscopy. Copper-doped nickel(II) and zinc(II) complexes were also prepared. The EPR spectra were examined in detail. The N-phenyl-anthranilate and flufenamate complexes are dimeric. Zero field splitting parameters are reported.
CHAPTER 1

INTRODUCTION

Copper is one of the most biologically important and widely studied transition metals. Ubiquitous in biological systems, copper is an active component of metalloenzymes involved with oxygen transport and oxidation-reduction processes (1). Copper is an essential trace metal for human health (2), and interest is growing in its role, particularly in the in vivo regulation of a variety of human disorders, in the form of low molecular weight complexes. In recent review articles (3, 4), Sorenson has discussed the role of copper in rheumatoid arthritis and other degenerative connective tissue diseases, fertility control, infectious bacterial and viral diseases, Menke's Syndrome (congenital hypocupremia); copper as an antineoplastic agent; and copper deficiency in infants.

In the case of certain inflammatory diseases, elevated levels of pharmacologically inert, albumin-bound copper in blood serum is observed (5). It is speculated that the resulting loss of copper from tissues induces chronic inflammation. It has been demonstrated that copper complexes with a variety of ligands, possess anti-inflammatory activity (6-11). Recently, interest in the copper bracelet as a "folk remedy" for inflammatory types of arthritis (12) has been
stimulated by demonstration of the ability of bis(glycinato) copper(II) to perfuse cat skin (13), of the physical and psychological benefit derived by use of copper bracelets (14), and of the ability of metallic copper to dissolve in human sweat (15). The mechanisms proposed for the anti-inflammatory activity of copper include superoxide scavenging (3, 4, 16-21), and regulation of prostaglandin synthesis (3, 4, 8, 9).

Bis(anthranilato) copper(II) is among the numerous copper complexes that have been tested for anti-inflammatory activity (6-8). Although this complex is considerably more active than anthranilic acid alone, or other copper complexes, it may be argued that the extreme insolubility of this complex is evidence against the existence of a pharmacologically active anthranilate complex in biological fluids. This problem prompted the present study.

The purpose of this investigation is to study the influence of ligand modification on the interaction of copper with a homologous series of anthranilic acid-like amino-carboxylic acids. The ligands and their abbreviations are listed in Table 1.1. Although complexes with several ligands in this series have been reported previously in the literature, this investigation is the first detailed comparative study and includes extensive analysis of electron paramagnetic resonance spectra. Previous studies are reviewed in Chapter 4.
## TABLE 1.1

**LIGANDS AND ABBREVIATIONS**

<table>
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<tr>
<th>Abbreviation</th>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Structure</th>
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<tbody>
<tr>
<td>Hpro</td>
<td>L-(-)-proline</td>
<td>L-pyrrolidine-2-carboxylic acid</td>
<td><img src="structure1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Hpip</td>
<td>pipecolinic acid</td>
<td>2-piperidine carboxylic acid</td>
<td><img src="structure2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Hpic</td>
<td>picolinic acid</td>
<td>2-pyridine carboxylic acid</td>
<td><img src="structure3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Common Name</td>
<td>IUPAC Name</td>
<td>Structure</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
<td>--------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hanth</td>
<td>anthranilic acid</td>
<td>o-aminobenzoic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Hcanth</td>
<td>4-chloroanthranilic acid</td>
<td>2-amino,4-chloro-benzoic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Hdcanth</td>
<td>3,5-dichloroanthranilic acid</td>
<td>2-amine,3,5-dichloro-benzoic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Common Name</td>
<td>IUPAC Name</td>
<td>Structure</td>
</tr>
<tr>
<td>--------------</td>
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<td>---------------------------------</td>
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</tr>
<tr>
<td>Hnanth</td>
<td>4-nitro-anthranilic acid</td>
<td>2-amino,4-nitro-benzoic acid</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Hpanth</td>
<td>N-phenyl-anthranilic acid</td>
<td>[N-phenyl-2-amino-benzoic acid]</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Hfluf</td>
<td>flufenamic acid</td>
<td>[N-(a,a,a-trifluorom-tolyl)-2-amino-benzoic acid]</td>
<td><img src="image3.png" alt="Structure" /></td>
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CHAPTER 2

THEORY: ELECTRONIC AND MAGNETIC PROPERTIES

2.1. States Derived from Electron Configuration

The state of an atom is specified by its electron configuration, orbital angular momentum, and electron spin. Each state is a multiplet of components with different energies and different values of total angular momentum. The Russell-Saunders or LS coupling scheme is used to derive the state of atoms in the first transition series (22).

For copper(II), with a d⁹ electron configuration, L = 2; M_L = ±2, ±1, 0; S = ½, M_S = ±½; 2S + 1 = 2; and J = L + S, |L - S| = 5/2, 3/2. Since the number of d electrons is greater than five, the spin orbit coupling constant is negative (λ = -828 cm⁻¹), and the high energy component of the multiplet has J = 3/2. Therefore, the ground state term symbol is ²D₅/₂. The ground state of the free ion has 5-fold orbital degeneracy and 2-fold spin degeneracy; the total degeneracy is (2L + 1)(2S + 1) = 5 x 2 = 10. Ground state degeneracy is removed by spin-orbit coupling, crystal field interactions, and magnetic field interactions.

2.2. Description of d-Orbital Splittings Using Crystal Field Theory

In crystal field theory, the interaction between the metal ion and the ligands is assumed to be purely electrostatic
or ionic. Depending on its symmetry, the crystal field removes to some extent the 5-fold degeneracy of the d-orbitals of the metal. In octahedral ($O_h$ or $m3m$) and elongated tetrahedral ($D_{2d}$ or $42m$), or tetrahedral ($T_d$ or $43m$) crystal fields, the ground state is doubly or triply degenerate, respectively. Orbitally degenerate ground states are not generally observed for copper(II) complexes due to distortion of crystal field symmetry. The Jahn-Teller theorem (23) predicts that a nonlinear molecule with a degenerate ground state experiences distortions which lower the symmetry of the crystal field, remove the degeneracy of the ground state, and lower the total energy of the d-orbitals. Group theory predicts the type of distortion that occurs, but not the magnitude of the distortion, or the d-orbital energies. The requirement for Jahn-Teller distortion is that the distortion be any of the non-totally symmetric normal vibrations contained in the irreducible representations obtained by the direct product of the ground state representation with itself (24). Representations corresponding to rotation ($R_x$, $R_y$, $R_z$) or translation ($x$, $y$, $z$) are excluded. In octahedral symmetry the ground state direct product is

$$e_g \times e_g = a_{1g} + a_{2g} + e_g$$

(2.2.1)

The non-totally symmetric normal vibrations are contained in the $e_g$ representation and correspond to $x^2 - y^2$ and $z^2$. Thus distortion will occur along the metal ligand bonds. In
the limit of compression along $z^2$ (with concomitant elongation along $x^2 - y^2$), a linear molecule results, having a $dz^2$ ground state. Conversely, in the limit of elongation along $z^2$ (with compression along $x^2 - y^2$) a square coplanar geometry is obtained, and the ground state is $dx^2 - y^2$. In a tetrahedral crystal field, the ground state direct product

$$t_2 \times t_2 = a_1 + e + t_1 + t_2 \quad (2.2.2)$$

contains normal modes corresponding to the $x^2 - y^2$, $xy$, $xz$ and $yz$ directions. If compression occurs along $x^2 - y^2$ and $xy$, compressed tetrahedral geometry is obtained with $dxy$ as the ground state.

These distortions are summarized in Figure 2.1. An important feature of these splitting diagrams is that a continuum of possible geometries exists between the theoretical limits of distortion, and therefore the relative order of the d-orbital energies can not be predicted with certainty. The ground state refers to the orbital containing the unpaired electron and thus, as a consequence of Hund's Rule, refers to the highest energy orbital. Note the existence of orbitally degenerate excited states in each case.

2.3. Electron Transitions

An understanding of the nature of electron transitions in a $d^9$ system is facilitated by use of the "hole formalism." According to this theorem, a $d^9$ electron configuration can
Figure 2.1. Crystal field splitting of d-orbitals.
be treated as an inverted d^1 "positive hole" or positron configuration. The d^9 ground state in D_{4h} (4/mmm) symmetry is ^2B_1g where the electron configuration is (dz^2)^2(dxz,dyz)^4 (dxy)^2(dx^2 - y^2)^1, while the d^1 ground state is also ^2B_{1g} but the positron configuration is simply (dx^2 - y^2)^1. The excited states are easily envisioned in the d^1 system as ^2B_{2g}[ (dx^2 - y^2)^0(dxy)^1], ^2E_g[(dx^2 - y^2)^0(dxy)^0(dxz,dyz)^1], and ^2A_{1g}[ (dx^2 - y^2)^0(dxy)^0(dxz,dyz)^0(dz^2)^1]. Thus, electron transitions in the d^9 system are equivalent to one-positron promotions from the ground state to the various excited states in the d^1 system. Note that the ground state and all the excited states are spin doublets.

The rules governing electron transitions are the Laporte rule (\Delta L = \pm 1) and spin multiplicity rule (\Delta S = 0). Since the d^9 electron configuration yields only doublet states, all the d-d transitions are spin-allowed. However, the Laporte rule requires transitions between states with different L values (e.g., ^2F \leftrightarrow ^2D or ^2D \leftrightarrow ^2P). This means the d-d transitions are forbidden (i.e., have transition moments equal to zero). Breakdown of the Laporte rule arises from mechanisms which mix ungerade character into the gerade d-orbitals, such as vibronic coupling and d-p orbital mixing.

2.4. Molecular Orbital Approach and Bonding Parameters

Since crystal field theory assumes metal-ligand interactions to be purely electrostatic, it ignores the effects of \sigma- and \pi-bonding. However, especially for the interpretation
of EPR data, it is necessary to include covalent bonding in the description of coordination complexes.

According to molecular orbital theory (MOT), molecular orbitals are constructed by taking linear combinations of metal atomic orbitals and ligand atomic orbitals or ligand group orbitals (LGO; linear combinations of ligand atomic orbitals) (26). Bond formation occurs if the symmetry of the metal and ligand orbitals is the same and if overlap is positive (i.e., the orbitals have the same sign in the region of overlap). If the symmetry is different, there is no overlap, and the atomic orbital becomes a nonbonding molecular orbital. For every bonding M.O., there exists a corresponding antibonding M.O. with negative overlap and higher energy. The energy difference between the bonding and antibonding M.O.'s is directly related to the degree of overlap between atomic orbitals. Generally overlap decreases in the following order (26, 27):

\[
\begin{align*}
\sigma &> \sigma \text{ interactions} \\
p_{\sigma} &> p_{\sigma} \\
d_{\sigma} &> d_{\sigma}
\end{align*}
\]

and

\[ \sigma > \pi > \delta \]

The unnormalized molecular orbitals for a heteronuclear bond have the form

\[
\psi = \phi_A + \lambda \phi_B \quad \text{(bonding)}
\]  
(2.4.1)
where λ is a mixing coefficient. For large energy differences between atomic orbitals, λ will be small and the orbitals will not mix efficiently. For transition metal complexes, the antibonding M.O.'s are said to have "metal character" (i.e., energies similar to metal atomic orbital energies) while bonding orbitals have predominantly "ligand character," indicating a relatively small degree of mixing. Since information about the metal d-orbital electrons can be obtained by observation of the electronic and magnetic properties of transition metal complexes, only the antibonding molecular orbitals are of interest. The normalized antibonding molecular orbitals in D₄h (4/mmm) symmetry (28) are

\[
\psi^* = \phi_A - \lambda \phi_B \quad \text{(antibonding)} \quad (2.4.2)
\]

where \( \psi^* \) is a normalized mixing coefficient. The following conditions apply (29): \( <i|i> = 1 \) and \( <i|j> = 0 \). When overlap
is large, the overlap integral, $S$, must be introduced to account for non-orthogonality (29), where $S = \langle i | j \rangle \neq 0$.

Normalization of the $B_{1g}$ antibonding orbital yields

$$
\langle \phi_{dx^2-y^2} | \phi_{LGO,x^2-y^2} \rangle = a^2 \langle \phi_{dx^2-y^2} | \phi_{dx^2-y^2} \rangle
- 2aa' \langle \phi_{dx^2-y^2} | \phi_{LGO,x^2-y^2} \rangle
+ a'^2 \langle \phi_{LGO,x^2-y^2} | \phi_{LGO,x^2-y^2} \rangle
= a^2 - 2aa'S + a'^2 \quad (2.4.8)
$$

where $S$ is needed to account for relatively large $\sigma$ bond overlap. For the other antibonding orbitals, overlap is small and can be neglected; normalization yields

$$
\langle \phi_{dxy} | \phi_{LGO,dxy} \rangle = \beta_1^2 + \beta_1'^2 = 1 \quad (2.4.9)
$$

$$
\langle \phi_{dz^2} | \phi_{LGO,dz^2} \rangle = \alpha_1^2 + \alpha_1'^2 = 1 \quad (2.4.10)
$$

$$
\langle \phi_{dxz} | \phi_{LGO,dxz} \rangle = \langle \phi_{dyz} | \phi_{LGO,dyz} \rangle = \\
\beta^2 + \beta'^2 = 1 \quad (2.4.11)
$$

The physical significance of the $a$'s and $\beta$'s can now be discussed (28, 30). The unprimed symbols refer to the amount of metal electron density remaining in metal orbitals; the primed symbols to metal electron density delocalized into ligand orbitals via covalent bonding. The parameter $a^2$ is related to the degree of covalency through $\sigma$-bonding. When
\( \alpha^2 = 1 \), no delocalization of metal electron density occurs as in ionic bonding; when \( \alpha^2 = 0.5 \), electron density is equally distributed in metal and ligand orbitals, indicating completely covalent \( \sigma \)-bonding. Likewise, the parameters \( \beta_2^2 \) and \( \beta_1^2 \) measure the degree of covalency through \( \pi \)-bonding. \( \beta_1^2 \) refers to in-(xy) plane \( \pi \)-bonding and \( \beta_2^2 \) refers to out-of-(xy) plane \( \pi \)-bonding. As will be shown later, electron-nuclear hyperfine coupling constants and \( g \)-values from EPR spectra are related to these mixing coefficients and can reveal the extent of covalent bonding in a complex.

Molecular orbital diagrams for \( D_{4h} (4/mmm) \) symmetry are shown in Figure 2.2. One corresponds to \( \sigma \)-bonding only, as with four nitrogen ligands; the other to \( \sigma + \pi \) bonding, as with four oxygen ligands. The M.O. description of a complex with two N and two O ligands is intermediate to the two situations.

The first important feature of the M.O. diagram is that the ground state of the copper atom is the same as that predicted by crystal field theory. The splitting of the d-orbitals is only slightly modified by covalent bonding. The effect of \( \pi \)-bonding depends on the energy of the ligand \( \pi \)-orbitals relative to the metal orbitals, and on whether the ligand \( \pi \)-orbitals are filled or empty. For oxygen ligands which possess filled \( \pi \)-orbitals of lower energy than the metal orbitals, the interaction destabilizes the metal orbitals and thus decreases the electron transition energies relative to the \( \sigma \)-bonding only situation.
Figure 2.2. Molecular orbital diagram for D$_{4h}$ (4/mmm) symmetry: (A) $\sigma$-bonding only, and (B) $\sigma$-bonding and $\pi$-bonding.
Generally, ammonia and alkyl amines do not participate in π-bonding because the nitrogen atom lacks filled π-orbitals or empty π*-orbitals; d-orbitals lie too high in energy to contribute. However, pyridine, which is isoelectronic with benzene, has filled bonding π and empty antibonding π*-orbitals which are available for π-bonding with the metal. In this case, the effect of π-bonding on electron transition energies is not easy to predict since the empty and filled ligand orbitals have competing effects.

2.5. Origin of Magnetism

Diamagnetism is a general property of all forms of matter, arising in an external magnetic field from the induction of a magnetic moment by the orbital motion of electrons in closed shells. Diamagnetic substances are repelled from magnetic fields and have negative magnetic susceptibility. Paramagnetism, antiferromagnetism, and ferromagnetism are properties of substances with a permanent magnetic dipole moment which arises from the spin and orbital angular momenta of one or more unpaired electrons. Substances of this type are drawn into a magnetic field and have a positive magnetic susceptibility (22).

The classical model of the origin of a magnetic moment is analogous to induction of a magnetic field in a closed electric circuit (31). An electron moving in a circular orbit constitutes a current, i, which induces a magnetic field, B, perpendicular to the plane of the orbit and equal to
where \( k \) is a proportionality constant and \( R \) is the radius of the orbit. The deBroglie wavelength associated with the electron is \( \lambda = \frac{h}{p} \). In order to prevent destructive interference, the circumference of the orbit must be an integral multiple of deBroglie wavelengths. It follows that angular momentum, \( p_{\phi} \), is quantized in units of \( \frac{h}{2\pi} \), as shown below (31).

\[
\lambda = \frac{h}{p} \quad (2.5.2)
\]

\[
2\pi r = m\lambda, \quad (m \equiv \text{integer}) \quad (2.5.3)
\]

\[
r = \frac{m h}{2\pi p} \quad (2.5.4)
\]

\[
p_{\phi} = pr = \frac{m h}{2\pi} \quad (2.5.6)
\]

In atoms, the motions of electrons are not restricted to a two-dimensional plane. Orbital angular momentum arises from the apparent motion of electrons over the surface of a sphere. Spherical harmonics, which describe the angular dependence of wave functions, leads to quantization of orbital and spin angular momenta in units of \([l(l + 1)]\frac{h}{2\pi} \) and \([S(S + 1)]\frac{h}{2\pi} \), where the allowed values of \( l \) and \( S \) are \(-l, -l + 1, \ldots l - 1, \ldots l \) and \(-S, -S + 1, \ldots S - 1, S\), respectively. The projection of the angular momentum vectors
along a fixed direction are restricted to \( m_s \) and \( m_l \); in each case there are \( 2L + 1 \) values of \( m_l \) and \( 2S + 1 \) values of \( m_s \).

The components of the magnetic moment along a fixed direction are similarly restricted. The component of the electron spin moment along the direction of the applied magnetic field (designated \( z \) by convention) is

\[
\mu_z = \gamma m_s \frac{\hbar}{\gamma} = -g\beta m_s \tag{2.5.7}
\]

where \( \gamma \) is the magnetogyric ratio and \( \beta \) is the Bohr magneton. Thus, the magnetic moment is quantized and has the units of the Bohr magneton, which is defined as

\[
1 \text{ B.M.} = \frac{e\hbar}{4\pi mc}
\]

where \( e \) is the electron charge, \( h \) is Planck's constant, \( m \) is the electron mass and \( c \) is the speed of light.

If the magnetic moment arises from both spin and orbital angular momenta, the predicted moment (22) is

\[
\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \tag{2.5.8}
\]

When orbital angular momentum is quenched by removal of orbital degeneracy by the ligand field, the magnetic moment arises solely from spin angular momentum, and the predicted moment (22) is
\[ \mu_S = g \sqrt{S(S + 1)} \quad (2.5.9) \]

where \( g = 2.0 \). For copper(II) the predicted range of magnetic moments is from \( \mu_S = 1.73 \) B.M. to \( \mu_{S+L} = 3.00 \) B.M. Experimental magnetic moments fall within the range 1.7 - 2.2 B.M. (22, 30, 32), indicating incomplete quenching of orbital angular momentum.

The effective magnetic moment is measured indirectly by measurement of magnetic susceptibility (22, 33). The volume susceptibility, \( \kappa \), is the ratio of the intensities of the bulk magnetization of the sample, \( B \), to the magnetic field, \( H \).

\[ \frac{B}{H} = \kappa \quad (2.5.10) \]

The molar susceptibility is related to the volume susceptibility by

\[ \chi_M = \frac{\kappa M}{d} \quad (2.5.11) \]

where \( d \) is the density and \( M \) is the molecular weight of the substance. Since diamagnetic and paramagnetic susceptibilities are opposite in sign, \( \chi_M \) must be corrected for the diamagnetic susceptibility according to

\[ \chi_M^{\text{corr}} = \chi_M - \chi_{\text{dia}} \quad (2.5.12) \]
where $\chi_{\text{dia}}$ is a sum of contributions from all the ligand atoms (34). Another correction is for the temperature independent paramagnetism (TIP) of the metal. TIP is an induced paramagnetism produced by coupling of ground and excited states in a magnetic field. For copper(II), the TIP is $60 \times 10^{-6}$ cgs units/mole (35).

Paramagnetic susceptibilities depend inversely on temperature and generally obey the Curie Law (22, 36)

$$\chi_M^{\text{corr}} = \frac{C}{T} \quad (2.5.13)$$

where $C$ is the Curie constant and $T$ is the absolute temperature. The effective magnetic moment is related to the magnetic susceptibility by

$$\chi_M^{\text{corr}} = \frac{N \mu_{\text{eff}}^2}{3kT} \quad (2.5.14)$$

where $N$ is Avogadro's number, and $k$ is the Boltzmann constant. It follows that

$$\mu_{\text{eff}} = \sqrt{\frac{3k}{N}} \sqrt{\chi_M^{\text{corr}}} \quad T = 2.84 \sqrt{\chi_M^{\text{corr}}} \quad T \quad (2.5.15)$$

Deviations from Curie Law behavior are frequently observed in the temperature dependence of magnetic susceptibilities. The Curie-Weiss law (22, 36) is

$$\chi_M^{\text{corr}} = \frac{C}{T - \theta} \quad (2.5.16)$$
where the Weiss constant, $\theta$, is a correction for simple, relatively weak interionic or intermolecular interactions. Ferromagnetism and antiferromagnetism result from relatively strong magnetic exchange interactions between spin moments. In both cases the temperature dependence of the magnetic susceptibility is described by the so-called Bleaney-Bowers (37) equation which is derived from the Heisenberg-Dirac-Van Vleck (38-40) model of magnetic exchange. The equation is

$$x_M^{corr} = \left[1 + \frac{1}{3}\exp\left(-\frac{2J}{kT}\right)\right]^{-1} + N_\alpha$$  \hspace{1cm} (2.5.17)

where $N_\alpha$ is the temperature independent paramagnetism.

In order to illustrate these phenomena, consider an $s = \frac{1}{2}$ system which forms exchanged-coupled dimers, as in the case of copper(II). If the dimer has a singlet ground state ($S_1 - S_2 = 0$) and a triplet excited state ($S_1 + S_2 = 1$), the coupling is described as antiferromagnetic. The maximum magnetic susceptibility occurs at the Néel temperature, $T_N$, where $J/kT_N = -4/5$ (36). Conversely, if the dimer has a triplet ground state and a singlet excited state, the coupling is described as ferromagnetic. The exchange energy, $J$, is a measure of the strength of the interaction. $J$ is negative for antiferromagnetism and positive for ferromagnetism. In either case, the singlet-triplet energy separation is $2J$ (36, 38-40). The exchange energy is measured by fitting $J$ as a parameter to the Bleaney-Bowers equation.
The classic example of an exchanged-coupled copper(II) dimer is copper acetate. The nature of the exchange interaction has been debated in the literature (41-46) for several years, but the controversy remains unresolved. Proposed mechanisms for spin-spin coupling are indirect exchange (superexchange) and direct exchange (38-40, 47, 48).

The structure of Cu$_2$(OAc)$_4$·2H$_2$O was determined by van Niekerk and Schoening (49, 50). The acetate groups bridge the two copper atoms which are separated by 2.64 Å. The short copper-copper separation led to the proposal of copper-copper bond formation and direct magnetic exchange. Exchange is antiferromagnetic and $2J = -334$ cm$^{-1}$ (41, 47). EPR parameters were determined for zinc-doped copper acetate (51) as $g_x = 2.052$, $g_y = 2.082$, $g_z = 2.344$, $A_x = 18 \times 10^{-4}$ cm$^{-1}$, $A_y = 23 \times 10^{-4}$ and $A_z = 147 \times 10^{-4}$ cm$^{-1}$. The magnetic tensors are rhombic and the two copper atoms within the dimer are magnetically equivalent.

Both $\sigma$-bonding (44) by end-to-end $dz^2$-$dz^2$ overlap and $\delta$-bonding (41-43, 45) by lateral $dx^2$-$y^2$-$dx^2$-$y^2$ overlap have been proposed. Forster and Ballhausen (44) have shown, using molecular orbital theory, that $\sigma$-bond formation is consistent with the observed behavior of copper acetate. They argue in favor of a $\sigma$-bond rather than a $\delta$-bond on the basis of the magnitudes of the overlap integrals for the two types of bonds.

The superexchange mechanism involves propagation of spin density by delocalization through orbitals centered on
atoms in the ligand bridge. Goodenough (52) has formulated schemes for predicting the outcome of exchange based on the geometry of orbitals and the number of intervening atoms. Chemical modification studies are consistent with this model (38, 47). The exchange interaction appears to be relatively insensitive to the copper-copper separation and solvent effects, but directly related to the length of the ligand bridge. Consequently, scores of carboxylate-bridged copper (II) dimers and higher polymers are known, exhibiting behavior similar to copper acetate, regardless of the copper-copper separation (35, 38, 47, 53-61). Recently, weak ferromagnetic and antiferromagnetic lattice interactions between copper ions have been observed at very low temperatures (62-64).
3.1. Introduction: Excitation and Relaxation Processes

The three most important features of the electron paramagnetic resonance phenomenon are:

1. Removal of spin degeneracy in a magnetic field
2. Absorption of a quantum of energy at microwave frequency which induces transitions from the low energy to the high energy spin state
3. Relaxation

These features are illustrated in Figure 3.1.

As a consequence of quantization of angular momentum (Section 2.5), there are only $2S + 1$ orientations of the spin moment $\mathbf{\mu}$ with respect to the applied magnetic field direction. For an $S = \frac{1}{2}$ system there are two such orientations, corresponding to the $\alpha$ spin state in which $\mu_z$ is aligned parallel with the field, and to the $\beta$ spin state in which $\mu_z$ is aligned antiparallel, as shown in Figure 3.1. Since parallel alignment is energetically unfavorable relative to antiparallel alignment, the two spin states move apart in energy as the magnetic field increases. Since the energy of interaction between the spin moment and the magnetic field is given by
Figure 3.1. Excitation and relaxation processes.
$m_s = \pm 1/2$

$A E = \frac{h\nu}{(\text{excitation})}$

$m_s = 1/2$ (α spin state)

$m_s = -1/2$ (β spin state)

Δ$E = h\nu$ (excitation)

$\tau_{R, T_1, T_2}$ (relaxation)

Magnetic Field, $H$

(removal of spin degeneracy)
and since $\mu_z$ is quantized, $E$ must be quantized. From $E = g \beta m_s H$, it is evident that $m_s = +\frac{1}{2}$ corresponds to the high energy spin state and $m_s = -\frac{1}{2}$ to the low energy spin state.

The EPR selection rule is a consequence of orthogonality of spin functions and predicts that the EPR transition moment integral will be nonzero if $\Delta m_s = \pm 1$ and $\Delta m_I = 0$, where $m_I$ is the nuclear spin quantum number of metal or ligand nuclei.

In a sample containing $N$ spin moments, the distribution of spins between the two states is given by the Boltzmann distribution law.

\[ N = N_\alpha + N_\beta \]  \hspace{1cm} (3.1.2)

\[ \frac{N_\alpha}{N_\beta} = e^{-\Delta E/kT} \]  \hspace{1cm} (3.1.3)

Since $\Delta E$ is on the order of 0.31 cm$^{-1}$ at X-band frequency (9.5 GHz) and $kT \approx 200$ cm$^{-1}$ at room temperature, the population difference is small, but $N_\beta > N_\alpha$. The population difference is enhanced at lower temperatures. Application of microwave frequency induces transitions from the $\beta$ to $\alpha$ spin state. Conversely, relaxation processes depopulate the excited state and tend to restore the original Boltzmann distribution. When the rate of relaxation equals the rate of excitation, $N_\alpha = N_\beta$, and the system becomes saturated,
which results in a loss of EPR signal intensity.

There are several pathways for relaxation which fall into three broad categories: spin-rotation, spin-spin, and spin-lattice relaxation. All three mechanisms give rise to line broadening by increasing the uncertainty in the energy levels of the \( \alpha \) and \( \beta \) spin states. In all relaxation processes, the EPR spectrometer can "see" only those events which happen at a frequency less than the frequency of the spectrometer.

Spin-rotation relaxation is important in liquid samples (65-67). If the solution containing the paramagnetic species is dilute (\(-10^{-3}\) M), the spin-rotation effect arises from the tumbling of the molecule, which generates a local, fluctuating magnetic field from the magnetic dipole moment of the molecule, and thus modulates the transition energies. The range of rotational frequencies from macromolecules to small molecules is \(10^6-10^{12}\) Hz. The rotational correlation time, \( \tau_R \), is given by the Debye equation

\[
\tau_R = \frac{4}{3}\frac{\pi a^3}{kT} \xi \tag{3.1.4}
\]

where the shape of the molecule is approximated by a sphere with radius \( a \), and \( \xi \) is the viscosity of the solution. Large molecules, or small molecules in highly viscous solution, tumble at a frequency less than the frequency of the spectrometer and appear to be stationary on the EPR timescale. Anisotropic EPR spectra are observed. Small molecules
tumbling at a frequency greater than the spectrometer frequency have isotropic EPR spectra with relatively sharp lines. When \( \frac{1}{\tau_R} = v_{\text{spectrometer}} \), line broadening effects are most severe.

Spin-spin (\( T_2 \)) relaxation arises from electron-electron (68), electron-nuclear (69), and nuclear-nuclear magnetic dipole interactions, in decreasing order of their line broadening effect. The dipole interaction is proportional to \( \frac{\mu_1 \cdot \mu_2}{r^3} \), where \( r \) is the distance between the interacting spin moments, \( \mu_1 \) and \( \mu_2 \). The electron-electron relaxation effect can be removed by diluting the sample (increasing \( r \)). Electron-nuclear interactions are responsible for hyperfine structure in the EPR signal and provide useful chemical information.

Spin-lattice relaxation arises from "lattice-induced" transitions between spin states in which the excited states couple or exchange energy with the lattice surroundings (31, 70). Spin-lattice relaxation differs from other relaxation processes by being independent of magnetic interactions. The spin-lattice relaxation time, \( T_1 \), is the inherent lifetime of an excited spin state in the absence of magnetic exchange interactions. The Uncertainty Principle

\[
\Delta E \Delta t = \frac{\hbar}{2\pi} \quad (3.1.5)
\]

predicts that as the lifetime of a species (\( T_1 \)) and the uncertainty in the lifetime (\( \Delta t \)) increase, the uncertainty in
the energy ($\Delta E$) decreases. Therefore, the longer the lifetime of the excited state, the sharper will be the EPR signal. Since spin-lattice interactions include coupling with vibrations and rotations, lowering the temperature of the sample increases $T_1$, and sharpens the EPR signal. For transition metals, spin orbit coupling also contributes to spin-lattice relaxation (31), such that $T_1$ decreases in the following order.

\[
T_1 \text{ (organic radicals) } > T_1 \text{ (1st row transition metals) } > T_1 \text{ (2nd and 3rd row transition metals)}
\]

If $1/T_1 >> \nu$ ‘spectrometer,’ an EPR signal may be difficult to observe except at very low (e.g., liquid He) temperatures. At low temperatures, it is easier to saturate spin populations and a lower microwave power must be used. Microwave power settings are typically 5 and 50-100 mW for liquid nitrogen and room temperature, respectively.

An additional contribution to EPR linewidths is motional or orientation averaging of $g$ and a anisotropy (65, 71, 72). This phenomenon is distinct from spin-rotation relaxation and leads to the dependence of linewidth on the metal nuclear spin quantum number, $m_I$. The result is that lines at the high and low field extremes of the EPR spectrum are broader than lines in the center of the spectrum.

Instrument parameters can cause artificial line broadening and line shape distortion. Typical scan times are 8-16
minutes depending on the noise filter. Faster scan rates yield distorted spectra. To avoid line broadening due to overmodulation, the general practice is to set the modulation amplitude at about one-fifth the narrowest peak-to-peak linewidth in the spectrum (73).

3.2. The Spin Hamiltonian (31, 74)

In this section, the spin Hamiltonian is introduced and the effect of spin orbit coupling is examined.

The Schrödinger Equation is an eigenvalue equation which relates the Hamiltonian operator \( \hat{H} \), operating on an eigenfunction \( \psi_n(x,y,z) \), to the total energy corresponding to the state, \( n \), that is specified by variables \( x, y, \) and \( z \),

\[
\hat{H} \psi_n(x,y,z) = E_n \psi_n(x,y,z)
\]  

(3.2.1)

where \( \hat{H} = \sum_{i} \hat{H}_i \) for \( m \) interactions. For a paramagnetic ion the appropriate Hamiltonian is

\[
\hat{H}_{\text{total}} = \hat{H}_{\text{electron-nuclear}} + \hat{H}_{\text{electron-kinetic}} + \hat{H}_{\text{electron-energy}} + \hat{H}_{\text{electron-repulsion}}
\]

\[
\hat{H}_{\text{crystal}} + \hat{H}_{\text{magnetic-field interactions}} + \hat{H}_{\text{spin-orbit coupling}}
\]  

(3.2.2)

The first two terms operate on the one-electron hydrogen-like wavefunctions. With the third term, the one-electron wavefunctions become the orbitals of the free atom. As seen
in Chapter 2, the five-fold degeneracy of the 3d orbitals is removed by operation of \( \hat{H}_{\text{crystal field}} \). The remaining terms contain electron spin operators and describe the electron paramagnetic resonance phenomenon.

Neglecting electron-nuclear coupling and other magnetic interactions for the moment, \( \hat{H}_{\text{magnetic interactions}} \) contains the electron Zeeman interaction which removes spin degeneracy and is proportional to the magnetic moment from both spin and orbital angular momenta.

\[
\hat{H}_{\text{electron}} = g_e H \cdot (\hat{\mathbf{L}} + g_e \hat{\mathbf{S}}) \quad \text{Zeeman, spin-only} 
\]

If orbital angular momentum were completely quenched by the ligand field, terms containing \( \hat{\mathbf{L}} \) could be neglected, and the Zeeman interaction would be simply

\[
\hat{H}_{\text{electron}} = g_e \beta H \cdot \hat{\mathbf{S}} \quad \text{Zeeman, spin-only} 
\]

The \( g \) value would be equal to the free electron value, \( g = 2.0023 \), as with organic radicals. For transition metals, complete quenching of orbital angular momentum is prevented by spin-orbit coupling which is described by

\[
\hat{H}_{\text{spin-orbit}} = \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad \text{spin-orbit coupling} 
\]

By combining (3.2.3) with (3.2.5) and collecting terms in
\[ \hat{H}_{\text{corrected}} = g_e \beta \hat{\mathbf{H}} \cdot \hat{\mathbf{S}} + (\beta \hat{\mathbf{H}} + \lambda \hat{\mathbf{S}}) \cdot \hat{\mathbf{L}} \]  
(3.2.6)

Using perturbation theory, new wavefunctions corrected to first order to include the effect of spin-orbit coupling are given by

\[ \psi = \phi_G - \sum_n \frac{\langle \phi_n \mid (\beta \hat{\mathbf{H}} + \lambda \hat{\mathbf{S}}) \cdot \hat{\mathbf{L}} \mid \phi_G \rangle}{\varepsilon_n - \varepsilon_G} \]  
(3.2.7)

where \( G \) refers to the ground state and \( n \) to the excited states before spin-orbit coupling. Corrections to the spin-only Hamiltonian are obtained by evaluation of

\[ (\hat{H})_{m_s, m_s'} = -\sum_n \frac{|\langle G, m_s \mid (\beta \hat{\mathbf{H}} + \lambda \hat{\mathbf{S}}) \cdot \hat{\mathbf{L}} + g_e \beta \hat{\mathbf{H}} \cdot \hat{\mathbf{S}} | n, m_s' \rangle|^2}{\varepsilon_n - \varepsilon_G} \]  
(3.2.8)

where the prime refers to the excited state, and \( \varepsilon_n, \varepsilon_G \) are zero order energies. This reduces to

\[ (\hat{H})_{m_s, m_s'} = \langle m_s \mid \beta^2 \hat{\mathbf{L}} \cdot \hat{\mathbf{A}} \cdot \hat{\mathbf{H}} + 2\lambda \beta \hat{\mathbf{L}} \cdot \hat{\mathbf{A}} \cdot \hat{\mathbf{S}} + \lambda^2 \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{A}} \cdot \hat{\mathbf{S}}_2 | m_s' \rangle \]  
(3.2.9)
where $\Lambda$ is a tensor which describes mixing of ground and excited states by spin-orbit coupling. The components of $\Lambda$ have the form

$$
\Lambda_{ij} = \frac{\langle G|\hat{L}_i|n\rangle\langle n|\hat{L}_j|G\rangle}{\varepsilon_n - \varepsilon_G}
$$

(3.2.10)

The first term in (3.2.9) describes the temperature independent paramagnetism and can be neglected in the EPR experiment. The second term contains the contribution of orbital angular momentum to the $g$ value. The third term is an electron-electron interaction which gives rise to zero field splitting of spin degeneracy in systems with $S \geq 1$.

The spin-only Hamiltonian containing $\hat{S}$ operators only and corrected for the effect of spin-orbit coupling is now

$$
\hat{H}_{\text{spin}} = \beta\hat{H}\cdot g\cdot \hat{S} + \hat{S}\cdot D\cdot \hat{S}
$$

(3.2.11)

only

where $g = g_e^1 + 2\lambda_\Lambda$ ($g$ tensor), $1$ = unit tensor, and $D = \lambda_\Lambda^2$ (zero field splitting tensor). $\hat{S}$ is now an effective spin operator and includes the effect of $\hat{L}$.

The principal axes of the $g$ tensor are those axes which diagonalize the tensor matrix. The diagonal tensor has off-diagonal elements, $g_{ij}$ ($i \neq j$), equal to zero, and principal values, $g_{ij}$ ($i = j$), equal to $g_{xx}$, $g_{yy}$, $g_{zz}$. Strictly speaking, the values $g_{xx}$, $g_{yy}$, and $g_{zz}$ are obtained from single crystal studies. The more commonly encountered values,
\( g_x, g_y, \) and \( g_z \), are approximately equal to \( g_{xx}, g_{yy}, \) and \( g_{zz} \), respectively, and are obtained more easily from polycrystalline or frozen solution spectra. In the second case, the result is that

\[
\hat{H}_{\text{electron}} = \beta (H_x \hat{S}_x + H_y \hat{S}_y + H_z \hat{S}_z) \quad (3.2.12)
\]

simplifies in nonaxial symmetry to

\[
\hat{H}_{\text{electron}} = \frac{\beta}{2} (H_x \hat{S}_x + H_y \hat{S}_y + H_z \hat{S}_z) \quad (3.2.13)
\]

and in axial symmetry to

\[
\hat{H}_{\text{electron}} = g_x \beta H_x \hat{S}_x + g_y \beta H_y \hat{S}_y + g_z \beta H_z \hat{S}_z \quad (3.2.14)
\]

when the \( g \) tensor is diagonal.

The anisotropy in \( g \) is observed in single crystal EPR spectra which depend on the orientation of the crystalline axes relative to the direction of the applied magnetic field. Polycrystalline or frozen solution samples contain microcrystallites or molecules trapped in random orientation in the rigid matrix, and their EPR spectra are summations over all orientations of single crystal spectra. In liquid solution, the anisotropy in \( g \) is averaged to zero by molecular
tumbling, and an isotropic g value, \( g_0 = \frac{g_x + g_y + g_z}{3} = \frac{g_H + 2g_L}{3} \), is observed.

Additional terms can now be added to the spin Hamiltonian to account for a variety of other interactions.

\[
\hat{H}_{\text{spin}} = \hat{H}_{\text{electron}} + \hat{H}_{\text{electron- metal}} + \hat{H}_{\text{electrons- nucleus}} + \hat{H}_{\text{electron- Zeeman}} + \hat{H}_{\text{electron- quadrupole}} + \hat{H}_{\text{nuclear Zeeman}}
\]

where \( \hat{H}_{\text{electron}} \) is the electron spin Hamiltonian, \( \hat{H}_{\text{electron- metal}} \) and \( \hat{H}_{\text{electron- nucleus}} \) are the electron-metal and electron-nucleus Zeeman couplings, \( \hat{H}_{\text{electron- quadrupole}} \) is the electron-nuclear quadrupole coupling, and \( \hat{H}_{\text{nuclear Zeeman}} \) are the nuclear Zeeman couplings.

The Hamiltonians for the electron-nuclear hyperfine couplings have the form

\[
\hat{H}_{\text{electron- nucleus}} = A \cdot \hat{S} \cdot \hat{I}
\]

where \( A \) is a measure of the strength of interaction between electron and nuclear spin moments, and \( \hat{I} \) is the nuclear spin operator which is physically and mathematically analogous to the electron spin operator, \( \hat{S} \). Any nuclei with \( I \neq 0 \) will give rise to hyperfine couplings. The nuclei of interest in this study are listed in Table 3.1.

There are two contributions to electron-nuclear hyperfine couplings. The isotropic or Fermi contact interaction arises from the presence of unpaired spin density at the nucleus. This means that s-d and s-p atomic orbital mixing
<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Nuclear Spin, I</th>
<th>$\gamma_N \times 10^4$ rad sec$^{-1}$G$^{-1}$</th>
<th>$g_N = \frac{\gamma_N^H B_N}{B_N}$</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1H$</td>
<td>$\frac{1}{2}$</td>
<td>2.67510</td>
<td>5.5851</td>
<td>99.985%</td>
</tr>
<tr>
<td>$^{14}N$</td>
<td>1</td>
<td>0.19324</td>
<td>0.40345</td>
<td>99.63 %</td>
</tr>
<tr>
<td>$^{63}Cu$</td>
<td>3/2</td>
<td>0.70904</td>
<td>1.4803</td>
<td>69.09 %</td>
</tr>
<tr>
<td>$^{65}Cu$</td>
<td>3/2</td>
<td>0.75958</td>
<td>1.5859</td>
<td>30.91 %</td>
</tr>
</tbody>
</table>
must occur because pure p and d orbitals have nodes, and therefore zero electron density, at the nucleus. The Hamiltonian operator for this interaction is

\[ \hat{H}_{\text{isotropic}} = \frac{8\pi}{3} g_s g_N \beta_N |\psi(0)|^2 \hat{S}_z \cdot \hat{I}_z \]

where \( g_N \) is the nuclear g value, \( \beta_N \) is the nuclear magneton, and \( |\psi(0)|^2 \) is the electron density at the nucleus for a hydrogen-like s orbital.

The second contribution to hyperfine couplings is through-space coupling of electron and nuclear dipole moments. For rapidly tumbling molecules, or when the unpaired electron resides in an s orbital, this effect is averaged to zero. The dipolar hyperfine interaction appears when the electron occupies a p or d orbital and the individual moments are frozen in stationary orientations. The Hamiltonian for this interaction is

\[ \hat{H}_{\text{dipolar}} = -g_s g_N \beta_N \left[ \frac{\hat{S} \cdot \hat{I}}{r^3} - \frac{3 (\hat{S} \cdot \hat{r}) (\hat{I} \cdot \hat{r})}{r^5} \right] \]  

(3.2.18)

where \( r \) is the vector joining the electron and nuclear dipole moments. Expansion of the vector products leads to

\[ \hat{H}_{\text{dipolar}} = \hbar \frac{\hat{S} \cdot \hat{T} \cdot \hat{I}}{r} \]  

(3.2.19)
where $T$ is the anisotropic hyperfine tensor which describes the angular dependence of the dipole interaction.

An electron-nuclear hyperfine tensor $\hat{A}$ including both isotropic and dipolar contributions is obtained when $\hat{H}_{\text{isotropic hyperfine}}$ and $\hat{H}_{\text{dipolar hyperfine}}$ are combined.

\[
\hat{H}_{\text{electron- nuclear hyperfine}} = \hat{H}_{\text{isotropic hyperfine}} + \hat{H}_{\text{dipolar hyperfine}}
\]

\[
= hA_0 \hat{S} \cdot \hat{I} + h\hat{S} \cdot \hat{T} \cdot \hat{I}
\]

\[
= h\hat{S} \cdot \hat{A} \cdot \hat{I}
\]

(3.2.20)

The $A$ tensor is analogous to the $g$ tensor and is given by

\[
A = A_0 I + T
\]

(3.2.21)

The principal values of the diagonalized hyperfine tensor are $A_{xx}$, $A_{yy}$, and $A_{zz}$, so that the Hamiltonian

\[
\hat{H}_{\text{electron- nucleus coupling}} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_x \\ \hat{I}_y \\ \hat{I}_z \end{pmatrix}
\]

simplifies in nonaxial symmetry to

\[
\hat{H}_{\text{electron- nucleus coupling}} = A_{xx} \hat{S}_x \hat{I}_x + A_{yy} \hat{S}_y \hat{I}_y + A_{zz} \hat{S}_z \hat{I}_z
\]

(3.2.23)
and in axial symmetry to

\[ \hat{H}_{\text{electron-nucleus coupling}} = A_S \hat{S}_z \hat{I}_z + A_\perp (\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y) \]  \hspace{1cm} (3.2.24)

for polycrystalline or frozen solution spectra.

The relationship between the isotropic \( A_\text{iso} \) and dipolar \( A_\text{dip} \) contributions to the hyperfine coupling constants in axial symmetry is approximated by

\[ A_S = A_\text{iso} + A_\text{dip}(3\cos^2 \theta - 1) = A_\text{iso} + 2A_\text{dip} \]  \hspace{1cm} (3.2.25)

\[ A_\perp = A_\text{iso} + A_\text{dip}(3\cos^2 \theta - 1) = A_\text{iso} - A_\text{dip} \]  \hspace{1cm} (3.2.26)

where \( \theta \) is the angle between \( \vec{r} \) and \( \vec{H} \), and \( A_\text{dip} \) is negative. \( A_\text{iso} \) is assumed to be negative for the copper nuclear hyperfine interaction (75). The sign of \( B_0 \) for ligand nuclear super-hyperfine coupling depends on the pathway or mechanism of spin delocalization, and can be determined by nuclear magnetic resonance experiments (76-83).

Additional terms arise from copper nuclear quadrupole coupling (84-86)

\[ \hat{H}_{\text{quadrupole coupling}} = \vec{r} \cdot \hat{Q} \cdot \hat{r} \]  \hspace{1cm} (3.2.27)

where the tensor \( \hat{Q} \) describes the interaction between the
nucleus and the electric field gradient at the nucleus; and from the nuclear Zeeman interaction.

\[ \hat{H}_{\text{nuclear}} = -g_N \beta_N H_z \hat{I}_z \]  

(3.2.28)

The nuclear Zeeman interaction is the basis for the nuclear magnetic resonance experiment at microwave frequencies in the MHz range. Both these effects promote "forbidden" or "double spin-flip" transitions where \( \Delta m_I \neq 0 \), and contribute to \( T_2 \) relaxation.

The Hamiltonian for zero field splitting was introduced previously (3.2.11) where the \( D \) tensor describes the dipolar interaction between electron spin moments, and is mathematically equivalent to the \( T \) tensor. An additional term is necessary to take into account exchange interactions

\[ \hat{H}_{\text{electron}} = \hat{H}_{\text{zero}} + \hat{H}_{\text{exchange}} \]

where \( J \) is the exchange energy (see Section 2.6), and the interaction is between pairs of spins.

In summary, the spin Hamiltonian is composed of Hamiltonian operators which describe magnetic interactions involving electron and nuclear spin operators, \( \hat{S} \) and \( \hat{I} \). These interactions have a dual orientation dependence, and are
described by second rank tensors. In the following sections, the spin Hamiltonian is applied to \( S = \frac{1}{2} \) and coupled \( S_1 = \frac{1}{2}, S_2 = \frac{1}{2} \) copper spin systems.

3.3. \( S = \frac{1}{2} \) Spin Systems

In magnetically dilute samples where electron-electron spin coupling, quadrupole coupling, and nuclear Zeeman effects are small and negligible, except as pathways for \( T_2 \) relaxation, the EPR spectrum of an \( S = \frac{1}{2} \) copper complex can be fitted to

\[
\hat{H} = g_z \beta H_z \hat{S}_z + g_y \beta H_y \hat{S}_y + g_x \beta H_x \hat{S}_x \\
+ A_z \hat{S} \hat{I}_z + A_y \hat{S} \hat{I}_y + A_x \hat{S} \hat{I}_x \\
+ B_z \hat{S} \hat{I}_z + B_y \hat{S} \hat{I}_y + B_x \hat{S} \hat{I}_x
\]

(3.3.1)

where \( A_{x,y,z} \) are the principal values of the copper nuclear hyperfine tensor and \( B_{x,y,z} \) are the principal values of the ligand nuclear superhyperfine tensor. In Figure 3.2, EPR transitions for a hypothetical copper complex with one nitrogen ligand, are shown for the parallel orientation where the projections of \( \hat{S} \) and \( \hat{I} \) on \( H_n \) are \( m_S \) and \( m_I \), respectively. Since \( A \) is assumed to be negative, the EPR lines are labelled from negative to positive \( m_I \) from left to right. There are \((2I_{Cu} + 1)(2I_{N} + 1) = (2 \cdot 3/2 + 1)(2 \cdot 1 + 1) = 12\) allowed transitions with \( \Delta m_S = \pm 1, \Delta m_{Cu}^I = 0, \) and \( \Delta m_{N}^I = 0 \). The observed hyperfine splittings, corresponding to the coupling constants \( A_n \) and \( B_n \), are \( a_n \) and \( b_n \), as shown in Figure 3.2.
Figure 3.2. EPR transitions for hypothetical copper complex with one nitrogen ligand ($S = \frac{1}{2}$, $I = 1$); parallel orientation.
TRANSITION ENERGIES:
\[ \Delta E_1 = g_\| \beta H_{ii} \cdot 3/2 A_{ii} B_{ii} \]
\[ \Delta E_2 = g_{\|} \beta H_{ii} \cdot -3/2 A_{ii} \]
\[ \Delta E_3 = g_{\|} \beta H_{ii} \cdot 3/2 A_{ii} B_{ii} \]
\[ \Delta E_4 = g_{\|} \beta H_{ii} \cdot -1/2 A_{ii} B_{ii} \]
\[ \Delta E_5 = g_{\|} \beta H_{ii} \cdot -1/2 A_{ii} \]
\[ \Delta E_6 = g_{\|} \beta H_{ii} \cdot 1/2 A_{ii} B_{ii} \]
\[ \Delta E_7 = g_{\|} \beta H_{ii} \cdot 1/2 A_{ii} B_{ii} \]
\[ \Delta E_8 = g_{\|} \beta H_{ii} \cdot 1/2 A_{ii} \]
\[ \Delta E_9 = g_{\|} \beta H_{ii} \cdot 3/2 A_{ii} B_{ii} \]
\[ \Delta E_{10} = g_{\|} \beta H_{ii} \cdot 3/2 A_{ii} \]

CORRESPONDING EPR SPECTRUM
There will be an additional twelve lines each for $H_x$ and $H_y$.

For $g_x = g_y = g_\perp$ the intensity of the perpendicular lines will be greater than the intensity of the parallel lines.

Since spin-orbit coupling mixes ground state and excited state configurations according to the crystal field symmetry, EPR parameters are sensitive to the coordination geometry as well as the ground state of the complex. Expressions for $g$ and $A$ parameters are derived by using the ground state antibonding molecular orbital, corrected for admixture of excited state character by spin orbit coupling, as the eigenfunction for the spin Hamiltonian. The solutions which are obtained depend on the crystal field symmetry.

In $D_{4h}$ ($4/mmm$) symmetry, the ground state is $B_{1g}$ ($dx^2 - y^2$) and does not mix with the $A_{1g}$ ($dz^2$) excited state. The observed $g$ values are predicted (28, 30, 75) by

$$g_\parallel - 2.0023 = \frac{-8\lambda \alpha \beta_1}{\Delta E_{dx^2-y^2+dxy}} \left[ \alpha \beta_1 - \alpha' \beta_1 S - \alpha' (1-\beta_1^2)^{1/2} \right] T(n)/2$$  \hspace{1cm} (3.3.2)

$$g_\perp - 2.0023 = \frac{-2\lambda \alpha \beta}{E_{dx^2-y^2+dxz, yz}} \left[ \alpha \beta - \alpha' \beta S - \alpha' (1-\beta^2)^{1/2} T(n)/2 \right]$$  \hspace{1cm} (3.3.3)

where $\alpha$, $\beta_1$, $\beta$ are the bonding parameters introduced in Chapter 2; $\Delta E$ is the electron transition energy; $\lambda$ is the spin orbit coupling constant; $T(n)$ is a function of the metal-ligand distance, nuclear charge, and extent of $s$-$p$
hybridization of ligand orbitals. The overlap integral is defined as

\[ S = \langle dx^2 - y^2 | \psi_{LGO}, x^2 - y^2 \rangle / 2 \]

\[ = \langle dx^2 - y^2 | \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \rangle / 2 \] (3.3.4)

where \( \sigma_i = np_i \pm (1 - n^2)^{1/2}s_i \) to account for s-p hybridization of ligand orbitals. Evaluation of \( S \) using hydrogen-like wavefunctions yields \( S_{\text{nitrogen}} = 0.093 \) and \( S_{\text{oxygen}} = 0.076 \), assuming \( sp^2 \) hybridization (28). The difference in the values of \( S \) for \( sp^2 \) and \( sp^3 \) hybridization is probably small. On the other hand, \( T(n) \) is sensitive to the metal-ligand distance as well as to the extent of \( sp \) hybridization, where

\[ T(n) = n - \frac{(1-n^2)^{1/2} R 8(z_p z_s)^{5/2}(z_s - z_p)}{(z_s + z_p)^5 a_o} \] (3.3.5)

and where \( z_p \) and \( z_s \) are the effective nuclear charges for p and s electrons, \( R \) is the metal-ligand distance, and \( n \) is the fraction of p orbital character. Using \( z_s = 4.50 \), \( z_p = 3.54 \) for nitrogen, and \( z_s = 5.25 \), \( z_p = 4.06 \) for oxygen (28), and \( R \) from crystallographic data (see Table 4.1), the \( T(n) \)'s for nitrogen and oxygen are calculated for bis(prolinato)copper(II) dihydrate, bis(anthranilato)copper(II), and bis(picolinato)copper(II) dihydrate and listed in Table 3.2. Since there is evidence that \( sp^2 \) hybridization is not a good approximation for aromatic nitrogen or for oxygen (87, 88),
<table>
<thead>
<tr>
<th></th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pic)$_2$·2H$_2$O</td>
<td>$R = 1.963$ Å</td>
<td>$R = 1.940$ Å</td>
</tr>
<tr>
<td></td>
<td>$sp^2, n = (0.67)^{\frac{1}{2}}$</td>
<td>$sp^2, n = (0.67)^{\frac{1}{2}}$</td>
</tr>
<tr>
<td></td>
<td>$T(n) = 0.325$</td>
<td>$T(n) = 0.218$</td>
</tr>
<tr>
<td>Cu(anth)$_2$</td>
<td>$R = 2.024$ Å</td>
<td>$R = 1.973$ Å</td>
</tr>
<tr>
<td></td>
<td>$sp^3, n = (0.75)^{\frac{1}{2}}$</td>
<td>$sp^2, n = (0.67)^{\frac{1}{2}}$</td>
</tr>
<tr>
<td></td>
<td>$T(n) = 0.428$</td>
<td>$T(n) = 0.209$</td>
</tr>
<tr>
<td>Cu(pro)$_2$·2H$_2$O</td>
<td>$R = 1.959$</td>
<td>$R = 2.028$</td>
</tr>
<tr>
<td></td>
<td>$sp^3, n = (0.75)^{\frac{1}{2}}$</td>
<td>$sp^2, n = (0.67)^{\frac{1}{2}}$</td>
</tr>
<tr>
<td></td>
<td>$T(n) = 0.442$</td>
<td>$T(n) = 0.192$</td>
</tr>
</tbody>
</table>
differences among the calculated values of $T(n)$ may not be significant.

Depending on the experimental uncertainty in the measurement of EPR parameters, terms in $S$ and $T(n)$ may be relatively unimportant. Simplified equations (30) can then be used:

\[
g_{\parallel} - 2.0023 = \frac{-8\alpha^2 \beta_1^2}{\Delta E_{dx^2-y^2 \rightarrow dxy}} \tag{3.3.6}
\]

\[
g_{\perp} - 2.0023 = \frac{-2\alpha^2 \beta_2^2}{\Delta E_{dx^2-y^2 \rightarrow dxz,dyz}} \tag{3.3.7}
\]

When the crystal field symmetry is nonaxial, three $g$ values may be observed. In $D_{2h}$ (mmm) symmetry, the in-(xy) plane anisotropy arises from splitting of the dxz and dyz orbitals and the $g$ values are

\[
g_z - 2.0023 = \frac{-8\alpha^2 \beta_1^2}{\Delta E_{dx^2-y^2 \rightarrow dxy}} \tag{3.3.8}
\]

\[
g_y - 2.0023 = \frac{-2\alpha^2 \beta_2^2}{\Delta E_{dx^2-y^2 \rightarrow dxz}} \tag{3.3.9}
\]

\[
g_x - 2.0023 = \frac{-2\alpha^2 \gamma^2}{\Delta E_{dx^2-y^2 \rightarrow dyz}} \tag{3.3.10}
\]

where $\beta^2$ and $\gamma^2$ are the bonding parameters corresponding to the dxz and dyz antibonding molecular orbitals, respectively. In $C_{2v}$ (mm) symmetry, the in-(xy) plane anisotropy also arises from admixture of $dx^2-y^2$ and $dz^2$ orbital character, and
\[ g_z - 2.0023 = -\frac{8\lambda^2\beta^2 (\sin^2 \delta)}{\Delta E_{dx^2-y^2-dxy}} \] (3.3.11)

\[ g_y - 2.0023 = -\frac{2\lambda a^2 \beta^2 (\sqrt{3} \cos \delta + \sin \delta)^2}{\Delta E_{dx^2-y^2-dxz}} \] (3.3.12)

\[ g_x - 2.0023 = -\frac{2\lambda a^2 \gamma^2 (\sqrt{3} \cos \delta - \sin \delta)^2}{\Delta E_{dx^2-y^2-dyz}} \] (3.3.13)

where \( \sin^2 \delta = 0.9956 \) and \( \cos^2 \delta = 0.0044 \) are mixing coefficients (51, 89).

When \( dz^2 \) is the ground state, as in distorted octahedral symmetry, the lowest \( g \) value is very close to the free electron value and

\[ g_\perp = 2.0023 \] (3.3.14)

\[ g_\parallel - 2.0023 = -\frac{3a^2\lambda}{\Delta E_{dz^2-dxz,yz}} \] (3.3.15)

The hyperfine coupling constants are also related to the bonding parameters. In \( D_{4h} (4/mmm) \) symmetry (28, 30, 75),

\[ A_\parallel = \mu \left[ a^2 (-\kappa_o - 4/7) + (g_\parallel - 2.0023)Z_\parallel + \frac{3/7(g_\perp - 2.0023)Z_\perp} \right] \] (3.3.16)

\[ A_\perp = \mu \left[ a^2 (-\kappa_o + 2/7) + 11/14(g_\perp - 2.0023)Z_\perp \right] \] (3.3.17)

where \( \kappa_o \) is the Fermi contact term, and
\[ P_0 = 2.0023 \, g_N^2 \beta_N <r^{-3}> d x^2 - y^2 \]  \hspace{1cm} (3.3.18)

\[ Z_\parallel = \alpha_\parallel^{1/2} \left[ \alpha_\parallel - \alpha' \beta_1 \left( 1 - \beta_1^2 \right) \frac{1}{2} T(n) \right] = 1 \]  \hspace{1cm} (3.3.19)

\[ Z_\perp = \alpha_\perp \left[ \alpha_\parallel - \alpha' \beta_1 S_1 - \alpha' \left( 1 - \beta_1^2 \right) \frac{1}{2} T(n) \right] = 1 \]  \hspace{1cm} (3.3.20)

The free atom values of \( P_0 \) are 388 \( \times 10^{-4} \) cm\(^{-1}\) and 416 \( \times 10^{-4} \) cm\(^{-1}\) for \(^{63}\)Cu and \(^{65}\)Cu, respectively (75). However, to account for the reduction of \( P_0 \) by covalent bonding, an average value, \( P = 360 \times 10^{-4} \) cm\(^{-1}\), is usually employed (90).

The Fermi contact term, \( \kappa_0 \), is approximately 0.43, and it is usually assumed to be constant (91). Kuska and Rogers (92) found that this assumption is not generally valid. The two contributions to \( \kappa_0 \) are opposite in sign. The negative contribution from exchange polarization of electron spin density in filled \( s \) orbitals, is covalency dependent, and is related to the hyperfine couplings by \( a^2 \). The positive term arises from unpaired electron density in the 4s copper orbital, and is sensitive to both covalency and the ground state-excitited state energy separation. The relative importance of the two terms can vary independently in such a way that the hyperfine couplings decrease, rather than increase, as covalency decreases (\( a^2 \) approaches 1). This was observed by Kuska and Rogers (92), and Yokoi (93) in their studies of the effect of ligand substitution on EPR hyperfine splittings in copper acetylacetonates.
Similar expressions for the ligand hyperfine couplings (94) are given by

\[
B = |g_e g_N g_N| \left( \frac{\alpha'^2}{4} \right) \times \{ 4n^2 \langle r^{-3} \rangle_{2p} \\
+ \frac{8\pi}{3}(1-n^2) \psi_{2s}^2(0) \} \tag{3.3.21}
\]

\[
B_- = |g_e g_N g_N| \left( \frac{\alpha'^2}{4} \right) \times \{ -\frac{2n^2}{5} \langle r^{-3} \rangle_{2p} \\
+ \frac{8\pi}{3}(1-n^2) \psi_{2s}^2(0) \} \tag{3.3.22}
\]

where \( \alpha' \) is the molecular orbital coefficient for the ligand term in the antibonding orbital, \( n \) is the fraction of s-p hybridization of ligand orbitals, \( \psi_{2s}^2(0) \) is the electron density of the ligand atomic 2s orbital at the ligand nucleus, and \( \langle r^{-3} \rangle_{2p} \) is the radial integral over the ligand 2p orbital. For nitrogen, \( \langle r^{-3} \rangle_{2p} \) is 2.37 a.u., and \( \psi_{2s}^2(0) \) is 4.49 a.u. (94).

To further complicate interpretation of EPR parameters, covalent bonding reduces the spin-orbit coupling constant below the free ion value (90) by as much as 30-40%. For example, Kokoszka and Allen (51) calculated \( \lambda = -475 \ \text{cm}^{-1} \) compared to \( \lambda_0 = -828 \ \text{cm}^{-1} \) for zinc-doped copper acetate monohydrate.

3.4. Coupled \( S_1 = \frac{1}{2}, S_2 = \frac{1}{2} \) Systems

Electron-electron interactions must be considered when the copper-copper distance becomes small, as in magnetically
Concentrated samples or in dimeric copper complexes. The Hamiltonian operators for the dipolar and exchange interactions were introduced in Section 3.2. The observed zero field splitting arises from both the dipolar interaction, and anisotropy in the exchange interaction. Isotropic exchange does not contribute to zero field splitting, but reduces nuclear hyperfine splittings by a factor of one-half (31).

For a given orientation two transitions occur as shown in Figure 3.3. The effective spin Hamiltonian, neglecting nuclear hyperfine interactions, is (58, 95)

\[
\hat{H} = \frac{g_\beta H_S}{2} + D S_z^2 + E (S_x^2 - S_y^2) - \frac{2}{3} D
\]  

(3.4.1)

where \( E \) is the rhombic component of the zero field splitting (not shown in Figure 3.3). A general solution of this equation is not possible. However, the six principal \( \Delta m_s = \pm 1 \) resonance positions are approximately as given by (95)

\[
H_1^2 = \left( \frac{g_e}{g_x} \right)^2 [(H_o - D' + E')(H_o + 2E')]
\]  

(3.4.2)

\[
H_2^2 = \left( \frac{g_e}{g_x} \right)^2 [(H_o + D' - E')(H_o - 2E')]
\]  

(3.4.3)

\[
H_3^2 = \left( \frac{g_e}{g_y} \right)^2 [(H_o - D' - E')(H_o - 2E')]
\]  

(3.4.4)

\[
H_4^2 = \left( \frac{g_e}{g_y} \right)^2 [(H_o + D' + E')(H_o + 2E')]
\]  

(3.4.5)
Figure 3.3. EPR transitions in coupled $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ system (H $\parallel$ Z).
$E_4 = g_{||} \beta H_{||} - \frac{1}{2} J_o + \frac{1}{3} D$  
($s_z = +1$)

$E_3 = +\frac{1}{2} J_o - \frac{2}{3} D$  
($s_z = 0$)

$E_2 = -g_{||} \beta H_{||} - \frac{1}{2} J_o + \frac{1}{3} D$  
($s_z = -1$)

$E_1 = +\frac{3}{2} J_o$

$h\nu = \Delta E_{3,4} = g_{||} \beta (H_{||,1})_o - D$

$h\nu = \Delta E_{2,3} = g_{||} \beta (H_{||,2})_o + D$
where $H = \frac{g_e}{g_z}$, $D' = \frac{D}{g_e}$, and $E' = \frac{E}{g_e}$. When $E = 0$, four lines appear at

$$H_{1,1} = \frac{g_e}{g_{\perp}} (H_0 - \frac{D'}{2})$$ (3.4.8)

$$H_{1,2} = \frac{g_e}{g_{\perp}} (H_0 + \frac{D'}{2})$$ (3.4.9)

$$H_{\|,1} = \frac{g_e}{g_{\|}} (H_0 - D')$$ (3.4.10)

$$H_{\|,2} = \frac{g_e}{g_{\|}} (H_0 + D')$$ (3.4.11)

where the observed separation is $2|D'|$ for the outermost lines and just $|D'|$ for the inner pair of lines (31).

The observed zero field splitting, $D$, has two components

$$D = D_{\text{exchange}} - D_{\text{dipolar}}$$ (3.4.12)

where $D_{\text{dipolar}} = 2g_{\|}^2 \beta^2 / r^3$, $r$ is the copper-copper distance, and

$$D_{\text{exchange}} = -\frac{3}{4} \left\{ \frac{1}{4} (g_{\|} - 2)^2 - (g_{\perp} - 2)^2 \right\}$$ (3.4.13)
assuming a $dx^2-y^2$ ground state (58, 96). In this equation, $J$ is the exchange energy that is obtained from the temperature dependence of magnetic susceptibility (58).

The exchange interaction can be a direct process resulting from overlap of metal d orbitals, or an indirect superexchange process which is propagated through bridging ligand atoms. The debate regarding the nature of the exchange interaction in copper acetate was reviewed in Chapter 2.
Anthranilic acid is used as a reagent for gravimetric determination of divalent and trivalent transition metals (97, 98). In 1960, Hill and Curran (99) reported infrared and ultraviolet absorption studies of divalent manganese, zinc, cadmium, nickel, and copper complexes, and sodium, potassium, calcium, barium, and strontium salts with anthranilic acid. It was found that the N-H stretching frequencies were shifted by 149-187 cm\(^{-1}\) to lower frequency for the transition metal complexes, with the greatest shift observed in the spectrum of copper complex. These shifts are larger than those typically observed in the spectra of aliphatic amino acid complexes. Since very small shifts were observed for peaks in the 1625-1500 cm\(^{-1}\) region, the authors concluded that the COO\(^{-}\)-M\(^{2+}\) bonds in anthranilate complexes are electrostatic. Hill and Curran also reported that the ultraviolet spectra of these complexes in absolute ethanol indicate that the N-M bond is broken, and that in 95% ethanol the nickel complex is completely dissociated, and the copper, zinc, and cadmium complexes are "appreciably hydrolyzed." This behavior was attributed to the electrostatic character of the COO\(^{-}\)-M\(^{2+}\) bond and "the gain in resonance stabilization" when the nitrogen-metal bonds are broken. It was concluded
that the anthranilate ion is a weak ligand.

In a later study, Sandhu et al. (100), reported infrared and magnetic susceptibility measurements on the 2:1 anthranilate complexes with divalent manganese, nickel, zinc, cadmium, cobalt, and copper. On the basis of the insolubility of these complexes and infrared data, it was suggested that these complexes have a polymeric structure, that the ligands are tridentate due to the involvement of both oxygens of the carboxylate group in coordination, and that the coordination geometry around the metal ion is distorted octahedral. Further evidence for octahedral stereochemistry are the room temperature magnetic moments for the bis(anthranilato) nickel(II) and cobalt(II) complexes, which were reported as 3.2-3.4 B.M. and 5.00-5.05 B.M., respectively (100, 101). The magnetic moment of bis(anthranilato) copper(II) has been variously reported as 2.0 B.M. (100) and 1.84 B.M. (102). On the basis of electron paramagnetic resonance spectra of magnetically concentrated, polycrystalline bis(anthranilato) copper(II), a square planar geometry was suggested (102, 103). However, the crystalline g-values reported by Ismailov (102) as $g_1 = 2.069$ and $g_2 = 2.250$ are not necessarily equal to the molecular g-values, due to Cu-Cu interactions in the undiluted lattice, and might be misleading. As with other ligand bridged copper complexes (62-64, 104), and as suggested by the observed (102) Weiss constant, $\theta = -2^\circ$, a weak magnetic interaction between copper ions is expected.

Other reports of infrared spectra of metal anthranilates
have appeared in the literature (105-108). Shepard et al. (108) reported M-O stretching frequencies for divalent manganese, cobalt, nickel, copper, and zinc complexes of anthranilic acid, and of 5-methyl, 5-chloro, 5-bromo, and 5-iodo anthranilic acids. Splitting of the Cu-O stretching band but not the Cu-N stretching band was observed. The splitting was attributed to tetragonal distortion of octahedral symmetry, and the presence of two types of Cu-O bonds (i.e., equatorial and axial). It was observed also that the M-O stretching frequency shifts toward lower frequency as the inductive, electron-withdrawing capacity of the ligand substituent decreases. The substituent effect on the M-N stretching frequencies showed a tendency to shift the M-N band in the opposite direction compared to the M-O band.

In 1975, Lange and Haendler (109) reported the crystal and molecular structure of bis(anthranilato) copper(II). This work confirmed the polymeric structure proposed by Sandhu (100), in which the copper ion is in a distorted octahedral environment. Two amino nitrogens and two carboxylate oxygens occupy trans equatorial positions. A carbonyl oxygen from a ligand on an adjacent complex molecule occupies the axial coordination site. The polymeric carboxylate-bridged network is further stabilized by N-H⋯O=C hydrogen bonds, and is probably responsible for the extreme insolubility of this complex. Crystallographic data are summarized in Table 4.1.

The thermal properties of complexes of divalent nickel,
TABLE 4.1
SUMMARY OF CRYSTAL DATA

<table>
<thead>
<tr>
<th>Complex</th>
<th>Cu(anth)$_2$</th>
<th>Cu(pro)$_2$$\cdot$2H$_2$O</th>
<th>Cu(pic)$_2$$\cdot$2H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P_2_1$/C</td>
<td>$P_2_1$/n</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>a</td>
<td>12.95 Å</td>
<td>5.61 Å</td>
<td>5.122 Å</td>
</tr>
<tr>
<td>b</td>
<td>5.25</td>
<td>17.86</td>
<td>7.717</td>
</tr>
<tr>
<td>c</td>
<td>9.39</td>
<td>7.12</td>
<td>9.216</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90°</td>
<td>90°</td>
<td>101.07°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>93.3°</td>
<td>108°</td>
<td>95.60°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90°</td>
<td>90°</td>
<td>110.45°</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cu-N</td>
<td>2.024 Å</td>
<td>1.959</td>
<td>1.963</td>
</tr>
<tr>
<td>Cu-O</td>
<td>1.973</td>
<td>2.028</td>
<td>1.940</td>
</tr>
<tr>
<td>Cu-L$_{\text{axial}}$</td>
<td>2.415(C=O*)</td>
<td>2.538(H$_2$O*)</td>
<td>2.752(C=O*)</td>
</tr>
</tbody>
</table>

See Table 1.1 for ligand abbreviations.
copper, and zinc with o-, m-, and p-aminobenzoates have been studied using thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (110). It was found that the activation energy for decomposition followed these sequences

\[ E_{\text{Cu(II)}}^* > E_{\text{Zn(II)}}^* = E_{\text{Ni(II)}}^* \]
\[ E_{\text{ortho}}^* > E_{\text{para}}^* > E_{\text{meta}}^* \]

whereas the procedural decomposition temperatures (pdt) decreased in the order Ni > Zn > Cu. While \( E^* \) reflects complex stability and metal-ligand bond strength, the pdt's are related to the strength of intermolecular bonding. Examination of the above trends reveals the effects of crystal field stabilization energy and chelate ring formation on \( E^* \). The trend in pdt's suggests that Jahn-Teller distortion weakens the intermolecular interactions in the copper complexes. Both \( E^* \) and pdt correlate well with stability constants and free energies of formation of the complexes.

Although Hill and Curran (99) originally proposed that the COO⁻-M²⁺ bond was electrostatic in anthranilate complexes, a more recent study (111) has shown that the COO⁻-M²⁺ bond is not completely ionic in character. Oxygen (Is) binding energies from photoelectron spectra were larger and indicated greater covalency for anthranilate complexes compared to the corresponding sodium salt. A correlation between the shifts in nitrogen (Is) binding energies with N-H frequency shifts in the infrared spectra, established that amine stretching
frequencies decrease as the covalent character of the M-N bond increases.

The N-substituted derivatives of anthranilic acid are known as the fenamic acids and constitute an important group of nonsteroidal anti-inflammatory drugs, noted for their ability to inhibit prostaglandin synthesis (112-115). Yatsimirskii et al. (116) first described the ability of the copper fenamate complexes to catalyze oxidation of ascorbic acid and degradation of hydrogen peroxide. The catalytic activity of the complexes was correlated with the anti-inflammatory activity of the free ligand. They also found that the 1:1 complexes had greater catalytic activity than the 2:1 complexes. Later it was found that the fenamic acids are able to extract copper from ceruloplasmin and form low molecular weight copper fenamate complexes in the presence of the protein (117). Addition of N-(2,3-dimethyl-phenyl)-anthranilate to ceruloplasmin increased the rate of ascorbic acid oxidation, presumably through the formation of low molecular weight copper complexes having greater catalytic activity than the native protein. Grigor'eva et al. (118) have reviewed the role of copper in the mechanism of anti-inflammatory action of the fenamic acids.

Several reports have appeared by Russian investigators of the ability of the copper fenamates to dimerize in organic solvents (119-121). Electron paramagnetic resonance spectroscopy was used to determine the dimerization constants in aqueous dioxane solution for the 2:1 complexes with
N-(2,3-dimethylphenyl)-anthranilate, N-phenyl-anthranilate, N-(3-trifluoromethylphenyl)-anthranilate and N-(3,4-dimethylphenyl)-anthranilate, in decreasing order of magnitude of the dimerization constant. It was found that the stability constants of the analogous monomeric complexes decrease in the reverse order. The singlet-triplet energy separation, 2J, measured from the temperature dependence of the magnetic susceptibility, was found to be -260 cm\(^{-1}\) and -240 cm\(^{-1}\) for the N-(2,3-dimethylphenyl) and N-(3-trifluoromethylphenyl) anthranilate complexes, isolated as dimers from N,N'-dimethylformamide solution (122). The copper-copper distance in the dimeric 2,3-dimethyl complex is 2.613 Å (123). The complete X-ray structure determination has not been published to date.

Copper complexes with α-amino acids have been studied as models for copper-protein binding sites (1, 124-127). The crystal and molecular structure (128, 129) of bis(L-(−)-prolinato) copper(II) dihydrate has been determined (see Table 4.1). In the solid state, the proline ring has a non-planar, envelope conformation. The axial coordination sites are occupied by water molecules which participate in H\(_2\)O...H-N and C=O...H-O hydrogen bond formation.

Numerous investigations concerned with resolution of optical isomers are reported (130-133). Extensive electron paramagnetic resonance (EPR) work has also been performed (134-137). Slight differences in EPR parameters exist between bis(L-(−)-prolinato) copper(II) dihydrate and bis-(D,L-prolinato) copper(II) dihydrate. For example, in frozen
dilute aqueous methanol solution, the EPR parameters for
the optically pure and racemic complexes are \( g_\| = 2.261, g_\perp = 2.058, A_\| = 188 \times 10^{-4} \text{ cm}^{-1} \), and \( g_\perp = 2.266, g_\| = 2.058, A_\perp = 179 \times 10^{-4} \text{ cm}^{-1} \), respectively (135, 136). Despite these
differences among isomers, the EPR parameters for most ali­
phatic (135-138) and aromatic (139) \( \alpha \)-amino acid complexes
are very similar, and in most cases the \( g \) and \( A \) tensors are
axially symmetric (135-139).

In concentrated polycrystalline samples of \( \text{Cu(pro)}_2 \cdot 2\text{H}_2\text{O} \), magnetic coupling between adjacent copper atoms is
evident from the crystal \( g \)-values, \( g_\perp = 2.075 \) and \( g_\| = 2.191 \)
(134), which do not equal the molecular \( g \)-values (135, 136).
Sastry and Sastry (134) analyzed the variation in linewidth
for rotation of a single crystal around the \( b \)-axis, accord­
ing to Van Vleck's theory of mean square second moments
(140), to obtain the exchange energy and Curie temperature.
In this case, exchange is ferromagnetic with \( 2J = +0.108 \text{ cm}^{-1} \)
and \( T_C = 0.24^\circ \text{K} \). Ferromagnetic exchange is relatively rare
for copper(II) complexes but has been observed for diammine
copper(II) carbonate (104) and [(4-nitroquinoline N-oxide)-
CuCl\(_2\)]\(_2\) (141).

Numerous studies of transition metal complexes with
pyridine carboxylic acids have appeared in the literature.
Complexes of picolinic, nicotinic, and isonicotinic acids
with divalent manganese, iron, cobalt, nickel, copper, zinc,
and silver are known (142, 143). Kleinstein and Webb (143)
initially proposed tetragonal geometry with axial coordination
of solvent molecules for the bis(picolinato) dihydrate complexes, but octahedral geometry and a polymeric carboxylate-bridged lattice network for the analogous nicotinate and isonicotinate complexes. Later, the X-ray structure of bis(picolinato) copper(II) dihydrate (144) (see Table 4.1) and bis(picolinato) copper(II) dihydrate (145) demonstrated the existence of a polymeric structure for the copper complex, but not the cobalt complex. The waters of hydration in the copper complex are interstitial and participate in $O-H \cdots O=C$ and $O-H \cdots O_H$ hydrogen bonding (144), whereas the water molecules are axially coordinated in the cobalt complex. The crystalline dimorphs of bis(picolinato) copper(II) dihydrate differ in the positions of the water molecules in the crystal lattice (146). Upon removal of water, two moles of selenourea (147, 148), potassium selenocyanide (148), thiourea (149), or allylthiourea (149) can be incorporated into the crystal lattice per mole of copper, by coordination through selenium or sulfur at the axial positions on copper.

The thermal properties of the pyridine carboxylate complexes (150) are similar to the properties of the aminobenzoate complexes (110). The thermal stability of the pyridine carboxylates decreases in the following sequences

$$Mn > Zn = Fe > Co > Ni > Cu,$$
$$\text{picolinate} > \text{nicotinate} > \text{isonicotinate},$$

where the effects of crystal field stabilization energy and
chelate ring formation are apparent.

Picolinic acid is able to coordinate in the acid form in nonaqueous media. Mixed free acid and acid anion plus chloride or bromide complexes with copper(II) are known (151). Weight loss percentages in the thermogravimetric analyses of Cu(pic)(Hpic)Br and Cu(pic)(Hpic)Cl·0.5C₂H₅OH correspond to copper(II) oxide as the residue of decomposition, in contrast to copper(II) monohalobenzoates which form copper(I) halide residues (152).

Ammeter et al. (94) demonstrated the dependence of g, metal hyperfine and nitrogen superhyperfine interactions, and optical d-d transitions on the host lattice and the extent of axial coordination, using bis(picolinato) copper(II) doped into diamagnetic lattices or dissolved in a variety of solvents. Solvent effects are particularly important, and the following trends are generally observed as the strength of the axial (solvent) ligand interaction increases:

1. Tetragonality, T, increases, where T is defined as the ratio of equatorial to axial bond lengths so that T = 1.0 for octahedral geometry and T = 0.5-0.6 for square planar geometry
2. The electron transition energies decrease
3. The contribution to the total spin moment from orbital angular momentum increases (i.e., the degree of "quenching" decreases)
4. Hyperfine coupling constants increase in a positive manner, i.e., |−A| decreases as a consequence of (3)
5. Equatorial σ-bond covalency decreases
6. Equatorial ligand hyperfine coupling constants decrease as a consequence of (5)
7. g-values increase as a result of (3) and (5)
8. $<r^{-3}>_{d\chi^2-y^2}$ increases as a result of (5), and parameters which are directly proportional to $<r^{-3}>$ increase (e.g., $P$, $\lambda$)

These trends are illustrated by the values of $g_o$ and $A_o$ for Cu(pic)$_2$ in pyridine, water, methanol, and ethanol, in decreasing order of the coordinating ability of the solvent. The $g_o$-values are 2.136, 2.133, 2.130, 2.130, and $A_o$ values are -65, -67, -70.5, -71 G for each solvent, respectively.

Theoretical aspects of EPR spectroscopy were discussed in Chapter 3.

Divalent zinc and nickel, but not copper, complexes with pipecolinic acid have been reported (153). It was found that the thermodynamic stability constants for the interaction of picolinate and pipecolinate anions with copper(II) in aqueous-propanol solution, are larger for the formation of 1:1 complexes compared to 2:1 complexes; for nickel compared to zinc; and for picolinate compared to pipecolinate. The relationship between $K_1$ and $K_2$ is expected on statistical grounds, whereas the relationship between nickel and zinc is predicted by crystal field stabilization energy. The relationship between the formation constants of picolinate and pipecolinate complexes suggests stabilization by delocalization of electrons arising from coplanarity of the chelate
ring and picolinate aromatic ring.

It is sometimes possible to correlate metal complex behavior with the acid dissociation constants of the ligand. For amino acids the following acid-base relationships must be considered.

\[
\begin{align*}
\text{NH}_3^+ - R - \text{COOH} & \leftrightharpoons \text{NH}_3^+ - R - \text{COO}^- \\
\text{NH}_2 - R - \text{COOH} & \leftrightharpoons \text{NH}_2 - R - \text{COO}^-
\end{align*}
\]

where \( K_A \) and \( K_D \) are dissociation constants for the carboxylic acid group; \( K_B \) and \( K_C \) are dissociation constants for the amino group; and \( K_Z \) is the equilibrium constant for rearrangement of the neutral molecule to the zwitterion (\( \text{NH}_3^+ - R - \text{COO}^- \)). The effective two-step concentration equilibrium constants for acid dissociation (153) are given by:

\[
\begin{align*}
K_{H1} &= K_A + K_B \\
K_{H2} &= \frac{1}{K_C} + \frac{1}{K_D}
\end{align*}
\]

One or both stepwise acid dissociation constants have been reported for some of the ligands in this study, and are summarized in Table 4.2. Complex stability constants are also listed. There is no stereoselectivity in complexation by optically active bidentate amino acids (157).
### Table 4.2

ACID DISSOCIATION CONSTANTS AND COPPER COMPLEX FORMATION CONSTANTS

<table>
<thead>
<tr>
<th>Acid</th>
<th>( pK_{H1} )</th>
<th>( pK_{H2} )</th>
<th>( T(°C), I(M) )</th>
<th>ref</th>
<th>( \log K_1^a )</th>
<th>( \log K_2^b )</th>
<th>( T(°C), I(M) )</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-(-)-proline</td>
<td>1.90</td>
<td>10.38</td>
<td>25,0.1</td>
<td>154</td>
<td>8.83</td>
<td>16.40</td>
<td>25,0.1</td>
<td>154</td>
</tr>
<tr>
<td>piperolic acid</td>
<td>--</td>
<td>10.52</td>
<td>25,0.1</td>
<td>154</td>
<td>7.5</td>
<td>13.9</td>
<td>20,0.1</td>
<td>154</td>
</tr>
<tr>
<td>picolinic acid</td>
<td>2.01</td>
<td>5.50</td>
<td>25,0.02</td>
<td>153</td>
<td>7.95</td>
<td>14.95</td>
<td>20,0.1</td>
<td>154</td>
</tr>
<tr>
<td>anthranilic acid</td>
<td>1.97</td>
<td>4.79</td>
<td>25,0.1</td>
<td>156</td>
<td>4.25</td>
<td>--</td>
<td>25,0</td>
<td>154</td>
</tr>
<tr>
<td>4-chloro-anthranilic acid</td>
<td>(1.74)</td>
<td>(4.32)</td>
<td>--</td>
<td>157</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>3,5-dichloro-anthranilic acid</td>
<td>(1.23)</td>
<td>(4.26)</td>
<td>--</td>
<td>157</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>4-nitro-anthranilic acid</td>
<td>(1.19)</td>
<td>(4.08)</td>
<td>--</td>
<td>157</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>N-phenyl-anthranilic acid</td>
<td>--</td>
<td>7.70</td>
<td>25,0.02</td>
<td>119</td>
<td>5.89</td>
<td>4.81</td>
<td>25,0.02</td>
<td>119</td>
</tr>
<tr>
<td>flufenamic acid</td>
<td>--</td>
<td>7.63</td>
<td>25,0.02</td>
<td>121</td>
<td>5.77</td>
<td>4.65</td>
<td>25,0.02</td>
<td>121</td>
</tr>
</tbody>
</table>

\[ \text{Cu}^{2+} + \text{LH} \xrightarrow{K_1} (\text{CuL})^+ + \text{H}^+ \]
TABLE 4.2 - Continued

\[ b(CuL)^+ + LH \xrightarrow[K_2]{\text{}} CuL_2 + H^+ \]

\(^c\text{Calculated using Hammett Equation, } pK_a = (pK_a)_0 - \sigma, \text{ with } (pK_a)_0 = (pK_{H1})_{\text{anthranilic acid}} = 1.97; \sigma(\text{m - NO}_2) = 0.71, \sigma(\text{p - NO}_2) = 0.78, \sigma(\text{m - Cl}) = 0.37, \sigma(\text{p - Cl}) = 0.23, \sigma(\text{o - Cl}) = 0.20.\]

\(^d\text{Calculated using Hammett Equation with } (pK_a)_0 = (pK_{H2})_{\text{anthranilic acid}} = 4.79.\]
5.1. Preparation of Complexes

The ligands (shown in Table 1.1) were purchased from Aldrich and used without further purification. Aqueous solutions of the sodium salts of the acids were prepared by dissolving the free acid in dilute (-0.5-1.0 M) sodium hydroxide solution. The pH was adjusted to 6.0-7.0 with dilute acetic acid, and the solution was then filtered. An aqueous solution of copper(II) acetate was added to the ligand solution in a 1:2 metal-ligand mole ratio. With the exception of that of L-(−)-proline, the complexes precipitated immediately as finely grained powders in quantitative yield. The products were collected on Buchner funnels, washed with deionized water, and air-dried. Copper-doped zinc(II) and nickel(II) complexes were prepared by the same procedure, using approximately 5 mol% copper(II) acetate in nickel(II) acetate or zinc(II) acetate. The bis(prolinato) copper(II) complex which is extremely soluble in water, was isolated by addition of acetone or ether to the aqueous solution of the complex.

Two preparative variations were followed with N-phenylanthranilic acid and flufenamic acid. Complexes with these ligands, originally prepared in aqueous solution and
designated CuL₂ A, were recrystallized from reagent grade methanol, which had been dried over 4A molecular sieves, forming CuL₂·MeOH complexes. Alternatively, hot concentrated methanol solutions of the free ligand and copper(II) acetate were combined, and the complexes isolated by crystallization upon slow evaporation of the solvent.

The complexes designated CuL₂ B were prepared by gentle heating of the CuL₂·MeOH complexes in the solid state for approximately 24 hours. The temperature did not exceed 50°C for Cu(fluf)₂ B or 120°C for Cu(panth)₂ B.

All complexes were analyzed for C, H, N composition using a Perkin Elmer 240B Elemental Analyzer, or F&M Model 185, Carbon, Hydrogen, Nitrogen Analyzer. Metal content was determined by gravimetric methods (98). In the analyses for metal, a sample (0.1-0.3 g) of the solid complex was decomposed in about 10 ml of concentrated (-12 M) hydrochloric acid. The copper, nickel, and zinc complexes with N-phenylanthranilic and flufenamic acids were dissolved in methanol prior to acid treatment to insure complete dissociation.

With the exception of proline, pipecolinic acid, and picolinic acid, the ligands precipitated as the free acids and were removed by filtration of the acidified solution. The presence of proline, pipecolinic acid, and picolinic acid in solution did not interfere with the analysis for copper. In the analyses of the copper complexes, the filtrate (-25 ml) was diluted to about 75 ml with deionized water, and treated with aqueous ethylenediamine solution (-9.0 wt%), followed
by addition of concentrated potassium tetraiodomercurate (II) solution to precipitate copper(II) as $[\text{Cu}(\text{en})_2][\text{HgI}_4]$ (98). In the analyses of the copper-doped zinc and nickel complexes, the pH of the filtrate was adjusted to about 6.0 with dilute (~0.5 M) sodium hydroxide solution prior to addition of aqueous sodium anthranilate solution (~3.0 wt.% to determine total metal, i.e., (Cu + Zn) or (Cu + Ni), as the anthranilate complex (98).

Solutions of the complexes were prepared by dissolving in volumetric flasks the solid complexes. Reagent grade methanol and benzene were stored over 4A molecular sieves and used without further purification. Reagent grade dioxane was not pretreated. Since N,N'-dimethylformamide decomposes in the presence of water to carbon monoxide and dimethylamine, and may also contain formic acid (159), this solvent was carefully purified immediately prior to use. Water was removed as the benzene or toluene azeotrope. The solvent was subsequently treated with barium oxide or phosphorous pentoxide, filtered, and fractionally distilled.

5.2. Thermal Analysis

The presence of solvent molecules in the solid complexes was determined by thermal gravimetric analysis (TGA). The enthalpy of desolvation was measured by differential scanning calorimetry (DSC) using indium metal as a calibrant. Adsorbed solvent was distinguished from coordinated solvent by the absence, in the former case, of a well-defined
transition in the DSC curve corresponding to solvent weight loss in the TGA curve.

The thermal decomposition of the complexes in air up to 500°C was studied by TGA also. Decomposition temperatures were measured by integration of the TGA curve using the formula (159)

\[ T_D = \frac{\text{Area Under Curve}}{\text{Total Area}} \times 500 + 40 \]  

(5.2.1)

Solid residues from thermal decomposition were analyzed by X-ray powder diffraction, and products identified by comparison with the standard diffraction file (160).

All the above studies employed a Perkin Elmer Thermobalance, Model TGS-1, and Differential Scanning Calorimeter, Model DSC-1B. Aluminum sample pans were used throughout the various studies.

5.3. Magnetic Susceptibility Measurements

The magnetic susceptibilities of the complexes in the solid state were measured by the Gouy method using a Varian Electromagnet (Model 4004), Power Supply (Model V-2300-A) and Current Regulator (Model 2301-A), and a Beckers Sons (Type RO,1) analytical balance. Measurements were performed at room temperature in a magnetic field of 5.8 kG. The calibration constant, \( \beta \), was determined using HgCo(CNS)\(_4\), and checked against \( (NH_4)_2Fe(SO_4)_2\cdot6H_2O \). The sample tube was open at each end so that the diamagnetic correction for the
glass was small or zero. The magnetic susceptibility, $\chi$, is given by

$$10^6 \chi = \frac{\alpha + \beta F'}{W}$$  \hspace{1cm} (5.3.1)

where $F'$ is the force in mg on the sample corrected for the diamagnetism of the glass, $W$ is the mass of the sample in g, and $\alpha$ and $\beta$ are calibration constants (33). Calculation of $\mu_{\text{eff}}$ was reviewed in Section 2.6.

5.4. Infrared and Visible Spectroscopy

Solution spectra were recorded on the Carey 14 scanning spectrophotometer using matched quartz cells (1 cm path-length) with pure solvent in the reference beam. Diffuse powder reflectance data were collected using the Beckman Model DU Quartz Spectrophotometer with reflectance attachment 2580. The reflectance, $R$, relative to the reflectance of magnesium carbonate was converted to absorbance by

$$A = \log \left( \frac{100}{R} \right)$$  \hspace{1cm} (5.4.1)

Single wavelength absorbances were plotted versus wavelength to give the absorption spectrum.

Infrared spectra were obtained using halocarbon mulls with sodium chloride plates, and a Perkin Elmer grating spectrometer, Model 337. The instrument was calibrated using the spectrum of polystyrene.
5.5. X-ray Diffraction

X-ray powder diffraction photographs were taken with a Philips 57.3 mm camera, and were exposed with nickel-filtered copper Kα radiation (λ = 1.5418 Å) either for 30 minutes to a General Electric X-ray unit set at 10 ma and 45 mV or for two hours to a Norelco X-ray unit set at 15 ma and 35 mV. Samples were contained in 0.3 mm glass capillaries.

5.6. Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectra were recorded on the Varian E-4 spectrometer operating at X-band frequency (-9.5 GHz) with 100 kHz field modulation. The magnetic field was calibrated with a proton nuclear magnetic resonance gaussmeter. Diphenylpicrylhydrazyl (DPPH, g = 2.0037 ± 0.0002) was used as a microwave frequency marker. Cylindrical quartz tubes (3 mm i.d.) were used for powders, dioxane and benzene solutions at room temperature, and for all solutions at liquid nitrogen temperature. A quartz flat cell was used for N,N'-dimethylformamide and methanol solutions at room temperature. A cylindrical quartz Dewar was inserted into the instrument cavity for measurement of spectra at liquid nitrogen temperature. Instrument settings were selected to avoid power saturation, overmodulation, and lineshape distortion. EPR parameters were refined by computer simulation of spectra. Simulated spectra were calculated using a Fortran program for S = \frac{1}{2} (84) systems (appendix A) on a DEC-10 computer, and were displayed on a Calcomp plotter.
Zero field splitting parameters (D and E) were measured by comparison of observed resonance positions with calculated positions (see appendix B).
CHAPTER 6

RESULTS AND DISCUSSION

6.1. Stoichiometry of the Complexes

Complexes with a 2:1 ligand:metal mole ratio were prepared. As shown in Table 6.1, the results of the analyses for carbon, hydrogen, nitrogen, and metal confirm this stoichiometry. In general, the observed percentages are in good agreement with predicted values. In several compounds, i.e., Cu(panth)$_2$ A, Cu(fluf)$_2$ A, Ni(anth)$_2$, Ni (panth)$_2$, Zn(panth)$_2$, and Zn(fluf)$_2$, where the differences between observed and calculated values are greater than the acceptable ±0.3% limit, thermal gravimetric analysis established the presence of adsorbed water in nonstoichiometric amounts (see Table 6.2 and Figures 6.1-6.5). Although weight loss corresponding to desorption of water is not observed in every case where the observed and calculated compositions differ, the presence of adsorbed water is inferred. The desorption process may be obscured by the decomposition process in these substances. The presence of adsorbed water is not unexpected since these complexes precipitate rapidly upon formation, and are similar in texture when dry to clay materials. The absence of a well-defined transition in the DSC curve corresponding to loss of water in the TGA curve, is indicative of physical adsorption rather than chemical solvation.

80
TABLE 6.1
ANALYTICAL DATA

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<tr>
<th>Empirical Formula</th>
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<th>% Composition</th>
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TABLE 6.1 - Continued

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$^a$Copper complexes analyzed for copper content by ethylenediamine method; copper-doped zinc and nickel complexes analyzed for total metal content by anthranilate method; see Section 5.1 for details.

$^b$Calculated assuming 5.0 mol% copper content.
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<th>Complex</th>
<th>( T_D ) (°C)(^a)</th>
<th>Temperature Range (°C)</th>
<th>Observed % Weight Loss</th>
<th>Volatile Product(^b)</th>
<th>Calculated % Weight Loss(^c)</th>
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<td>Calculated % Weight Loss</td>
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TABLE 6.2 - Continued

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<th>Complex</th>
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<th>Temperature Range (°C)</th>
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<th>Volatile Product*</th>
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\(^a\)Estimated by integration of TGA curve over temperature range 40-500°C; see Section 5.2.

\(^b\)Identity of product assumed. Chemical or spectral characterization was not performed.

\(^c\)Assuming formation of metal(II) oxide. As indicated by X-ray diffraction, the metal (II) oxide was always found in combination with other compounds (see Section 6.2). Agreement between calculated and observed % weight loss can be misleading.
TABLE 6.2 - Continued

dFreshly prepared sample.
eAged sample.
fLoss of sample occurred during explosive decomposition.
Figure 6.1. TGA curves for (A) Cu(pic)$_2$; (B) Cu(pip)$_2$·2H$_2$O; (C) Cu(pro)$_2$·2H$_2$O (old); and (D) Cu(pro)$_2$·2H$_2$O (new); sample weight: 1.916, 1.519, 1.396, 1.239 mg, respectively; mass range: x 2; heating rate: 40°/min; chart speed: 2''/min.
Figure 6.2. TGA curves for (A) Cu(nanth)$_2$; (B) Cu-(dcanth)$_2$$\cdot$2H$_2$O; (C) Cu(canth)$_2$; and (D) Cu(anth)$_2$; sample weight: 2.610, 0.746, 1.742, 2.673 mg, respectively; mass range: x 4, x 1, x 2, x 2, respectively; heating rate: 40°/min; chart speed: 2"/min.
Figure 6.3. TGA curves for (A) Cu(panth)$_2$ A; (B) Cu(panth)$_2$ B; (C) Cu(panth)$_2$·MeOH; (D) Cu(fluf)$_2$ A; (E) Cu(fluf)$_2$ B; and (F) Cu(fluf)$_2$·MeOH; sample weight: 1.103, 1.113, 1.445, 1.323, 3.498, 1.827 mg, respectively; mass range: x 2, x 2, x 2, x 2, x 4, x 2, respectively; heating rate: 40°/min; chart speed: 2"/min.
WEIGHT LOSS

Diagram showing weight loss over time with labeled sections A, B, C, D, E, F.

Legend:
- 0.1 g
- 0.25 mg
- Graph scale
Figure 6.4. TGA curves for (A) Zn(anth)$_2$; (B) Zn-(canth)$_2$; (C) Zn(dcanth)$_2$; (D) Zn(nanth)$_2$; (E) Zn(panth)$_2$; and (F) Zn(fluf)$_2$; sample weight: 2.544, 2.224, 2.532, 1.090, 3.120, 2.496, respectively; mass range: x 4, x 2, x 2, x 1, x 4, x 4, respectively; heating rate: 40°/min; chart speed: 2"/min.
Figure 6.5. TGA curves for (A) Ni(anth)$_2$; (B) Ni-(panth)$_2$; and (C) Ni(fluf)$_2$; sample weight: 2.724, 2.126, and 1.184 mg, respectively; mass range: x 4, x 2, x 1, respectively; heating rate: 40°/min; chart speed: 2"/min.
With Cu(pro)$_2$$\cdot$2H$_2$O, Cu(pip)$_2$$\cdot$2H$_2$O, Cu(dcanth)$_2$$\cdot$2H$_2$O, Cu(panth)$_2$$\cdot$MeOH, and Cu(fluf)$_2$$\cdot$MeOH, the presence of solvent molecules is indicated by transitions in the TGA curves, corresponding to loss of solvent, which are accompanied by transitions in the DSC curve (Figures 6.6 and 6.7). In these substances, the solvent molecules presumably are coordinated directly to the metal or participate in hydrogen bonding. The heats of transitions were measured, and will be discussed in Section 6.2.

The complexes Cu(panth)$_2$ A and Cu(fluf)$_2$ A can be re-crystallized from methanol to form the corresponding methanol solvates. The resulting complexes, Cu(panth)$_2$$\cdot$MeOH and Cu(fluf)$_2$$\cdot$MeOH, can be desolvated by gentle heating to produce Cu(panth)$_2$ B and Cu(fluf)$_2$ B. In turn, these complexes can be recrystallized from methanol to again form the methanol solvates.

6.2. Thermal Properties

The thermal decomposition of the copper, nickel, and zinc complexes was examined to assist in the determination of the stoichiometry of the complexes, and the interpretation of DSC results. The heating rate in these studies was more rapid than that normally employed for TGA (i.e., 40°/min rather than 5 or 10°/min) in order to correlate TGA and DSC curves. At lower heating rates, calorimeter sensitivity would be lost. Identical heating rates for TGA and DSC were considered desirable because pathways and products of thermal
Figure 6.6. DSC curves for (A) \( \text{Cu(pro)}_2 \cdot 2\text{H}_2\text{O} \); (B) \( \text{Cu(fluf)}_2 \cdot \text{MeOH} \); and (C) \( \text{Cu(panth)}_2 \cdot \text{MeOH} \); heating rate: 40\(^\circ\)/min; chart speed: 5"/min; recorder range: x 16, x 4, x 4, respectively; sample weight: 8.373, 8.710, 2.762 mg, respectively.
Figure 6.7. DSC curves for (A) Cu(pip)₂·2H₂O, and (B) Cu(dcanth)₂·2H₂O; heating rate: 40°/min; chart speed: 2"/min; recorder range: x 8; sample weight 5.017, 6.726 mg, respectively.
A) Cu(pip)$_2$·2H$_2$O

B) Cu(dcanth)$_2$·2H$_2$O

$T_d = 76$

$T_d = 151$
composition are sensitive to heating rate, as well as other experimental parameters such as sample size.

The thermal decomposition of Cu(pro)$_2$$\cdot$2H$_2$O depends on the age of the sample. A sample of freshly prepared complex exhibits an initial transition corresponding to loss of two water molecules. Over a period of several months, the complex develops a distinctive amine odor, and the low temperature portion of the TGA curve is altered. This observation suggests that ammonia is produced by time-dependent decomposition of the complex at room temperature via rearrangement of the ligand, but that it remains coordinated to copper and is released at elevated temperature. The possible presence of a secondary species such as an ammine adduct should be kept in mind in the evaluation of the magnetic and electronic properties of Cu(pro)$_2$$\cdot$2H$_2$O.

As shown in Table 6.2, the major steps in the decomposition of these complexes is loss of solvent molecules, followed by deterioration of the ligand and release of volatile products, presumably carbon oxides, nitrogen oxides, and water. In many cases, the observed weight loss is drastically different from weight loss calculated for decomposition to the divalent metal oxide. X-ray powder diffraction revealed that the residues are mixtures of products other than the simple divalent metal oxide. Metallic copper, copper(I) oxide, and copper(II) oxide are among the decomposition products for the copper complexes. Copper(I) chloride and copper(II) chloride are also formed for Cu(canth)$_2$ and
Cu(dcanth)$_2$. The complex Cu(nanth)$_2$ is unique in that it decomposes explosively with ignition of the sample and ejection of material from the sample pan.

Metallic nickel as well as nickel(II) oxide were identified as the decomposition products of the nickel complexes. Similarly, metallic zinc and zinc(II) oxide were found as the decomposition products of the zinc complexes. Although the residue for Zn(dcanth)$_2$ is amorphous, weight percentage calculations suggest the presence of zinc chlorides. On the other hand, X-ray diffraction indicates the presence of ZnCl$_2$·4Zn(OH)$_2$ in the residue of Zn(canth)$_2$. Although zinc(II) fluoride is present in the residue of Zn (fluf)$_2$, the residues from the thermal decomposition of the copper and nickel flufenamates can not be identified by comparison of X-ray diffraction patterns with previously published data (160). However, the powder patterns of the residues from the copper flufenamates resemble that of CuOCl$_2$, suggesting the presence of an isomorphous compound such as CuOF$_2$. In every case where halogen was present as a ligand substituent, the residue was shown to contain halide anion by precipitation of silver halide upon treatment with nitric acid and aqueous silver nitrate solution.

Additional studies at lower heating rates are necessary to establish whether or not the observed compounds are formed under conditions approaching equilibrium. Since the sample size is small (only 1-3 mg), it is possible that near equilibrium conditions did exist. If that is true,
then the formation of reduced, rather than oxidized species, such as the free metals and monovalent metal oxides in an oxygen-containing atmosphere, is unusual and warrants further investigation. These results suggest that the metal is reduced by the amine group which is presumably oxidized, and are therefore indicative of strong electron donation by the amine nitrogen to the metal.

Another interesting result is that decomposition is exothermic for Cu(pro)$_2$·2H$_2$O, Cu(pip)$_2$·2H$_2$O, Cu(pic)$_2$, Cu(anth)$_2$, Cu(canth)$_2$, Cu(dcanth)$_2$·2H$_2$O, and Cu(nanth)$_2$, but endothermic for the various Cu(panth)$_2$ and Cu(fluf)$_2$ complexes. Metal complexes with primary amines, such as ethylenediamine, give endothermic DTA peaks in helium (162), whereas secondary amine complexes, such as with N-benzoyl-N-phenylhydroxylamine show exothermic peaks in nitrogen (163). Peaks which are exothermic in air are usually endothermic in nitrogen or other inert atmospheres (164).

Thermal stability of coordination complexes is influenced by (a) the metal ion, (b) the ligand, (c) interionic or intermolecular interactions, and (d) chelate ring formation (164). In general, the order of thermal stability is the reverse of the Irving-Williams stability order (165). From Table 6.2 it is seen that, with the exception of Ni (fluf)$_2$, the nickel and zinc complexes have greater thermal stability than the analogous copper complexes, in agreement with predictions based on the Irving-Williams series, and with previous studies of the thermal stability of copper,
nickel, and zinc complexes with aminobenzoates (110). The anomalous behavior of Ni(fluf)$_2$ suggests a coordination environment in this complex different from that of the other complexes.

For the copper complexes, the relative order of thermal stability is

\[
\text{pro} \approx \text{pip} < \text{panth} < \text{anth} < \text{nanth} < \text{dcanth} < \text{fluf} < \text{pic} < \text{canth}
\]

Since thermodynamic stability imparted by chelation is reflected in enhanced thermal stability, the greater thermal stability of the anthranilate-type complexes relative to the prolinate and pipecolinate complexes, suggests that the six-membered chelate ring of the former is thermodynamically more stable than the five-membered chelate ring of the latter. The much greater thermal stability of the picolinate complex relative to Cu(pro)$_2$·2H$_2$O and Cu(pip)$_2$·2H$_2$O, probably arises from resonance stabilization imparted by delocalization of electrons in the chelate ring and the aromatic ring of the ligand. In a previous study (153), the larger formation constant for bis(picolinato) copper(II) relative to bis(pipecolinato) copper(II) was attributed to resonance stabilization.

The differences in thermal stability among the complexes with the various substituted anthranilates can arise from either differences in coordinating ability of the ligands,
or differences in other interactions such as hydrogen bonding between complex molecules via amine hydrogens and the various electronegative substituents, or via semi-coordination of these substituents to copper. The concept of semi-coordination has been discussed by Hathaway and Billing (30). However, since the order of thermal stability does not correlate with either the $pK_{H1}$ or $pK_{H2}$ values of the ligands (Table 4.2), it appears that the latter consideration is more important. Furthermore, since the order of thermal stability of the zinc complexes,

$$\text{panth} < \text{fluf} < \text{dcanth} < \text{nanth} < \text{anth} < \text{canth},$$

differs from the order observed for the copper complexes, differences in the crystal structures of the copper and zinc complexes are expected.

As previously mentioned, the heat of desolvation was measured by integration of the DSC peak corresponding to the transition. The results are summarized in Table 6.3. The calorimeter measures the heat absorbed or released by a process at constant pressure (i.e., atmospheric) as a function of temperature, relative to the heat capacities of products and reactants. The observed heat can be related to bond energies or other energies of interaction, but is not a standard enthalpy. The entropy contribution to the observed heat of reaction can be estimated on statistical grounds using
### TABLE 6.3
HEATS OF TRANSITION\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Transition</th>
<th>(T_d) (°C)(^b)</th>
<th>(\Delta H_{DSC}) (kcal/mole copper)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pro)(_2)·2H(_2)O</td>
<td>d</td>
<td>41</td>
<td>26.6</td>
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<tr>
<td>Cu(pip)(_2)·2H(_2)O</td>
<td>d</td>
<td>76</td>
<td>24.5</td>
</tr>
<tr>
<td>Cu(dcanth)(_2)·2H(_2)O</td>
<td>d</td>
<td>151</td>
<td>12.9</td>
</tr>
<tr>
<td>Cu(panth)(_2)·MeOH</td>
<td>d,e</td>
<td>71</td>
<td>22.2</td>
</tr>
<tr>
<td>Cu(fluf)(_2)·MeOH</td>
<td>d,e</td>
<td>45</td>
<td>5.1</td>
</tr>
<tr>
<td>Ni(fluf)(_2)</td>
<td>e</td>
<td>108</td>
<td>21.7</td>
</tr>
<tr>
<td>Zn(panth)(_2)</td>
<td>e</td>
<td>137</td>
<td>12.5</td>
</tr>
<tr>
<td>Zn(fluf)(_2)</td>
<td>e</td>
<td>140</td>
<td>26.4</td>
</tr>
</tbody>
</table>

\(^a\)Heating rate: 40°/min; measured by electronic integration by strip chart recorder; calibration factor determined using heat of fusion of indium metal (\(\Delta H_f = 6.8\) mcal/mg).

\(^b\)Minimum temperature of transition, corresponding to temperature at which deflection from baseline was initiated.

\(^c\)Estimated uncertainty: ±1-2 kcal/mol.

\(^d\)Desolvation process: \(M_{n}L_{2n} \cdot 2S(s) \rightarrow M_{n}L_{2n}(s) + 2S(g)\)

\(^e\)Monomerization process: \(M_{2}L_{4}(s) \rightarrow 2ML_{2}(s)\)
\[ \Delta S = k \ln \frac{W_{\text{product}}}{W_{\text{reactant}}} \quad (6.2.1) \]

where \( W \) is the number of moles of product or reactant. For a desolvation process such as

\[ \text{ML}_2 \cdot 2S (s) \rightarrow \text{ML}_2 (s) + 2S (g) \quad (6.2.2) \]

\( \Delta S \) is on the order of 0.65 kcal/mole at room temperature. Similarly, for the process

\[ \text{M}_2\text{L}_4 \cdot 2S (s) \rightarrow 2\text{ML}_2 (s) + 2S (g) \quad (6.2.3) \]

\( \Delta S \) is only 0.82 kcal/mole, at room temperature. The entropy effect is therefore small and negligible relative to experimental error (±1-2 kcal/mole).

For desolvation of a complex in the solid state via (6.2.2), the observed heat of reaction is

\[ \Delta H_{\text{DSC}} = -\Delta H_{\text{solvation}} = -\Delta H_{\text{H bond}} - \Delta H_{\text{coordination}} \quad (6.2.4) \]

The energy of a hydrogen bond can be calculated from the electrostatic dipole-dipole model using

\[ E_{D-D} = \frac{\mu_1 \mu_2 (3\cos^2 \theta - 1)}{r^3} \quad (6.2.5) \]
where $\mu_e$ is the electric dipole moment, $r$ is the dipole-dipole separation, and $\theta$ is the angle of orientation between the interacting dipole moments.

Assuming that $\theta = 0^\circ$, the dipole-dipole energies are:

\[
\begin{align*}
\text{H-N ••• H-O} & \quad \sim 0.5 \text{ kcal/mole-H bond} \\
\text{C-O ••• H-N} & \quad \sim 1.0 \\
\text{C-Cl••• H-O} & \quad 5.0 \\
\text{H-O ••• H-O} & \quad 4.0
\end{align*}
\]

Reported values of the heat of formation of the H-O ••• H-O hydrogen bond in ice are in the range $-(3-8)$ kcal/mole-H bond (166).

From Table 6.3, the enthalpy of desolvation by Cu(pro)$_2$·2H$_2$O is 26.6 kcal/mole-copper atom. In the crystalline state, the water molecules are coordinated to copper and are hydrogen bonded to carbonyl oxygens (129). There are four hydrogen bonds per copper atom. If a value of $-5.0$ kcal/mole is assumed for the heat of formation of a C-O ••• H-O hydrogen bond, an estimate of the heat of coordination of water to copper is $-3.3$ kcal/mole-H$_2$O. Similarly for Cu(pip)$_2$·2H$_2$O, assuming 4 C-O ••• H-O hydrogen bonds per copper atom, the heat of coordination is $-2.2$ kcal/mole-H$_2$O.

The heat of desolvation of CuCl$_2$·2H$_2$O as determined by DSC (167) was reported as 12.8 kcal/mole-copper atom, in rough agreement with the heat of solvation of CuCl$_2$. 
determined by the solubility method -14.6 kcal/mole-copper (168). By similar analysis, the existence of four Cl ... H-O hydrogen bonds each contributing 2.3 kcal/mole-H bond is predicted for CuCl₂·2H₂O as a crystalline solid, assuming 2 x 2.7 kcal/mole-H₂O for the coordination of water.

For Cu(dcanth)₂·2H₂O, analysis of the observed heat of desolvation predicts only two C-O ... H-O hydrogen bonds per copper atom in contrast to Cu(pro)₂·2H₂O. Alternatively, the observed heat of desolvation could arise from a combination of weaker hydrogen bonds involving the amino and chloro groups, in the absence of hydrogen bonding to the carbonyl oxygens. A possible structure for Cu(dcanth)₂·2H₂O is one analogous to Cu(anth)₂ (109) in which the carbonyl oxygens are coordinated at the axial sites of adjacent copper atoms, but in which the water molecules are located outside the coordination sphere and are hydrogen bonded to the chloro substituents.

As will be seen in subsequent sections, the complexes Cu(panth)₂·MeOH and Cu(fluf)₂·MeOH exhibit magnetic properties typical of coupled $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ spin systems, whereas the analogous CuL₂ A and CuL₂ B complexes are spin monomers, in the solid state. The reversibility of monomer and dimer formation by desolvation and recrystallization from methanol, respectively, and the indistinguishable behavior of the three types of complexes in organic solvents, indicate that these complexes form thermally labile dimers in non-aqueous solution. As originally proposed by Kriss et al. (119) the
dimer appears to be hydrogen bond-bridged rather than ligand bridged (either Cu-N-R-O-Cu or Cu-O-C-O-Cu). The proposed hydrogen bonds would be between carbonyl oxygen and amine hydrogen on different ligands bound to different copper atoms, as shown below.

\[
\Delta H_{\text{DSC}} = -\Delta H_{\text{solvation}} - \Delta H_{\text{dimerization}}
\]

The interactions with the dimer include both ligand-ligand interactions and metal-metal interactions \((\Delta H_{M-M})\). The ligand-ligand interactions include hydrogen bonding \((\Delta H_{H\text{-bond}})\) and aromatic ring interactions \((\Delta H_{\pi-\pi})\) which are in dimer analogous to nucleotide base stacking interactions in nucleic acids (169). It will be assumed that \(\Delta H_{\pi-\pi}\) is approximately \(-1\) kcal/mole-ring pair.

It was shown that the heat of solvation of \(\text{CuCl}_2\) by methanol is only 3.5 kcal/mole-copper (168). This is
similar to $\Delta H_{\text{coord}}$ for water; therefore it can be assumed that hydrogen bonding makes a negligible contribution to $\Delta H_{\text{solvation}}$ for methanol. From the observed heat of desolvation and monomerization of Cu(panth)$_2$.MeOH, a value for $\Delta H_{M-M}$ can be calculated.

$$-\Delta H_{M-M} = 2\Delta H_{\text{DSC}} + 2\Delta H_{\text{coordination}} + 4\Delta H_{\pi-\pi} + 2\Delta H_{\text{H-bond in dimer}}$$

$$= 44.4 - 5.4 - 4.0 - 2.0$$

$$= 33 \text{ kcal/mole-dimer} \quad (6.2.7)$$

This value for $\Delta H_{M-M}$ is reasonable for metal-metal bond energies and is on the same order of magnitude as the theoretical estimates of metal-metal $\sigma$-bond energies which are $9.9 \times 10^3$ or $2.8 \times 10^4 \text{ cm}^{-1}$ (28.3 or 80.0 kcal/mole) depending on the value of $\sigma$-bond overlap integral employed, and $\delta$-bond energy which is $6 \times 10^3 \text{ cm}^{-1}$ (17.2 kcal/mole) (46).

Discussion of $\Delta H_{\text{DSC}}$ for Cu(fluf)$_2$.MeOH is reserved until Section 6.6.

Predecomposition transitions were observed (Figure 6.8) for Ni(fluf)$_2$, Zn(panth)$_2$, and Zn(fluf)$_2$, but not for Ni (panth)$_2$. Since solvent molecules are not associated with these complexes, the observed transition presumably corresponds to monomerization of dimeric species in analogy to the copper N-phenyl-anthranilate and flufenamate complexes.

A bond order of zero is predicted for the zinc-zinc $(d^{10}-d^{10})$ interaction due to equal occupation of bonding
Figure 6.8. DSC curves for (A) Ni(fluf)$_2$; (B) Zn-(panth)$_2$; and (C) Zn(fluf)$_2$; heating rate: 40°/min; chart speed: 2"/min; recorder range: x 32, x 16, x 8, respectively; sample weight: 7.357, 14.16, 4.504 mg, respectively.
A) Ni(fluf)$_2$

B) Zn(panth)$_2$

C) Zn(fluf)$_2$

$T_d = 108$

$T_d = 147$

$T_d = 140$
and anti-bonding molecular orbitals. Consequently, it is assumed $\Delta H_{\text{M-M}} = 0$ for the dimeric zinc complexes. On the other hand, since nickel has a $d^8$ configuration, a bond order greater than 1 and a larger value of $\Delta H_{\text{M-M}}$ is expected for the dimeric nickel complex relative to the dimeric copper complex.

For Zn(panth)$_2$, the heat of formation for each of four hydrogen bonds within the dimer is predicted to be $-5.25$ kcal/mole-dimer. This is much larger than the value calculated by assuming a simple electrostatic dipole-dipole interaction, but is not atypical for hydrogen bonds. Therefore, in the zinc complex, the hydrogen bonds are stronger and more covalent than in the copper complex, and suggests that hydrogen bond strength is inversely related to the strength of the metal-ligand and metal-metal interactions. For Zn(fluf)$_2$, a value of $-12.2$ kcal/mole-dimer for each hydrogen bond within the dimer is obtained. This value may not be unreasonably large, but the existence of other interactions in the complex, such as participation by the trifluoro-tolyl group in hydrogen bonding, cannot be discounted.

For Ni(fluf)$_2$, the predicted value of $\Delta H_{\text{M-M}}$ is $-37.4$ kcal/mole-dimer assuming similar hydrogen bond strength compared to the copper complex. This value of $\Delta H_{\text{M-M}}$ is larger than those observed for Cu(panth)$_2\cdot$MeOH and Cu(fluf)$_2\cdot$MeOH, as expected on the basis of molecular orbital occupation, weaker metal-ligand bonding (viz., Irving-Williams series), and no metal-solvent interaction.
6.3. X-ray Powder Diffraction

Debyegrams are shown in Figures 6.9-6.14 and diffraction data are compiled in appendix C. In every case, the copper and zinc complexes are not isomorphous. This dissimilarity was predicted by the differences in the orders of thermal stability for the copper and zinc complexes (Section 6.2). The Ni(panth)\textsubscript{2} complex is amorphous, whereas Ni(anth)\textsubscript{2} is isomorphous with Zn(anth)\textsubscript{2}, but Ni(fluf)\textsubscript{2} is not isomorphous with Zn(fluf)\textsubscript{2}.

The complex, Cu(panth)\textsubscript{2} B, is amorphous. The crystal structure of Cu(panth)\textsubscript{2} A is not well-developed, as might be expected for rapid precipitation of the complex, and does not resemble the structure of Cu(panth)\textsubscript{2}·MeOH. In contrast, Cu(fluf)\textsubscript{2} A and Cu(fluf)\textsubscript{2} B are isomorphous, and both are similar, but not identical, in structure, to Cu(fluf)\textsubscript{2}·MeOH. The higher degree of crystallinity of Cu(fluf)\textsubscript{2} B compared to Cu(panth)\textsubscript{2} B, in addition to the similarity of structures of Cu(fluf)\textsubscript{2} A, Cu(fluf)\textsubscript{2} B, and Cu(fluf)\textsubscript{2}·MeOH, reflects the low thermal barrier to decomposition of Cu(fluf)\textsubscript{2}·MeOH to Cu(fluf)\textsubscript{2} B.

6.4. Infrared Spectral Characterization

Amine stretching frequencies are listed in Table 6.4 for the free ligands and corresponding metal complexes. Proline and pipecolinic acid have infrared spectra which are characteristic of amino acids in the zwitterion form (i.e., broad strong absorptions near 1600 cm\textsuperscript{-1} due to carboxylate anion,
Figure 6.9. Debyegrams for Cu(anth)$_2$, copper-doped Zn(anth)$_2$, and copper-doped Ni(anth)$_2$. 
RELATIVE INTENSITY

INTERPLANAR SPACING, d (Å)

Cu(anth)$_2$

Zn(anth)$_2$

Ni(anth)$_2$
Figure 6.10. Debyegrams for Cu(canth)$_2$ and copper-doped Zn(canth)$_2$. 
Figure 6.11. Debyegrams for Cu(dcanth)$_2$·2H$_2$O and copper-doped Zn(dcanth)$_2$. 
Figure 6.12. Debyegrams for Cu(nanth)$_2$ and copper-doped Zn(nanth)$_2$. 
Relative intensity

Cu(nanth)$_2$

Zn(nanth)$_2$

Interplanar spacing, d (Å)
Figure 6.13. Debyegrams for Cu(panth)$_2$ A, Cu(panth)$_2$. MeOH, and copper-doped Zn(panth)$_2$. 
Figure 6.14. Debyegrams for Cu(fluf)$_2$ A, Cu(fluf)$_2$ B, Cu(fluf)$_2$·MeOH, copper-doped Zn(fluf)$_2$, and copper-doped Ni(fluf)$_2$. 
<table>
<thead>
<tr>
<th>INTERPLANAR SPACING, d(Å)</th>
<th>CuCl₂</th>
<th>CuCl₂-MeOH</th>
<th>Cu₂Cl₂</th>
<th>Cu₂Cl₂-A</th>
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<tr>
<td>16</td>
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# TABLE 6.4
AMINE STRETCHING FREQUENCIES ($v_{\text{NH}}'$ in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Free $v_{\text{NH}}$</th>
<th>Copper Complex $v_{\text{NH}}$</th>
<th>Nickel Complex $v_{\text{NH}}$</th>
<th>Zinc Complex $v_{\text{NH}}$</th>
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<tbody>
<tr>
<td></td>
<td>$\delta^a$</td>
<td>$\Delta^b$</td>
<td>$\Delta^b$</td>
<td>$\Delta^b$</td>
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<tr>
<td>Hanth</td>
<td>3235 --</td>
<td>3214 -21</td>
<td>3205 -20</td>
<td>3226 -9</td>
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<tr>
<td></td>
<td>3316 --</td>
<td>3269 -47</td>
<td>3300 -16</td>
<td>3287 -29</td>
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<tr>
<td>Hcanth</td>
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<td></td>
<td>3488 +172</td>
<td>3264 -224</td>
<td>-- --</td>
<td>3289 -199</td>
</tr>
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<td>Hdcanth</td>
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</tr>
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<tr>
<td>Hfluf</td>
<td>3315 +39</td>
<td>3283$^f$ -32$^f$</td>
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<td>3291$^h$ -24$^h$</td>
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</table>

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$^a$Frequency shift relative to Hanth.

$^b$Frequency shift relative to corresponding free ligand, assuming no crossover.
<table>
<thead>
<tr>
<th>Table 6.4 - Continued</th>
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<tbody>
<tr>
<td><strong>Cu(panth)₂ A.</strong></td>
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<td><strong>Cu(panth)₂ B.</strong></td>
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<td><strong>Cu(panth)₂•MeOH.</strong></td>
</tr>
<tr>
<td><strong>Cu(fluf)₂ A.</strong></td>
</tr>
<tr>
<td><strong>Cu(fluf)₂ B.</strong></td>
</tr>
<tr>
<td><strong>Cu(fluf)₂•MeOH.</strong></td>
</tr>
</tbody>
</table>
and in the 3500-2100 cm\(^{-1}\) region due to the protonated amine group, \(-\text{NH}_3^+\). In contrast, the substituted anthranilic acids apparently exist in the solid state as \(\text{NH}_2^-\text{-R-COOH}\). This is indicated by sharp N-H stretching bands in the 3400-3200 cm\(^{-1}\) region which are characteristic of free amines, and a broad band in the 3200-2300 cm\(^{-1}\) region due to O-H stretching bands from the undissociated carboxylic acid group. It is known that the formation constant for the zwitterion is smaller for aromatic than for aliphatic amino acids (153).

Aromatic ring substitutions shift \(v_{\text{N-H}}\) to higher frequencies. The order of decreasing substituent effect is roughly

\[
n\text{anth} > \text{canth} > \text{dcanth}
\]

which parallels the order of increasing \(pK_{\text{H}_2}\) (see Table 4.2). The presence of electronegative substituents on the aromatic ring with the carboxylic acid substituent, produces an electron withdrawing inductive effect which decreases the basicity of the amine nitrogen relative to anthranilic acid. On the other hand, N-phenyl-anthranilic acid and flufenamic acid have larger \(pK_{\text{H}_2}\) values than anthranilic acid. Therefore, the N-phenyl substituent increases the electron density on the amine nitrogen which increases its basicity. The trifluoromethyl substituent on flufenamic acid slightly weakens this inductive effect, as reflected by the lower
frequency of $\nu_{N-H}$, and the small decrease in $pK_{H2}$ relative to N-phenyl-anthranilic acid.

Upon complexation, the broad O-H band is removed, and $\nu_{N-H}$ is shifted to lower frequency by as much as 262 cm$^{-1}$ depending on the metal. The largest shifts are observed for the copper complexes. The order of decreasing amine frequency shift is

nanth > canth > dcanth > anth > panth = fluf

The same order is observed for both copper and zinc complexes. The order of decreasing amine frequency shift roughly parallels the order of increasing $pK_{H2}$ (see Table 4.2), and therefore, the order of increasing nitrogen donor strength. Intuitively, amine frequency shifts are expected to increase in proportion to the strength of the metal-amine interaction. Observation of the inverse relationship suggests that the amine stretching frequency is more sensitive to other interactions within the complex such as hydrogen bonding.

The frequency shifts are nearly identical for Cu(panth)$_2$ A and Cu(panth)$_2$ B, and for Cu(fluf)$_2$ A and Cu(fluf)$_2$ B. Slightly smaller shifts are observed for the corresponding methanol solvates, indicating that dimerization occurs with concomitant perturbation of the amine group.

6.5. Visible Spectral Characterization

Reflectance data plotted as log (100/R) vs. wavelength
are presented in Figures 6.15-6.17. The complexes fall into three groups with distinct electronic environments:
(a) Cu(pro)$_2$·2H$_2$O, Cu(pip)$_2$·2H$_2$O and Cu(pic)$_2$ which are blue or purple and absorb near 600 nm; (b) Cu(anth)$_2$, Cu(canth)$_2$, and Cu(dcanth)$_2$ which are green and absorb near 675 nm; and (c) the flufenamate and N-phenyl-anthranilate complexes which are brown or green in color.

The reflectance spectrum of Cu(pro)$_2$·2H$_2$O is well-resolved with three major peaks at 675, 625, and 575 nm, which probably correspond to $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{xz,yz}$, and $d_{x^2-y^2} \rightarrow d_z^2$ transitions, respectively, assuming a tetragonally distorted complex with a $d_{x^2-y^2}$ ground state. In contrast, Cu(pip)$_2$·2H$_2$O and Cu(pic)$_2$ exhibit a single peak near 650 and 600 nm, respectively. The order of increasing tetragonality (Chapter 4) should parallel the order of increasing wavelength of the lowest energy transition, and is, therefore,

$$\text{Cu(pro)}_2\cdot2\text{H}_2\text{O} > \text{Cu(pip)}_2\cdot2\text{H}_2\text{O} > \text{Cu(pic)}_2$$

This order agrees with the greater value of $\Delta H_{\text{coordination}}$ calculated for Cu(pro)$_2$·2H$_2$O compared to Cu(pip)$_2$·2H$_2$O (see Section 6.2). However, this order suggests that the waters of coordination are more strongly bound to copper than the carbonyl oxygen which occupies the axial position in Cu(pic)$_2$ (144). This is supported by comparison of axial bond lengths (Table 4.1). Apparently, the flexible
Figure 6.15. Powder reflectance data for (A) Cu(pro)$_2$·2H$_2$O, (B) Cu(pic)$_2$, and (C) Cu(pip)$_2$·2H$_2$O, plotted as log (100/R) versus wavelength.
Figure 6.16. Powder reflectance data for (A) Cu-(dcanth)$_2$$\cdot$2H$_2$O, (B) Cu(nanth)$_2$, (C) Cu(canth)$_2$, and (D) Cu(anth)$_2$, plotted as log (100/R) versus wavelength.
A) Cu(dcanth)$_2$ \cdot 2$H$_2$O
B) Cu(nanth)$_2$
C) Cu(canth)$_2$
D) Cu(anth)$_2$
Figure 6.17. Powder reflectance data for (A) Cu-(panth)$_2$ B, (B) Cu(fluf)$_2$ B, (C) Cu(fluf)$_2$·MeOH, (D) Cu-(panth)$_2$·MeOH, (E) Cu(fluf)$_2$ A, and (F) Cu(panth)$_2$ A, plotted as log (100/R) versus wavelength.
conformation of the chelate ring and congestion of the coordination sphere in Cu(pro)$_2$$ \cdot $2H$_2$O and Cu(pip)$_2$$ \cdot $2H$_2$O prevents approach by an adjacent complex molecule and consequent axial coordination of the carbonyl oxygen. The planar chelate ring of Cu(pic)$_2$ reduces the congestion.

Similarly, the order of increasing tetragonality is

$$ \text{Cu(dcanth)}_2$$ $ \cdot $2H$_2$O $ > $ Cu(Cl-anth)$_2$ $ > $ Cu(anth)$_2$$ \cdot $2H$_2$O

where the values of $\lambda_{\text{max}}$ are 700, 675, and 650 nm, respectively. A broad, intense absorption occurs near 575 nm for Cu(nanth)$_2$. This band presumably arises from ligand transitions as the ligand is intensely colored. A shoulder at 700 nm suggests an electronic environment in Cu(nanth)$_2$ similar to that of Cu(dcanth)$_2$$ \cdot $2H$_2$O. As a group, these complexes appear to have greater tetragonal character than the previous group of complexes, suggesting that the ligands are tridentate with coordination by carbonyl oxygen, as observed for Cu(anth)$_2$ (109). The order of decreasing tetragonality parallels the order of increasing base strength of the amine group of the ligand (Table 4.2). Support for this observation lies in the Cu-N and Cu-O bond lengths. In Cu(pro)$_2$$ \cdot $2H$_2$O the Cu-N bond is shorter than the Cu-O bond (see Table 4.1), but in Cu(anth)$_2$ and Cu(pip)$_2$, the Cu-N bond is longer than the Cu-O bond. Therefore, axial coordination by carbonyl oxygen, but not water, is inversely related to Cu-N bond strength.
In the third group of complexes only Cu(panth)$_2$·MeOH and Cu(fluf)$_2$·MeOH which are green, display a distinct feature near 650 nm. The complexes designated A are tan while those designated B are darker brown. The spectra of these complexes are flat and featureless, but the spectra of the A complexes are of weaker intensity than the spectra of the B complexes. The band near 650 nm is attributed to an intradimer transition since this feature is absent in the spectra of the A and B complexes.

Visible spectra were collected for the various complexes in solution. Qualitative solubility is summarized in Table 6.5. Like Cu(anth)$_2$, Cu(canth)$_2$ is insoluble in all the solvents tested, while Cu(pro)$_2$·2H$_2$O, Cu(pip)$_2$·2H$_2$O and Cu(pic)$_2$ are soluble only in the more polar solvents. The Cu(panth)$_2$ and Cu(fluf)$_2$ complexes are soluble in a wide range of solvents including polar and nonpolar solvents. The Cu(dcanth)$_2$·2H$_2$O and Cu(nanth)$_2$ complexes are soluble in only dimethylsulfoxide, N,N' -dimethylformamide, and dioxane. According to Jolly (170), the order of decreasing coordinating ability of these solvents is

MeOH > DMF > dioxane > benzene

The degree of tetragonality of a complex should increase as the coordinating ability of the solvent increases. Solution spectral data are gathered in Table 6.6 while representative spectra in each solvent are shown in Figures 6.18-6.21.
### TABLE 6.5

**SOLUBILITY OF COPPER COMPLEXES\(^{a,b,c}\)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>(H_2O)</th>
<th>DMSO(^d)</th>
<th>DME(^d)</th>
<th>MeOH(^d)</th>
<th>EtOH(^d)</th>
<th>Acetone</th>
<th>Benzene</th>
<th>Dioxane</th>
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</thead>
<tbody>
<tr>
<td>Cu(pro)(_2\cdot2H_2O)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Cu(pip)(_2\cdot2H_2O)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Cu(pip)(_2)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Cu(canth)(_2)</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>Cu(dcanth)(_2\cdot2H_2O)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td>Cu(nanth)(_2)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td>Cu(panth)(_2)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>S</td>
</tr>
<tr>
<td>Cu(panth)(_2)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Cu(panth)(_2\cdotMeOH)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Cu(fluf)(_2)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Cu(fluf)(_2)</td>
<td>I</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

\(^{a}\)At room temperature.
TABLE 6.5 - Continued

\( S \) = soluble, \( I \) = insoluble.

\(^c\) Identical behavior observed for analogous zinc and nickel complexes.

\(^d\) Solvent abbreviations: DMSO = dimethylsulfoxide, DMF = N,N'-dimethylformamide, MeOH = methanol, EtOH = ethanol.
### TABLE 6.6

**VISIBLE SPECTRAL DATA FOR SOLUTIONS**

<table>
<thead>
<tr>
<th>Complex</th>
<th>DMF $\lambda_{\text{max}}$</th>
<th>MeOH $\lambda_{\text{max}}$</th>
<th>Dioxane $\lambda_{\text{max}}$</th>
<th>Benzene $\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu(pro)}_2 \cdot 2\text{H}_2\text{O}$</td>
<td>596 47</td>
<td>600 73</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Cu(pip)}_2 \cdot 2\text{H}_2\text{O}$</td>
<td>592 79</td>
<td>596 95</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Cu(pic)}_2$</td>
<td>627 35</td>
<td>630 68</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Cu(4canth)}_2 \cdot 2\text{H}_2\text{O}$</td>
<td>750 86</td>
<td>--</td>
<td>663 81</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Cu(nanth)}_2$</td>
<td>675 77</td>
<td>--</td>
<td>675 15</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Cu(panth)}_2 \ A$</td>
<td>738 112</td>
<td>731 66</td>
<td>668 252</td>
<td>682 49</td>
</tr>
<tr>
<td>$\text{Cu(panth)}_2 \ B$</td>
<td>729 135</td>
<td>732 70</td>
<td>669 256</td>
<td>688 73</td>
</tr>
<tr>
<td>$\text{Cu(panth)}_2 \cdot \text{MeOH}$</td>
<td>738 138</td>
<td>736 68</td>
<td>669 247</td>
<td>688 63</td>
</tr>
<tr>
<td>$\text{Cu(fluf)}_2 \ A$</td>
<td>759 74</td>
<td>725 78</td>
<td>672 166</td>
<td>711 44</td>
</tr>
<tr>
<td>$\text{Cu(fluf)}_2 \ B$</td>
<td>753 81</td>
<td>731 73</td>
<td>671 213</td>
<td>718 56</td>
</tr>
<tr>
<td>$\text{Cu(fluf)}_2 \cdot \text{MeOH}$</td>
<td>753 92</td>
<td>738 60</td>
<td>675 242</td>
<td>709 62</td>
</tr>
</tbody>
</table>

---

a Solvent abbreviations in Table 6.5.
b $\lambda_{\text{max}}$ in nm.
c $\varepsilon$ in cm$^{-1}$ M$^{-1}$ (M expressed in moles copper atom/liter).
Figure 6.18. Visible spectra of (A) Cu(pip)$_2$·2H$_2$O, $c = 4.7 \times 10^{-3}$ M; (B) Cu(nanth)$_2$, $c = 1.9 \times 10^{-3}$ M; and (C) Cu(panth)$_2$ B, $c = 3.4 \times 10^{-3}$ M, in N,N'-dimethylformamide solution.
Figure 6.19. Visible spectra of (A) Cu(pro)$_2$·2H$_2$O, $c = 5.4 \times 10^{-3}$ M; and (B) Cu(fluf)$_2$ B, $c = 2.8 \times 10^{-3}$ M; in methanol solution.
Figure 6.20. Visible spectra of (A) Cu(nanth)$_2$, $c = 3.9 \times 10^{-3}$ M; (B) Cu(dcanth)$_2$$ \cdot 2$H$_2$O, $c = 2.6 \times 10^{-3}$ M; (C) Cu(panth)$_2$$ \cdot$MeOH, $c = 2.3 \times 10^{-3}$ M; and (D) Cu(fluf)$_2$$ \cdot 3$B$_2$, $c = 3.5 \times 10^{-3}$ M; in dioxane solution.
Figure 6.21. Visible spectra of (A) Cu(fluf)$_2$·MeOH, 
$c = 1.8 \times 10^{-3}$ M; and (B) Cu(panth)$_2$·MeOH, $c = 2.6 \times 10^{-3}$ M; 
in benzene solution.
In both N,N'-dimethylformamide and methanol, the prolinato, pipecolinato, and picolinato complexes absorb near 600 nm. The order of decreasing tetragonality is

\[ \text{MeOH} > \text{DMF} \]

and

\[ \text{pic} > \text{pro} > \text{pip} \]

The spectra of Cu(dcanth)$_2\cdot2\text{H}_2\text{O}$, and the Cu(fluf)$_2$ and Cu(panth)$_2$ complexes in N,N'-dimethylformamide are similar with absorption near 750 nm, while Cu(nanth)$_2$ absorbs near 675 nm. The spectra of Cu(dcanth)$_2\cdot2\text{H}_2\text{O}$, Cu(nanth)$_2$, and the Cu(panth)$_2$ and Cu(fluf)$_2$ complexes in dioxane are similar with absorption occurring near 670 nm, but much larger extinction coefficients are observed for the Cu(panth)$_2$ and Cu(fluf)$_2$ complexes. In benzene, the Cu(panth)$_2$ and Cu(fluf)$_2$ complexes absorb at slightly longer wavelengths with much smaller extinction coefficients. The benzene spectra are dominated by an intense absorption below 400 nm which is presumably a ligand band, or ligand-metal charge transfer band. In addition a shoulder on the charge transfer band appears near 400 nm for Cu(panth)$_2\cdot\text{MeOH}$ in dioxane (Figure 6.20C) and Cu(fluf)$_2\cdot\text{MeOH}$ in benzene (Figure 6.21A). Bimetallic carboxylate-bridged complexes characteristically display bands near 700 nm and 400 nm (35). The complexes Cu(panth)$_2\ A$, Cu(panth)$_2\ B$, and Cu(panth)$_2\cdot\text{MeOH}$ exhibit
identical visible spectra in solution, as do the Cu(fluf)$_2$ A, Cu(fluf)$_2$ B, and Cu(fluf)$_2$·MeOH complexes. If dimerization occurs in solution, and if the dimer is hydrogen bond-bridged rather than ligand-bridged, the bands near 700 nm and 400 nm are characteristic of the intermetallic interaction in copper dimers, rather than of the carboxylate-bridged structure.

The brown color of the benzene solutions in comparison to the tan color of Cu(panth)$_2$ A and Cu(fluf)$_2$ A, and brown color of Cu(panth)$_2$ B and Cu(fluf)$_2$ B, suggests that the electronic environment of these complexes in the solid state is similar to that in benzene solution.

6.6. Powder Susceptibility and EPR Spectra

The magnetic susceptibilities of the polycrystalline complexes are summarized in Table 6.7. Among the copper complexes, the magnetic moments are in the range 1.8-2.0 B.M., with the exceptions of Cu(panth)$_2$·MeOH and Cu(fluf)$_2$·MeOH which have magnetic moments of 1.4 and 1.3 B.M., respectively. The observed moments of the majority of the copper complexes are in agreement with previously observed moments of 1.84 B.M. (102) and 2.0 B.M. (100) for Cu(anth)$_2$.

Spin-spin coupling characteristic of dinuclear structures is indicated for Cu(panth)$_2$·MeOH and Cu(fluf)$_2$·MeOH and supports the formulation of these complexes as dimers. Copper(II) acetate has a room temperature magnetic moment of 1.39 B.M. (47). Grigor'eva et al. first observed room
<table>
<thead>
<tr>
<th>Complex</th>
<th>T(°K)</th>
<th>$\chi(10^6)$</th>
<th>$\chi_{\text{dia}}(10^6)$</th>
<th>$\chi_M'(10^3)$</th>
<th>$\mu_{\text{eff}}$(B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(pro)$_2$·2H$_2$O</td>
<td>294</td>
<td>3.72</td>
<td>-142.7</td>
<td>1.36</td>
<td>1.8</td>
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<tr>
<td>Cu(pip)$_2$·2H$_2$O</td>
<td>298</td>
<td>3.71</td>
<td>-165.9</td>
<td>1.49</td>
<td>1.8</td>
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<tr>
<td>Cu(pic)$_2$</td>
<td>298</td>
<td>4.52</td>
<td>-56.9</td>
<td>1.45</td>
<td>1.8</td>
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<tr>
<td>Cu(anth)$_2$</td>
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<td>-71.4</td>
<td>1.54</td>
<td>1.9</td>
</tr>
<tr>
<td>Cu(canth)$_2$</td>
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<td>1.9</td>
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<tr>
<td>Cu(dcanth)$_2$·2H$_2$O</td>
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<td>-166.9</td>
<td>1.51</td>
<td>1.9</td>
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<td>1.83</td>
<td>2.0</td>
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<td>296</td>
<td>2.85</td>
<td>-106.2</td>
<td>1.50</td>
<td>1.8</td>
</tr>
<tr>
<td>Cu(panth)$_2$ B</td>
<td>293</td>
<td>3.34</td>
<td>-106.2</td>
<td>1.74</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu(panth)$_2$·MeOH</td>
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<td>1.44</td>
<td>-128.6</td>
<td>0.88</td>
<td>1.4</td>
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<td>Cu(fluf)$_2$ A</td>
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<td>-150.2</td>
<td>1.65</td>
<td>1.9</td>
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<tr>
<td>Cu(fluf)$_2$ B</td>
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<td>-150.2</td>
<td>1.56</td>
<td>1.9</td>
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<tr>
<td>Cu(fluf)$_2$·MeOH</td>
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<td>3.57$^a$</td>
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</tr>
<tr>
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<td>1.53</td>
<td>-150.2</td>
<td>0.59$^a$</td>
<td>1.2</td>
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</table>

$^a$Corrected for presence of 5 mol% copper(II) and TIP of Ni(II) ($N_a = 500 \times 10^{-6}$, ref. 170).
temperature magnetic moments of 1.35 and 1.40 B.M. for copper complexes of N-2,3-dimethyl-phenyl-anthranilic acid and flufenamic acid isolated from aqueous-dimethylformamide solution, respectively (122). Exchange energies obtained from the temperature dependence of the magnetic susceptibilities were $2J = -260 \text{ cm}^{-1}$ and $2J = -240 \text{ cm}^{-1}$, respectively (122).

Among the nickel complexes, Ni(anth)$_2$ and Ni(panth)$_2$ have magnetic moments of 2.9 B.M. A room temperature magnetic moment of 3.2-3.4 B.M. was previously reported for Ni(anth)$_2$ (100, 101). In contrast, the magnetic moment of Ni(fluf)$_2$ is only 1.2 B.M. The observed magnetic moments of Ni(anth)$_2$ and Ni(panth)$_2$ fall within the range of values typically observed for nickel complexes with octahedral geometry (2.9-3.4 B.M.). Therefore these complexes are probably similar in structure to Cu(anth)$_2$ (109). The magnetic moment of Ni(fluf)$_2$ is much lower than typically observed values. The existence of a dinuclear complex with antiferromagnetic spin-spin coupling is indicated. The magnitude of the magnetic moment suggests that the Neél temperature for antiferromagnetic exchange is above room temperature, and therefore that the $S = 2$ excited state is high in energy. Recall that a predecomposition transition was observed for Ni(fluf)$_2$, but not for Ni(panth)$_2$ (Section 6.2.).

The room temperature EPR spectra of the magnetically undiluted polycrystalline complexes are shown in Figures
6.22-6.24. Corresponding EPR data are summarized in Table 6.8. Typical polycrystalline EPR line-shapes were classified by Hathaway and Billing (30) as six characteristic types:

A. Axial, \( g_1 < g_2, g_1 > 2.04 \)
B. Axial, \( g_1 < g_2, g_1 < 2.03 \)
C. Rhombic, \( g_1 < g_2 < g_3, g_1 > 2.04 \)
D. Rhombic, \( g_1 < g_2 < g_3, g_1 < 2.03 \)
E. Isotropic (\( g_1 \))
F. Exchanged coupled (\( g_1 < g_2 \))

Accordingly, Cu(pip)\(_2\)\(\cdot\)2H\(_2\)O, Cu(panth)\(_2\) \(A\) and \(B\), and Cu(fluf)\(_2\) \(A\) and \(B\) have isotropic spectra (Type E), while Cu(pro)\(_2\)\(\cdot\)2H\(_2\)O has an exchange-coupled spectrum (Type F). These spectra are uninformative except to reveal the presence of dipole and/or exchange coupling between adjacent copper atoms in the crystal lattice. In Cu(pro)\(_2\)\(\cdot\)2H\(_2\)O, the shortest copper-copper separation in the crystal lattice is 5.61 Å (129). Based on the simple magnetic dipole-dipole interaction which has the same form as the electric dipole-dipole interaction (6.2.5), the magnitude of dipole coupling between adjacent copper atoms in Cu(pro)\(_2\)\(\cdot\)2H\(_2\)O is in the range 104-231 \(\times\) \(10^{-4}\) cm\(^{-1}\) which is similar in energy to copper nuclear hyperfine interactions.

Among the other complexes, Cu(dcanth)\(_2\)\(\cdot\)2H\(_2\)O is unique for having a spectrum characteristic of magnetic environments with rhombic symmetry. With the other complexes, the lowest g-value, \( g_1 \), is greater than 2.04, indicating axial
Figure 6.22. EPR spectra of polycrystalline (A) Cu(pro)$_2$·2H$_2$O, (B) Cu(pip)$_2$·2H$_2$O, and (C) Cu(pic)$_2$, at room temperature; microwave power: 50 mW; scan time: 8 min; time constant: 0.30 sec; modulation amplitudes: $0.82 \times 10^1$, $1.0 \times 10^1$, $0.82 \times 10^1$ G, respectively; receiver gain: $2 \times 10^2$, $1.25 \times 10^2$, $6.2 \times 10^1$, respectively.
Figure 6.23. EPR spectra of polycrystalline (A) Cu(anth)$_2$, (B) Cu(canth)$_2$, (C) Cu(dcanth)$_2$, and (D) Cu(nanth)$_2$, at room temperature; microwave power: 50 mW; modulation amplitude: $0.82 \times 10^1$ G; scan time 8 min; time constant: 0.30 sec; receiver gain: $3.2 \times 10^2$, $6.2 \times 10^0$, $5.0 \times 10^1$, $6.2 \times 10^2$, respectively.
Figure 6.24. EPR spectra of polycrystalline
(A) Cu(panth)$_2$ A, (B) Cu(panth)$_2$ B, (C) Cu(panth)$_2$·MeOH,
(D) Cu(fluf)$_2$ A, (E) Cu(fluf)$_2$ B, and (F) Cu(fluf)$_2$·MeOH,
at room temperature; microwave power: 20 mW; modulation
amplitude: $1.0 \times 10^1$ G; scan time: 8 min; time constant:
1.0 sec; receiver gain: $3.2 \times 10^3$ for spectra (A)-(C) and
(F), and $6.2 \times 10^3$ for spectra (D) and (E).
A) Cu(panth)$_2$ A

B) Cu(panth)$_2$ B

C) Cu(panth)$_2$ MeOH

D) Cu(fkif)$_2$ A

E) Cu(fkif)$_2$ B

F) Cu(fkif)$_2$ MeOH

G) DPPH

MAGNETIC FIELD (GAUSS)

ROM TEMPERATURE
TABLE 6.8

POWDER g-VALUES$^a$

<table>
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<tr>
<th>Complex</th>
<th>Type of Spectrum</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>$G^c$</th>
<th>$R^d$</th>
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<td>2.17</td>
<td>--</td>
<td>2.83</td>
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<td>--</td>
<td>1.00</td>
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<tr>
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<td>--</td>
<td>2.83</td>
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<td>2.25</td>
<td>--</td>
<td>3.57</td>
<td>--</td>
</tr>
<tr>
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<tr>
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$^a$Estimated uncertainty, ±0.005.

$^b$See ref. 30 and ref. 32.

$^c G = \frac{g_\parallel - 2.0023}{g_\perp - 2.0023}$ where $g_\parallel = g_2$ and $g_\perp = g_1$.

$^d R = \frac{g_2 - g_1}{g_3 - g_2}$. 
symmetry corresponding to tetragonal-octahedral, square-coplanar, or square-based pyramidal coordination geometry (30). In axial symmetry the relationship between g-values is predicted by the expression (30, 32)

\[ G = \frac{g_{||} - 2}{g_{\perp} - 2} \approx 4.0 \]  

(6.6.1)

When G is 4.0-4.5, dipole and exchange coupling interactions are negligible. Further, when G is 3.5-5.0, coupling interactions may be small and the observed g-values meaningful. Interactions in the undiluted lattice which give rise to line broadening effects shift the observed inflections in polycrystalline EPR spectra, with the result that the "crystall" g-values are not necessarily equal to the "molecular" g-values (170). For Cu(pic)\textsubscript{2} and Cu(nanth)\textsubscript{2}, the G-values are outside the acceptable range. Therefore the powder (crystal) g-values will be different from g-values observed in dilute solution where line broadening effects are diminished (see Section 6.7 and 6.8). The value of G is acceptable for Cu(anth)\textsubscript{2} and Cu(canth)\textsubscript{2} and predicts close agreement of the powder g-values with molecular g-values (see Section 6.8). For a rhombic spectrum, a value of \( R > 1 \) is indicative of a \( dz^2 \) ground state and tetragonal-octahedral coordination geometry. Therefore, axial coordination is strong in Cu(dcanth)\textsubscript{2} \cdot 2H\textsubscript{2}O. Since \( \Delta H_{\text{desolvation}} \) is smaller for Cu(dcanth)\textsubscript{2} \cdot 2H\textsubscript{2}O than Cu(pro)\textsubscript{2} \cdot 2H\textsubscript{2}O and Cu(pip)\textsubscript{2} \cdot 2H\textsubscript{2}O (see Section 6.2), axial coordination in this complex
probably involves carbonyl oxygen rather than water of hydration.

The room temperature, polycrystalline EPR spectra of Cu(panth)$_2$ A, Cu(panth)$_2$ B, Cu(panth)$_2$·MeOH, Cu(fluf)$_2$ A, Cu(fluf)$_2$ B, and Cu(fluf)$_2$·MeOH are shown in Figure 6.24. As previously mentioned the spectra of the A and B complexes are isotropic with g-values near 2.1. Although the room temperature magnetic moments of these complexes are in the range 1.8-2.0 B.M. and therefore do not reveal the existence of spin-spin coupling, some dipolar and possibly exchange coupling evidently does occur which gives rise to the broadened spectra. No zero field splitting occurs, however, indicating relatively weak spin coupling. Therefore, the A and B complexes are probably copper monomers which interact only weakly with copper atoms in adjacent complex molecules. The weak, broad signal in the region 600-2800 G is attributed to a broad envelope of $\Delta M_s = \pm 2$ (forbidden) transitions which arise from weak dipolar coupling (58).

In contrast, the methanol solvates display distinct zero field splitting, and are therefore copper dimers. The reversibility of monomer and dimer formation (Section 6.1), the thermal instability of the methanol solvate (Section 6.2), and the observation of shifts in the amine stretching frequency in the infrared spectra of these complexes (Section 6.4) demonstrate that the dimeric complexes are not analogous to the well-studied carboxylate-bridged copper
dimers (35, 38, 47). Coordination of nitrogen to copper occurs in the N-phenyl-anthranilate and flufenamate complexes, and the bonds holding together the dimeric structure are easily broken and reformed. This supports the hypothesis (119) that the two 2:1 ligand-metal complex molecules are held together in a dimeric structure by hydrogen bonds. Confirmation of this structure awaits X-ray studies. It will be shown below that the observed zero field splitting is consistent with a small copper-copper distance similar to that observed for copper(II) acetate.

In appendix C, resonance field positions are calculated for hypothetical values of D and E, using equations 3.4.2-3.4.7 (94, 171). Although coordinate axes are usually chosen so that $D > E$, the relative magnitudes of D and E are unimportant. For the present discussion, field positions were calculated for E set at 0.00, 0.05 and 0.15 cm$^{-1}$ for values of D ranging from 0 to 0.30 cm$^{-1}$.

There are several important features revealed by this calculation. First, the resonance fields corresponding to parallel ($H_{z_1}$, $H_{z_2}$) and perpendicular ($H_{x_1}$, $H_{x_2}$, $H_{y_1}$, $H_{y_2}$) orientations crossover at small values of D, regardless of the magnitude of E. Therefore, the "outermost pair of lines" does not necessarily correspond to $H_{z_1}$ and $H_{z_2}$, as at larger values of D. Second, $H_{x_1}$, $H_{y_1}$, and $H_{z_1}$ converge near zero field as D approaches the frequency of the spectrometer (in this case, ~0.30 cm$^{-1}$ at X-band). Third, the effect of the rhombic component of zero field splitting, E, is
small at large values of D. Splitting of \( H_{y_1} \) and \( H_{x_1} \) at low field, and \( H_{y_2} \) and \( H_{x_2} \) at high field due to \( E \) may not be resolved if the signal is broad. However, at small values of D, the splitting due to \( E \) becomes more important. Four to six lines will be observed over a fairly narrow range of field positions. This result will be of importance in later discussion.

The EPR spectra of the polycrystalline methanol solvates, \( \text{Cu(panth)}_2 \cdot \text{MeOH} \) and \( \text{Cu(fluf)}_2 \cdot \text{MeOH} \), are assigned as follows:

A. The signal near zero field to \( H_{\perp 1}, H_{\parallel 1} \)

B. The signal in the 600-2800 G region to \( \Delta m_s = \pm 2 \) transitions arising from weak dipolar coupling between residual monomers or between dimer clusters

C. The weak signal near 3000 G to \( \Delta m_s = \pm 1 \) transitions due to residual monomer complex

D. The signal near 4400 G to \( H_{\perp 2} \)

The spectra are too broad to resolve a rhombic component in the zero field splitting.

The spectrum of \( \text{Cu(fluf)}_2 \cdot \text{B} \) retains some of the features of \( \text{Cu(fluf)}_2 \cdot \text{MeOH} \), indicating incomplete thermal decomposition of the dimer in preparation of the monomer (see Section 6.1). This would account for the similarity of the reflectance spectra of \( \text{Cu(fluf)}_2 \cdot \text{B} \) and \( \text{Cu(fluf)}_2 \cdot \text{MeOH} \) (Figure 6.17). In Section 6.2, it was assumed that desolvation and monomerization occur at the same temperature in the analysis of \( \Delta H_{\text{DSC}} \) of \( \text{Cu(panth)}_2 \cdot \text{MeOH} \). If the transition corresponding
to $\Delta H_{\text{M-M}}$ (metal bond rupture) occurs at a higher temperature than disruption of ligand-ligand ($\Delta H_{\text{H-bond in dimer}}$, $\Delta H_{\pi-\pi}$) and solvent-complex ($\Delta H_{\text{coordination}}$) interactions in Cu(fluf)$_2$·MeOH, $\Delta H_{\text{DSC}}$ can be satisfactorily accounted for:

$$\Delta H_{\text{DSC}} = -\Delta H_{\pi-\pi} - \Delta H_{\text{H-bond in dimer}} - \Delta H_{\text{coordination}}$$

$$\Delta H_{\text{DSC}} = -4(-1) - 4(-0.5) - 2(-2.7)$$

$$10.2 \approx 11.4 \text{ kcal/mole-dimer}$$

The conclusion here is that a strong metal-metal bond exists independent of other interactions within the dimer. However, no other predecomposition transition was observed in the DSC curve; therefore, further information regarding the existence of a metal-metal bond is unavailable from calorimetry experiments.

The zero field splitting, $D$, is ~0.30 cm$^{-1}$ for both Cu(fluf)$_2$·MeOH and Cu(panth)$_2$·MeOH. Using 3.6.12 and 3.6.13, and an approximate value of $|{-2J}|$ equal to 250 cm$^{-1}$ (122), the value of $D_{\text{exchange}}$ is calculated to be ~0.625 cm$^{-1}$ which leads to a copper-copper distance in these complexes of about 2.4 Å. This value is smaller than the copper-copper distance (2.64 Å) in copper(II) acetate (49, 50), but this may be attributed to a larger value of the exchange energy for dimeric complexes obtained from aqueous-dimethylformamide solution (122) as opposed to those obtained from methanol.
6.7. EPR Spectra of Dilute Solutions at Room Temperature and Liquid Nitrogen Temperature

EPR spectra at room temperature and at liquid nitrogen temperature can provide useful information regarding the electronic environment and molecular structure of the complexes in solution. Solution spectra are shown in Figures 6.25-6.38, and parameters are compiled in Tables 6.9 and 6.10.

In methanol (Figure 6.25) and dimethylformamide (Figure 6.26) solution at room temperature, the prolinato, pipocolinato and picolinato complexes display the typical isotropic spectrum of copper with four hyperfine lines arising from the interaction of the unpaired electron with the copper nucleus \( I^{Cu} = 3/2, 2I + 1 = 4 \). Values for the isotropic parameters, \( g_Q \) and \( A_Q \) (Table 6.9), were refined by computer simulation. The order of decreasing \( g_Q \)-values is

\[
\text{MeOH} > \text{DMF} \\
\text{pic} > \text{pro} > \text{pip}
\]

while \( A_Q \) values decrease in the reverse order. The differences between the \( g_Q \) and \( A_Q \) values with respect to the ligands are less pronounced than the solvent effect. This demonstrates that EPR parameters of copper complexes in solution are more sensitive to axial coordination than to the differences in the coordination environment induced by similar
Figure 6.25. EPR spectra of methanol solutions at room temperature: (A) Cu(pro)$_2$·2H$_2$O, $c = 3.0 \times 10^{-3}$ M; (B) Cu(pip)$_2$·2H$_2$O, $c = 3.0 \times 10^{-3}$ M; and (C) Cu(pic)$_2$, $c = 3.2 \times 10^{-3}$ M; microwave power: 100 mW; modulation amplitude: $0.82 \times 10^1$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: $5.0 \times 10^2$, $6.2 \times 10^2$, $8.0 \times 10^2$, respectively.
ROOM TEMPERATURE
MeOH SOLUTION

A) Cu(pro)$_2$ $\cdot$ 2H$_2$O

B) Cu(pip)$_2$ $\cdot$ 2H$_2$O

C) Cu(pic)$_2$

MAGNETIC FIELD (GAUSS)
Figure 6.26. EPR spectra of N,N'-dimethylformamide solutions at room temperature: (A) Cu(pro)$_2$·2H$_2$O, $c = 4.5 \times 10^{-3}$ M; (B) Cu(pip)$_2$·2H$_2$O, $c = 4.7 \times 10^{-3}$ M; (C) Cu(pic)$_2$, $c = 3.2 \times 10^{-3}$ M; (D) Cu(dcanth)$_2$·2H$_2$O, $c = 3.5 \times 10^{-3}$ M; and (E) Cu(nanth)$_2$, $c = 1.9 \times 10^{-3}$ M; microwave power: 50 mW for spectra (A)-(C), 100 mW for spectra (D) and (E); modulation amplitudes: 0.50 $\times 10^1$ G for spectra (A) and (B), 1.0 $\times 10^1$ G for spectra (C)-(E); scan time: 8 min; time constant: 1.0 sec; receiver gain: 2.0 $\times 10^3$, 2.0 $\times 10^3$, 3.2 $\times 10^3$, 2.5 $\times 10^3$, 2.5 $\times 10^3$, respectively.
Figure 6.27. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pro)$_2$·2H$_2$O in methanol, c = 3.0 x 10$^{-3}$ M; microwave power: 5 mW; modulation amplitude: 0.82 x 10$^1$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: 6.2 x 10$^1$. (B) Corresponding simulated spectrum.
Cu(pro)$_2$$\cdot$2H$_2$O, MeOH SOLUTION LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.28. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pip)$_2$$\cdot$2H$_2$O in methanol, c = $3.0 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $0.50 \times 10^1$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: $3.2 \times 10^2$. (B) Corresponding simulated spectrum.
Cu(pip)$_2$ $\cdot$ 2 H$_2$O, MeOH SOLUTION
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.29. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pic)$_2$ in methanol, c = 3.2 x $10^{-3}$ M; microwave power: 5 mW; modulation amplitude: 0.50 x $10^1$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: 3.2 x $10^2$. (B) Corresponding simulated spectrum.
Cu(pic)$_2$.MeOH SOLUTION
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated
Figure 6.30. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pro)$_2$·2H$_2$O in N,N'-dimethylformamide, c = 4.5 $\times$ 10$^{-3}$ M; microwave power: 5 mW; modulation amplitude: 0.5 $\times$ 10$^0$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: 1.25 $\times$ 10$^3$. (B) Corresponding simulated spectrum.
Cu\((pro)_{2}2H_{2}O, DMF SOLUTION\)
LIQUID N\(_{2}\) TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.31. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pip)$_2$.2H$_2$O in N,N'-dimethylformamide, $c = 4.7 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $0.50 \times 10^0$ G; scan time: 16 min; time constant: 0.30 sec; receiver gain: $1.25 \times 10^3$. (B) Corresponding simulated spectrum.
Cu(pip)$_2$H$_2$O, DMF Solution, Liquid N$_2$ Temperature

A) Experimental

B) Simulated

Magnetic Field (Gauss)
Figure 6.32. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(pic)$_2$ in N,N'-dimethylformamide, $c = 3.2 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $0.50 \times 10^0$ G; scan time: 16 min; time constant: 1.0 sec; receiver gain: $2.5 \times 10^3$. (B) Corresponding simulated spectrum.
Cu(pic)$_2$, DMF SOLUTION
LIQUID N$_2$ TEMPERATURE

A) experimental
B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.33. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(dcanth)$_2$·2H$_2$O in N,N'-dimethylformamide, $c = 3.5 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $1.0 \times 10^0$ G; scan time: 8 min; time constant: 1.0 sec; receiver gain: $1.5 \times 10^3$. (B) Corresponding simulated spectrum.
Cu(dcanth)$_2$.$2$H$_2$O, DMF SOLUTION
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.34. (A) Experimental EPR spectrum at liquid nitrogen temperature of Cu(nanth)$_2$ in N,N'-dimethylformamide, $c = 1.9 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $1.0 \times 10^0$ G; scan time: 8 min; time constant: 1.0 sec; receiver gain: $1.5 \times 10^3$. (B) Corresponding simulated spectrum.
Cu(nanth)$_2$, DMF SOLUTION
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated
Figure 6.35. Room temperature EPR spectra of Cu(panth)₂
B in (A) N,N'-dimethylformamide, c = 4.7 x 10⁻³ M; (B)
methanol, c = 5.1 x 10⁻³ M; (C) dioxane, c = 5.3 x 10⁻³ M;
and (D) benzene, c = 5.5 x 10⁻³ M; microwave power: 100 mW;
modulation amplitude: 1.0 x 10¹ G; scan time: 8 min; time
constant: 1.0 sec; receiver gain: 2.5 x 10³, 3.2 x 10³, 2.5
x 10³, 1.5 x 10³, respectively.
Cu(panth)$_2$

MAGNETIC FIELD (GAUSS)

DMF

METHANOL

DIOXANE

BENZENE

ROOM TEMPERATURE

0 400 800 1200 1600 2000 2400 2800 3200 3600 4000 4400 4800 5200 5600 6000
Figure 6.36. Room temperature EPR spectra of Cu(\textit{fluf})_2 B in (A) N,N'-dimethylformamide, \(c = 5.1 \times 10^{-3}\) M; (B) methanol, \(c = 5.5 \times 10^{-3}\) M; (C) dioxane, \(c = 6.3 \times 10^{-3}\) M; and (D) benzene, \(c = 4.5 \times 10^{-3}\) M; microwave power: 100 mW; modulation amplitude: \(1.0 \times 10^1\) G; scan time: 8 min; time constant: 1.0 sec; receiver gain: \(2.5 \times 10^3\), \(3.2 \times 10^3\), \(2.5 \times 10^3\), \(1.25 \times 10^3\), respectively.
Cu(fluf)$_2$  

MAGNETIC FIELD (GAUSS)
Figure 6.37. EPR spectra at liquid nitrogen temperature of Cu(panth)$_2$ B in (A) N,N'-dimethylformamide, $c = 4.7 \times 10^{-3}$ M; (B) methanol, $c = 5.1 \times 10^{-3}$ M; (C) dioxane, $c = 5.3 \times 10^{-3}$ M; and (D) benzene, $c = 5.5 \times 10^{-3}$ M; microwave power: 5 mW; modulation amplitude: $1.0 \times 10^0$ G; scan time: 8 min; time constant: 1.0 sec; receiver gain: $2.0 \times 10^3$, $3.2 \times 10^3$, $1.5 \times 10^3$, $1.5 \times 10^3$, respectively.
LIQUID N₂ TEMPERATURE

BENZENE

DIOXANE

DMF

MeOH

Cu(panth)₂

MAGNETIC FIELD (GAUSS)

2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400
Figure 6.38. EPR spectra at liquid nitrogen temperature of Cu(fluf)$_2$ B in (A) N,N'-dimethylformamide, c = 5.1 x 10$^{-3}$ M; (B) methanol, c = 5.5 x 10$^{-3}$ M; and (C) dioxane, c = 6.3 x 10$^{-3}$ M; microwave power: 5 mW; modulation amplitude: 1.0 x 10$^0$ G; scan time: 8 min; time constant: 1.0 sec; receiver gain: 2 x 10$^3$, 1.25 x 10$^3$, 10.0 x 10$^2$, respectively.
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<td>2.1814</td>
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<td>2.0686</td>
<td>2.3729</td>
<td>--</td>
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TABLE 6.9
EPR PARAMETERS FOR DILUTE SOLUTION

**Notes:**
- $q_o$ and $A_o$ are isotropic parameters.
- $g_x$, $g_y$, and $g_z$ are anisotropic parameters.
- $R^g$ is a parameter.
- Subscripts: $h$ for hexafluoroacetone, $i$ for isonicotinate.
- $^j$ indicates anisotropy values.
TABLE 6.9 - Continued

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>System</th>
<th>Isotropic</th>
<th>Anisotropic</th>
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</thead>
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<td>Cu(fluf)_2</td>
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<td>--</td>
<td>2.0524 2.0914 2.3822 0.13</td>
</tr>
<tr>
<td>Cu(fluf)_2</td>
<td>DX</td>
<td>14</td>
<td>--</td>
<td>2.0602 2.1884 2.3649 0.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>System</th>
<th>Isotropic</th>
<th>Anisotropic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(fluf)_2</td>
<td>MeOH</td>
<td>13</td>
<td>--</td>
<td>2.0524 2.0914 2.3822 0.13</td>
</tr>
<tr>
<td>Cu(fluf)_2</td>
<td>DX</td>
<td>14</td>
<td>--</td>
<td>2.0602 2.1884 2.3649 0.73</td>
</tr>
</tbody>
</table>

- a1-5 x 10^{-3} M concentration; parameters from computer simulation (see appendix A); estimated uncertainty in g-values is ±0.0005.
- bFrom room temperature spectra.
- cFrom frozen solution spectra at liquid nitrogen temperature.
- dSolvent abbreviations: DMF = N,N'-dimethylformamide, MeOH = methanol, DX = dioxane.
- eSame as Table 6.10.
- fIn 10^4 cm^{-1}.
- gR = \frac{g_3 - g_2}{g_2 - g_1} (see ref. 30 and 32).
- hSimulations performed using two sites for ^{63}Cu and ^{65}Cu isotopes; reported copper hyperfine coupling constants are for ^{63}Cu; multiply values by \gamma_N(^{65}Cu)/\gamma_N(^{63}Cu) = 1.0713 to obtain coupling constants for ^{65}Cu.
- iSimulations performed using one site with average copper hyperfine coupling constants.
- jApproximate values not refined by simulation.
TABLE 6.10
ADDITIONAL EPR PARAMETERS FOR DILUTE SOLUTION

<table>
<thead>
<tr>
<th>System</th>
<th>Copper Hyperfine</th>
<th>Nitrogen Hyperfine</th>
<th>Bonding Parameters</th>
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<td>$B_x$ $B_y$ $B_z$</td>
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<td>1</td>
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<td>3</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>--    --   --</td>
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<tr>
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</tr>
<tr>
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<td>10.0 15.0 10.0</td>
<td>0.88 0.12 0.94 1.84(?) 0.66</td>
</tr>
<tr>
<td>12</td>
<td>12.0  12.0  145.0</td>
<td>--    --   --</td>
<td>0.82 0.18 0.91 0.65 --</td>
</tr>
<tr>
<td>13</td>
<td>5.0   15.0  144.0</td>
<td>15.0 10.0 10.0</td>
<td>0.83 0.17 0.95 0.89 0.50</td>
</tr>
<tr>
<td>14</td>
<td>5.0   25.0  164.0</td>
<td>10.0 15.0 10.0</td>
<td>0.88 0.12 0.92 1.90(?) 0.59</td>
</tr>
</tbody>
</table>
TABLE 6.10 - Continued

See Table 6.9 for more details.

Systems defined in Table 6.9.

From frozen solution spectra at liquid nitrogen temperature; in $10^4 \text{ cm}^{-1}$; copper hyperfine couplings for systems 1-6 are for $^{63}\text{Cu}$ (see footnote h, Table 6.9).

Calculated using program in appendix D; for systems 1-6, average copper hyperfine coupling constants, weighted by isotope abundance, used in calculation; values of $E$ from visible solution spectra (Table 6.6) and values of $T(n)$ from Table 3.2.
equatorial ligands. As the degree of tetragonality of a copper complex increases, g-values increase and A values decrease (Chapter 4). Thus, the relative tetragonality of these complexes is the same as the order predicted by visible spectroscopy (Section 6.5) and confirms that methanol has greater coordinating ability toward copper than dimethylformamide.

The room temperature EPR spectra of Cu(nanth)\textsubscript{2} and Cu(dcanth)\textsubscript{2} \cdot 2H\textsubscript{2}O in dimethylformamide are broadened, and the copper hyperfine structure is poorly resolved (Figure 6.26). The appearance of these spectra could be due to the presence of two or more species in solution, such as complexes with different ligand-metal ratios. However, the presence of electro-negative substituents on the ligands (i.e., nitro and chloro groups) suggests that the greater ligand size and possibly solvent-ligand association increases the rotational correlation time by increasing the effective radius of the complex. As 1/τ\textsubscript{R} approaches the frequency of the spectrometer, the EPR spectrum is broadened by spin-rotation relaxation (Section 3.1). From 3.1.4, assuming the viscosity of dimethylformamide is similar to that of methanol (τ = 0.55 cp), and 1/τ\textsubscript{R} = 9.5 \times 10^{9} Hz, the effective dynamic radius of these complexes, a, is about 5.7 Å. Using crystallographic data (109), the approximate "radius" of Cu(anth)\textsubscript{2} is about 4.9 Å as shown below.
Therefore, ligand substitution increases the dynamic radius of the complex and retards molecular tumbling to produce line broadening effects. The approximate \( g_o \) and \( A_o \) values (Table 6.9) of \( \text{Cu(nanth)}_2 \) and \( \text{Cu(dcanth)}_2\cdot2\text{H}_2\text{O} \) in dimethylformamide suggest that the magnetic environments in these two complexes differ markedly.

In solution, the \( \text{CuL}_2 \text{A} \), \( \text{CuL}_2 \text{B} \), and \( \text{CuL}_2\cdot\text{MeOH} \) (\( L = \text{panth or fluf} \)) complexes have identical EPR spectra, as well as identical visible spectra (Section 6.5). In methanol and dimethylformamide solution, the complexes \( \text{Cu(panth)}_2 \text{B} \) and \( \text{Cu(fluf)}_2 \text{B} \) have room temperature EPR spectra (Figures 6.35 and 6.36) which are severely broadened. This broadening is probably produced by spin rotation relaxation effects arising from the larger size of the complexes due to the N-phenyl ligand substituent, as observed for the complexes with the nitro and dichloro substituted ligands.

On the other hand, in benzene and dioxane solution zero field splitting from spin-coupled dimer units is apparent, in addition to broad signals at \(-3000 \text{ G}\) and in the region \(500-2000 \text{ G}\), which arise from dipole-dipole
interactions between monomer units. Therefore, both monomers and dimers are present, indicating an equilibrium situation. Dimer interactions are weak in methanol and dimethylformamide solution, judging from the large difference in appearance of the EPR spectra compared to benzene and dioxane. Unlike benzene, the dioxane spectra reveal sharp features near 3100 G. Using appendix C, these features can be assigned to \( \Delta m_s = \pm 1 \) transitions within the spin triplet of the dimer, and correspond to a small D value (0.009–0.012 cm\(^{-1}\)) and large E value (0.1–0.15 cm\(^{-1}\)). A value of E of 0.1 cm\(^{-1}\) predicts a copper-copper distance of 2.67 Å assuming a negligible contribution of exchange coupling to the observed splitting. Resolution of these features in dioxane but not benzene suggests strong coordination by dioxane with a concomitant increase in the rotational correlation time and sharpening of features in the center of the spectrum.

The frozen solution spectra (Figures 6.27–6.32) of Cu(pro)\(_2\)·2H\(_2\)O, Cu(pip)\(_2\)·2H\(_2\)O, and Cu(pic)\(_2\) in methanol and dimethylformamide have parameters corresponding to axial symmetry which are typically observed for copper(II) complexes with α-amino acids (1, 127, 135–138). The feature indicated by a small arrow in the spectrum of Cu(pro)\(_2\)·2H\(_2\)O in methanol at room temperature (Figure 6.25) is attributed to an impurity arising from gradual decomposition of the complex as previously discussed (Section 6.2). A similar feature is not observed in the frozen methanol solution.
spectrum or in the dimethylformamide solution spectra at either temperature but it may simply be obscured by the perpendicular lines (see Figures 6.26 and 6.30).

Nitrogen hyperfine coupling constants are about $10^{-13} \times 10^{-4} \text{ cm}^{-1}$ (±$1-2 \times 10^{-4} \text{ cm}^{-1}$) (Table 6.10), and are consistent with covalent copper-nitrogen bonds. From 3.3.21, the observed nitrogen hyperfine coupling constants predict that the bonding parameters, $\alpha'^2$, range from 0.17-0.22, in agreement with the values of $\alpha'^2$ obtained using $g$ and $A$ values (Tables 6.9 and 6.10, appendix D).

As previously discussed in relation to room temperature spectra, the tetragonality of copper complexes can be predicted by the relative magnitude of $g$ and $A$ values. In frozen solution, the order of decreasing $g_\|$ is

$$\text{pic} > \text{pro} > \text{pip}$$

in both methanol and dimethylformamide, while the order of decreasing $g_\perp$ is

$$\text{pic} > \text{pip} > \text{pro}$$

in methanol, but

$$\text{pic} > \text{pip} = \text{pro}$$

in dimethylformamide. However, the anomaly in the order of $g_\perp$ values may simply reflect the uncertainty in $g_\perp$ (±0.0005).
Although the order of decreasing $g_{||}$ or $g_{\perp}$ with respect to solvent is

\[ \text{MeOH} > \text{DMF} \]

for the prolinato and pipecolinato complexes, as previously observed in the room temperature spectra, the reverse solvent order is observed for the picolinato complex. These trends in $g_{||}$ and $g_{\perp}$ are paralleled by reverse trends in $A_{||}$ and $A_{\perp}$, in agreement with theory (94).

The calculated bonding parameters (Table 6.10) are similar to one another for these complexes. Out-of-(xy)-plane $\pi$-bonding (presumably via the oxygen donor atoms) is enhanced in dimethylformamide relative to methanol for the prolinato and pipecolinato complexes, but lessened for the picolinato complex, according to the variation in the value of $\beta^2$.

Another important distinction between the prolinato or pipecolinato and picolinato complexes, is hydrogen nuclear hyperfine coupling. The simulated spectra of the prolinato and pipecolinato complexes were calculated assuming interaction of unpaired spin with two amine hydrogens, having hyperfine coupling constants of about $1-3 \times 10^{-4}$ cm$^{-1}$, and with additional hydrogens at the carbons alpha to the amine group, having coupling constants of about $1 \times 10^{-4}$ cm$^{-1}$. Hydrogen hyperfine coupling constants of similar magnitude were observed for copper(II)(DL-alaninato)$_2$$^\cdot$$H_2$O.
Although the hydrogen hyperfine interaction is difficult to ascertain by simulation of EPR spectra, in the case of Cu(pic)$_2$ in methanol, resolution of the hyperfine structure in the perpendicular region of the experimental spectrum is unusually good. Excellent agreement between the experimental and simulated spectra was obtained using the following hyperfine coupling constants: $B_{\perp}^{H1} = 4.0$ and $B_{\parallel}^{H1} = 5.5 \times 10^{-4}$ cm$^{-1}$ for two equivalent hydrogens (i.e., hydrogens at position 6 on the heterocyclic rings of the two ligands), and $B_{\perp}^{H2} = 2.2$ and $B_{\parallel}^{H2} = 2.5 \times 10^{-4}$ cm$^{-1}$ for six equivalent hydrogens (i.e., the remaining ring hydrogens on the two ligands at positions 3, 4, and 5). Although the calculated bonding parameters of Cu(pic)$_2$ (Table 6.10) do not differ significantly relative to complexes with saturated ligands, the hydrogen hyperfine interaction indicates extensive delocalization of unpaired spin density into the unsaturated heterocyclic ring of the ligand.

The frozen solution spectra of Cu(dcanth)$_2 \cdot 2$H$_2$O and Cu(nanth)$_2$ in dimethylformamide (Figures 6.33 and 6.34) also have EPR parameters corresponding to axial symmetry (Table 6.10). However, while the spectrum of Cu(nanth)$_2$ resembles those of the prolinato, pipecolinato, and picolinato complexes, the spectrum of Cu(dcanth)$_2 \cdot 2$H$_2$O is markedly different. The parallel region is poorly resolved and suggests the presence of more than one species. The calculated bonding parameters (Table 6.10) demonstrate that equatorial $\sigma$-bond strength ($\alpha^2$) and out-of-(xy)plane $\pi$-bond strength ($\beta^2$)
are comparable, but that in-(xy)plane π-bond strength \( (\beta_1^2) \) is reduced in the dichloroanthranilato complex, relative to the nitroanthranilato, picolinato, prolinato, and picolinato complexes.

The frozen solution spectra of Cu(panth)_2 B and Cu(fluf)_2 B in dimethylformamide, methanol, and dioxane (Figures 6.37 and 6.38) reveal that monomeric species are indeed present in solution despite the broadened room temperature spectra. In dimethylformamide, Cu(panth)_2 B and Cu(fluf)_2 B have spectra corresponding to axial symmetry with parameters dissimilar to those previously discussed, i.e., larger \( g_\perp \) and \( g_\parallel \), and smaller \( A_\perp \) and \( A_\parallel \). Nitrogen hyperfine coupling constants are small or zero indicating weak coordination through the amine nitrogen. In contrast, the spectra of these complexes in methanol and dioxane have parameters (Tables 6.9 and 6.10) corresponding to a magnetic environment of rhombic symmetry which is unusual for copper(II) complexes with amino acids. However, since \( R < 1 \), \( dx^2-y^2 \) rather than \( dz^2 \) ground states are predicted for these complexes.

The Cu(panth)_2 and Cu(fluf)_2 complexes in the three different solvents have reduced in-(xy)plane π-bonding (larger values of \( \beta_1^2 \), Table 6.10), suggesting that the N-phenyl substituent creates steric interference with copper-oxygen interactions. The magnetic anisotropy in the (xy)-plane in methanol and dioxane appears to originate in anisotropy of the metal-ligand interaction. It is more
appropriate in this situation, to recast the calculated bonding parameters in a new form: $a^2 = a_{\parallel}^2$, $a^2_{\beta} = a_{\perp,1}^2$, and $a^2_{\gamma} = a_{\perp,2}^2$. The values of interest are

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$a_{\parallel}^2$</th>
<th>$a^2_{\beta}$</th>
<th>$a_{\perp,1}^2$</th>
<th>$a^2_{\gamma}$</th>
<th>$a_{\perp,2}^2$</th>
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</thead>
<tbody>
<tr>
<td>Cu(panth)$_2$</td>
<td>MeOH</td>
<td>0.82</td>
<td>0.68</td>
<td>0.56</td>
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<tr>
<td>Cu(panth)$_2$</td>
<td>DX</td>
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<td>1.62</td>
<td>0.58</td>
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</tr>
<tr>
<td>Cu(fluf)$_2$</td>
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<tr>
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<td>DX</td>
<td>0.88</td>
<td>1.67</td>
<td>0.52</td>
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</table>

assuming no out-of-(xy)plane $\pi$-bonding ($\beta^2 = 1$, $\gamma^2 = 1$).

These values indicate stronger axial coordination by methanol relative to dioxane, where $a^2_{\parallel}$(MeOH) < $a^2_{\parallel}$(dioxane). Further, the observed xy-anisotropy in EPR parameters can be attributed to strongly covalent nitrogen-metal bonds and weaker coordination through oxygen. The coordinative anisotropy is more pronounced in dioxane than in methanol, and for Cu(fluf)$_2$ than for Cu(panth)$_2$. In dimethylformamide, the relative strength of the Cu-O and Cu-N bonds is apparently reversed judging from the absence of a nitrogen hyperfine interaction in this solvent.

In benzene, a broad isotropic signal is observed near 3130 G for Cu(panth)$_2$ B whereas no signal is detectable for Cu(fluf)$_2$ B. The significance of this observation is that while a monomer $\rightleftarrows$ dimer equilibrium apparently exists in solution, and a significant monomer population persists at liquid nitrogen temperature in the coordinating solvents,
formation of the dimer goes to completion for Cu(fluf)$_2$ and to near completion for Cu(panth)$_2$. In the latter case, the observed signal is indicative of strong dipole coupling and incipient dimerization of the remaining monomeric complexes. The absence of transitions at liquid nitrogen temperature corresponding to $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ spin triplet state of the dimer, demonstrates that the singlet-triplet energy separation, $|-2J|$ is large and that the EPR-silent singlet ground state is populated at this temperature. The minimum value of $|-2J|$ can be predicted by assuming that the temperature of maximum susceptibility ($T_m$) is above the liquid nitrogen temperature (−100°K). From $J/kT_m \approx -4/5$, one predicts that $|J| \geq 55$ cm$^{-1}$ or $|-2J| \geq 110$ cm$^{-1}$. Therefore exchange coupling is strong for dimers in solution, and the copper-copper separation of 2.67 Å calculated from zero field splitting at room temperature is reasonable.

6.8. EPR Spectra of Copper-doped Zinc Complexes

The EPR spectra of the polycrystalline copper-doped complexes at liquid nitrogen temperature are shown in Figures 6.39-6.44. Corresponding spectral parameters are gathered in Table 6.11. As might be expected, the spectra at liquid nitrogen temperature have sharper features and better resolution than spectra at room temperature. There are also slight differences in $g$ and $A$ values which presumably arise from a temperature dependence of the electron transition energies. The spectra are generally broader than
Figure 6.39. (A) Experimental EPR spectrum of polycrystalline copper-doped Zn(anth)₂ at liquid nitrogen temperature; microwave power: 5 mW; modulation amplitude: 0.50 x 10⁰ G; scan time: 16 min; time constant: 0.30 sec; receiver gain: 3.2 x 10². (B) Corresponding simulated spectrum.
Cu-doped Zn(anth)$_2$
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated
Figure 6.40. (A) Experimental EPR spectrum of polycrystalline copper-doped Zn(canth)$_2$ at liquid nitrogen temperature; microwave power: 5 mW; modulation amplitude: $0.50 \times 10^0$ G; scan time: 16 min; time constant: 0.30 sec; receiver gain: $3.2 \times 10^2$. (B) Corresponding simulated spectrum.
Cu-doped Zn(canth)$_2$

LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.41. (A) Experimental EPR spectrum of polycrystalline copper-doped Zn(dcanth)$_2$ at liquid nitrogen temperature; microwave power: 5 mW; modulation amplitude: $0.5 \times 10^0$ G; scan time: 16 min; time constant: 0.30 sec; receiver gain: $3.2 \times 10^2$. (B) Corresponding simulated spectrum.
Cu-doped Zn(dcanth)$_2$
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.42. (A) Experimental EPR spectrum of poly-crystalline copper-doped Zn(nanth)$_2$ at liquid nitrogen temperature; microwave power: 5 mW; modulation amplitude: $0.50 \times 10^0$ G; scan time: 16 min; time constant: 0.30 sec; receiver gain: $8.0 \times 10^2$. (B) Corresponding simulated spectrum.
Cu-doped Zn(nanth)$_2$
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.43. (A) Experimental EPR spectrum of polycrystalline copper-doped Zn(panth)$_2$ at liquid nitrogen temperature; microwave power: 20 mW; modulation amplitude: $2.5 \times 10^{0}$ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: $2.5 \times 10^{1}$. (B) Corresponding simulated spectrum.
Cu-doped Zn(panth)$_2$
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
Figure 6.44. (A) Experimental EPR spectrum of poly-crystalline copper-doped Zn(fluf)₂ at liquid nitrogen temperature; microwave power: 20 mW; modulation amplitude: 0.82 x 10⁰ G; scan time: 8 min; time constant: 0.30 sec; receiver gain: 10.0 x 10¹. (B) Corresponding simulated spectrum.
Cu-doped Zn(fluf)$_2$
LIQUID N$_2$ TEMPERATURE

A) experimental

B) simulated

MAGNETIC FIELD (GAUSS)
### TABLE 6.11

**EPR PARAMETERS FOR COPPER-DOPED ZINC COMPLEXES**

<table>
<thead>
<tr>
<th>Zinc Host</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$R^b$</th>
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<th>$A_y$</th>
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<th>$B_y$</th>
<th>$B_z$</th>
<th>$a^2$</th>
<th>$a_1^2$</th>
<th>$b_1^2$</th>
<th>$b_2^2$</th>
<th>$\gamma^2$</th>
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</thead>
<tbody>
<tr>
<td>1$^f$</td>
<td>2.0387</td>
<td>2.0961</td>
<td>2.3182</td>
<td>0.26</td>
<td>14.0</td>
<td>14.0</td>
<td>14.0</td>
<td>14.0</td>
<td>12.0</td>
<td>12.0</td>
<td>0.76</td>
<td>0.24</td>
<td>0.97</td>
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<td>0.45</td>
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<tr>
<td>2$^f$</td>
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<td>2.0888</td>
<td>2.3182</td>
<td>0.15</td>
<td>12.0</td>
<td>12.0</td>
<td>145.0</td>
<td>16.0</td>
<td>13.0</td>
<td>13.0</td>
<td>0.76</td>
<td>0.24</td>
<td>0.92</td>
<td>1.01</td>
<td>0.60</td>
</tr>
<tr>
<td>3$^f$</td>
<td>2.0356</td>
<td>2.1421</td>
<td>2.3418</td>
<td>0.53</td>
<td>28.0</td>
<td>40.0</td>
<td>126.0</td>
<td>15.0</td>
<td>13.0</td>
<td>13.0</td>
<td>0.74</td>
<td>0.26</td>
<td>0.98</td>
<td>1.62</td>
<td>0.39</td>
</tr>
<tr>
<td>4$^f$</td>
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<td>2.1480</td>
<td>2.108</td>
<td>0.86</td>
<td>29.0</td>
<td>58.0</td>
<td>112.0</td>
<td>12.0</td>
<td>10.0</td>
<td>10.0</td>
<td>0.67</td>
<td>0.33</td>
<td>0.99</td>
<td>1.87</td>
<td>0.08</td>
</tr>
<tr>
<td>5$^g$</td>
<td>2.0694</td>
<td>2.0694</td>
<td>2.430</td>
<td>2.40</td>
<td>5.8</td>
<td>5.8</td>
<td>120.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>0.82</td>
<td>0.18</td>
<td>1.24</td>
<td>0.76</td>
<td>--</td>
</tr>
<tr>
<td>6$^g$</td>
<td>2.0582</td>
<td>2.0872</td>
<td>2.402</td>
<td>2.40</td>
<td>0.8</td>
<td>1.8</td>
<td>139.5</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.83</td>
<td>0.18</td>
<td>1.11</td>
<td>0.95</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$Polycrystalline samples at liquid nitrogen temperature; parameters refined by computer simulation (see appendix A); estimated uncertainty in $g_z$ is ±0.0005; greater uncertainty associated with $g_x$ and $g_y$.

$^b$In $10^4$ cm$^{-1}$.

$^c$Calculated using computer program in appendix D, using values of E from powder reflectance spectra of corresponding copper complexes (Section 6.5.5), and values of T(n) from Table 3.2.

$^d$Zinc host complexes: 1 = Zn(anth)$_2$; 2 = Zn(canth)$_2$; 3 = Zn(dcanth)$_2$; 4 = Zn(nanth)$_2$; 5 = Zn(panth)$_2$; 6 = Zn(panth)$_2$.

$^e$E$_R$ = $g_3$ - $g_2$.
$\frac{g_2 - g_1}{g_2}$

$^f$Simulations performed using one site with average copper hyperfine coupling constant.

$^g$Simulations performed using two sites for $^{63}$Cu and $^{65}$Cu isotopes, see footnote h from Table 6.9.
the dilute frozen solution spectra, suggesting that the density of copper ions in the diamagnetic host lattice is too concentrated to completely eliminate weak dipole interactions between copper ions. However, spin-lattice relaxation effects may be stronger in the solid complex than in a frozen solvent matrix. Even so, the spectra are sufficiently well-resolved to identify major features.

The spectra of copper(II) in the host lattices of Zn(anth)_2, Zn(canth)_2, Zn(dcanth)_2, and Zn(nanth)_2 have parameters corresponding to rhombic symmetry. The calculated values of R are less than 1, indicating dx^2-y^2 rather than dz^2 ground states. The order of increasing rhombic or tetragonal character is

\[ \text{Zn(canth)}_2 < \text{Zn(anth)}_2 < \text{Zn(dcanth)}_2 < \text{Zn(nanth)}_2 \]

and roughly parallels the order of increasing magnitude of the shift of the amine stretching frequencies (Section 6.4), and decreasing basicity of the amine group (Table 4.2). These complexes are further characterized by weak in-(xy)-plane π-bonding (β_{\perp}^2 ≈ 1.0) and highly anisotropic equatorial coordination, where (a^2β^2 ≈ a_{\perp, 1}^2) > (a^2γ^2 ≈ a_{\perp, 2}^2). Although values of bonding parameters >1.0 or <0.5 are physically impossible, the results are indicative of inadequacies in the calculation of the bonding parameters to account for significant admixture of dz^2 character in the ground state representation, for local symmetry lower than
D$_{4h}$ or D$_{2h}$, or for reduction of the spin-orbit coupling constant.

Axial $\sigma$-bonds appear to be stronger than in the previously discussed copper complexes, where $a^2 = a_\parallel^2$ decreases (σ-bond strength increases) as the anisotropy in the EPR parameters increases. Therefore, as previously suggested for the origin of the xy-anisotropy in the EPR parameters of the frozen solution spectra of dichloroanthranilate, N-phenylanthranilate, and flufenamate complexes of copper(II) in various solvents (Section 6.7), the coordination of nitrogen to copper is strongly covalent while the interaction of the carboxylate group is weak and essentially electrostatic. Hill and Curran (99) originally suggested that the M$^{2+}$-COO$^-$ interaction in metal anthranilates is weak and electrostatic. Furthermore, copper(II) apparently prefers to coordinate with weaker bases because the anisotropy in the magnetic environment increases as the basicity of the amine group decreases. This accounts for the unusual infrared data. This conclusion is supported by smaller nitrogen hyperfine coupling constants observed for the copper-doped Zn(panth)$_2$ and Zn(fluf)$_2$ complexes. The amine groups of these ligands are slightly more basic than the amine group of anthranilic acid due to the electron-pushing inductive effect of the N-phenyl substituent. With the stronger amine group, EPR parameters corresponding to axial symmetry are observed, and axial $\sigma$-bonding is weakened ($a^2 = a_\parallel^2 = 0.82$) and the average equatorial $\sigma$-bonds are also weakened ($a^2_{\beta} = a_\perp^2$ =
0.62 - 0.79) relative to the nitro or chloro substituted anthranilate complexes.

The EPR parameters of copper(II) in Zn(panth)₂ and Zn (fluf)₂ are unusual in that \( g_\| \) is 2.40-2.44 and \( A_\| \) is small. These parameters do not resemble those obtained for copper-doped zinc(II) acetate (51) or zinc(II) propionate monohydrate (56), indicating that the Zn(fluf)₂ and Zn(panth)₂ are not carboxylate-bridged complexes.

Since the X-ray powder diffraction patterns of the copper and zinc complexes differ, it is not possible to correlate the magnetic parameters obtained for the copper-doped zinc complexes with the magnetic properties of the undiluted copper complexes. For instance, Cu(dcanth)₂•2H₂O has powder g-values \( g_1 = 2.06, g_2 = 2.21, \) and \( g_3 = 2.31, \) which differ greatly from the g-values for copper-doped Zn(dcanth)₂. However, the xy-anisotropy of the crystal g-values of Cu(dcanth)₂•2H₂O, and the similarity in the infrared data for the zinc and copper complexes are good indications that the substituted anthranilates behave similarly toward either metal.

6.9. Conclusions

Unlike α-amino acids, copper(II) complexes with substituted anthranilic acids display more diverse behavior. Electronegative substituents which decrease the basicity of the amine group have the effect of destabilizing the metal-carboxylate interaction while stabilizing the metal-amine
interaction. This effect produces a highly anisotropic ligand environment which results in rhombic EPR parameters.

In contrast, substitution by phenyl groups at the amine nitrogen increases the basicity of the amine group, but decreases the metal coordinating ability of the group. This may be a steric, rather than an electronic effect. Regardless, the copper complexes of N-phenyl anthranilates are soluble in a wide range of solvents, and exhibit a tendency to dimerize in non-polar, weakly coordinating solvents. The dimer is apparently held together, in solution and in the solid state, by hydrogen bonds, phenyl ring stacking interactions, and direct metal-metal bonding. These observations support arguments in favor of greater importance of direct metal-metal interactions, rather than indirect, super-exchange type of phenomena, in the behavior of copper dimers. In these complexes, ligand-bridging is relatively weak.

Future work on these complexes should include EPR studies at Q-band frequency to determine more accurately the xy-anisotropy in the magnetic environment. Crystallographic work is also necessary to confirm the proposed hydrogen bond-bridged dimeric structure.
APPENDIX A

EPRPOW COMPUTER PROGRAM

The original version of EPRPOW was modified by the author to include a fourth hyperfine interaction, and CALCOMP plot routines to label simulated spectra with a table of selected parameters.
EPRPOW was developed by Drs. L. K. White and R. L. Belford of the School of Chemical Sciences of the University of Illinois and subsequently modified by L. K. White, N. F. Allanece, and N. D. Chasteen at the University of New Hampshire to include both Lorentzian and Gaussian line shape functions, an I=7/2 nucleus, a fourth hyperfine interaction, and multiple sites having different line widths. Please acknowledge the original developers of the program, Drs. White and Belford, when reporting results based on the use of EPRPOW.

Thank you.

N. D. Chasteen
Chemistry Department
University of New Hampshire
November 2, 1978

*******************************************************************************

INTEGER ALPHA,GGX,GGY,GGZ,AX1,A Y1,AZ1,AX2,A Y2,AZ2,AX3,A Y3,AZ3,
1AX4,A Y4,AZ4,WX, WY,WZ,H,STAR,HAM,II
REAL KK, LX, LY, LZ,KH,LH
REAL*4 X(2502),Y(2502),STORE(2502)
DIMENSION CX(600),SX(600),SP(600),CP(600),DPHI(600),F1(600)
DIMENSION INT1(20),INT2(20),INT3(10),INT4(10)
DIMENSION PTITLE12)
DIMENSION LABEL(24)
DATA (LABEL(I1),I1=1,24)/ 'SITE#,*WT%*,GX*,GY*,GZ*,AAX1*,
1 AAY1*,AAZ1*,AAX2*,AAY2*,AAZ2*,AAX3*,AAY3*,
2 AAZ3*,AAX4*,AAY4*,AAZ4*,SPIN1*,SPIN2*,SPIN3*,SPIN4*,WWX*,
3 WWY*,WWZ*/

PLOT SETUP, INTEGRATION, FREQUENCY, AND LINELWIDTH DATA READ IN HERE
PLOT TITLE READ IN HERE
READ(5,11) PTITLE
WRITE(6,11) PTITLE
11 FORMAT(12A5)
READ(5,1) NN,MM,ALPHA,STAR,HAM
WRITE(6,1) NN,MM,ALPHA,STAR,HAM
1 FORMAT(5(2X,I3))
READ(5,2) LLOT,SPAC,PL,PHGT
2 FORMAT(2(2X,I5),2X,F6.3,2X,F5.2,2X,F5.2)
READ(5,3) XNU,NSITES
3 FORMAT(2X,F7.4,I3)
READ(5,10) WWX,WWY,WWZ
10 FORMAT(3(2X,F5.1))
CUTOFF=4.0
IF(STAR.EQ.1) CUTOFF=3.0
IF(HAM.EQ.1) CUTOFF=8.0
L=L*100
LTOT=LTOT*100
LINT=SPAC*100.0+0.5
WX=WWX*100.0+0.5
WY=WWY*100.0+0.5
WZ=WWZ*100.0+0.5
KLOT=(2*(WX+WY+WZ))/LINT
DEL=KLOT*LINT
KMAX=LTOT+DEL
KMIN=L-DEL
KDOT=((KMAX-KMIN)/LINT)
KTOT=(LTOT-KMIN)/LINT
WRITE(6,19) KLOT,KMAX,KMIN,KDOT,KTOT,L,LTOT,DEL,SPAC
19 FORMAT(7I8,2X,2F7.2)
WRITE(6,303)XNU
303 FORMAT(1X,F7.4,24HGHZ MICROWAVE FREQUENCY)
DO100 KL=1,KDOT
STORE(KL)=0
X(KL)=0.
Y(KL)=0.
100 CONTINUE
L=(L/LINT)*LINT
LTOT=(LTOT/LINT)*LINT
HMIN=L
HMAX=LTOT
92 NN3=3*NN
M =3*MM
C GAUSS-POINT SELECTION OF ANGLES, WEIGHTING FACTORS FOR INTEGRATION
C SELECTION USES LINEWIDTHS OF 1ST SITE ONLY.
C SUBROUTINE THETA SELECTS FOR XZ OR YZ PLANES
C SUBROUTINE PHI SELECTS FOR XY PLANE
IF(HAM.EQ.1) GO TO 89
CALL THETA(NN,CX,SX,D)
IF(HAM.EQ.2) GO TO 90
CALL ORTHRH(MM,CP,SP,DPHI,ALPHA)
GO TO 91
89 NN3=1
SX(1)=0.0000000
CX(1)=1.0000000
D(1)=1.0000000
90 MM3=1
CP(1)=1.0000000
SP(1)=0.0000000
DPHI(1)=1.0000000
C
C PLOT AND TABLE OF DATA INITIATED HERE
C HL=LETTER HEIGHT, WLINE=LINE SPACING, BX AND BY=X AND Y COORDINATES TO START TABLE
C
91
HL=0.25
WLINE=0.35
BX=2.0
BY=28.5
CALL PLOTS('C')
CALL PLOT(1.0,0.0,-3)
CALL SYMBOL(BX,BY+3*WLINE,HL,PTITLE,0.0,45)
CALL NUMBER(BX,BY+2*WLINE,HL,FLOAT(NN),0.0,-1)
CALL NUMBER(BX+2.0,BY+2*WLINE,HL,FLOAT(MM),0.0,-1)
CALL NUMBER(BX+4.0,BY+2*WLINE,HL,FLOAT(ALPHA),0.0,-1)
CALL NUMBER(BX+6.0,BY+2*WLINE,HL,FLOAT(START),0.0,-1)
CALL NUMBER(BX+8.0,BY+2*WLINE,HL,FLOAT(HAM),0.0,-1)
CALL NUMBER(BX,BY+WLINE,HL,FLOAT(L),0.0,-1)
CALL NUMBER(BX+2.0,BY+WLINE,HL,FLOAT(LDT),0.0,-1)
CALL NUMBER(BX+4.0,BY+WLINE,HL,SPAC,0.0,1)
CALL NUMBER(BX+6.0,BY+WLINE,HL,PL,0.0,1)
CALL NUMBER(BX+8.0,BY+WLINE,HL,PHGT,0.0,1)
DO 1000 II=1,124
CALL SYMBOL(BX,BY-WLINE,FLOAT(II-1),HL,LABEL(II),0.0,5)
1000 CONTINUE

C EPR_PARAMETERS READ IN FOR EACH SITE
C LINENUMBER OF A PARTICULAR SITE USED FOR LINESHAPE FUNCTION OF THAT SITE ONLY
C
DO 108IN=1,NSITES
IF(IN.EQ.1) GO TO 25
READ (5,10) WX,WWY,WWZ
WX=WX*100.0+0.5
WWY=WWY*100.0+0.5
WWZ=WWZ*100.0+0.5
25 CONTINUE
READ(5,4)GGX,GGY,GGZ,IWT
4 FORMAT(4(I2,15))
READ(5,5)AAAI,AAY1,AAZ1
5 FORMAT(3F10.5)
READ(5,5)AAAX2,AAY2,AAZ2
READ(5,5)AAAX3,AAY3,AAZ3
READ(5,5)AAAX4,AAY4,AAZ4
READ(5,8)SPIN1,SPIN2,SPIN3,SPIN4
8 FORMAT(4(2X,F3.1))
NSP1=2.*SPIN1+1.5
NSP2=2.*SPIN2+1.5
NSP3=2.*SPIN3+1.5
NSP4=2.*SPIN4+1.5
READ(5,9) ((INTI(I),I=1,NSP1),(INT2(J),J=1,NSP2),
DATA FOR EACH SITE PLOTTED HERE

1(INT3(K),K=1,NSP3),(INT4(LM),LM=1,NSP4)
9 F0RMAT(2014/2014)

BX=BX+2.5
CALL NUMBER(BX,BY,HL,FLOAT(IN),0.0,-1)
CALL NUMBER(BX,BY-3*WLINE,HL,FLOAT(GGX),0.0,-1)
CALL NUMBER(BX,BY-4*WLINE,HL,FLOAT(GGY),0.0,-1)
CALL NUMBER(BX,BY-5*WLINE,HL,AAX1,0.0,2)
CALL NUMBER(BX,BY-6*WLINE,HL,AAY1,0.0,2)
CALL NUMBER(BX,BY-7*WLINE,HL,AAZ1,0.0,2)
CALL NUMBER(BX,BY-8*WLINE,HL,AAX2,0.0,2)
CALL NUMBER(BX,BY-9*WLINE,HL,AAY2,0.0,2)
CALL NUMBER(BX,BY-10*WLINE,HL,AAZ2,0.0,2)
CALL NUMBER(BX,BY-11*WLINE,HL,AAX3,0.0,2)
CALL NUMBER(BX,BY-12*WLINE,HL,AAY3,0.0,2)
CALL NUMBER(BX,BY-13*WLINE,HL,AAZ3,0.0,2)
CALL NUMBER(BX,BY-14*WLINE,HL,AAX4,0.0,2)
CALL NUMBER(BX,BY-15*WLINE,HL,AAY4,0.0,2)
CALL NUMBER(BX,BY-16*WLINE,HL,AAZ4,0.0,2)
CALL NUMBER(BX,BY-17*WLINE,HL,SPIN1,0.0,1)
CALL NUMBER(BX,BY-18*WLINE,HL,SPIN2,0.0,1)
CALL NUMBER(BX,BY-19*WLINE,HL,SPIN3,0.0,1)
CALL NUMBER(BX,BY-20*WLINE,HL,SPIN4,0.0,1)
CALL NUMBER(BX,BY-21*WLINE,HL,WWX,0.0,2)
CALL NUMBER(BX,BY-22*WLINE,HL,WWY,0.0,2)
CALL NUMBER(BX,BY-23*WLINE,HL,WWZ,0.0,2)

SPIN=SPIN1*(SPIN1+1)
RALPH=ALPHA
ALP=ALPHA*0.0174533
SALP=SIN(ALP)
C=ALPHA*0.0174533
GX=GGX/10000.
GY=GGY/10000.
GZ=GGZ/10000.
WRITE(6,298)

298 F0RMAT(12A5/)
WRITE(6,299) IN,IWT
299 F0RMAT(14H***SITE NUMBER,14H***WEIGHT % ,I3,3H***)
WRITE(6,300) SPIN1,SPIN2,SPIN3,SPIN4

300 F0RMAT(2X,6SPIN1=F4.2,2X,6SPIN2=F4.2,2X,6SPIN3=F4.2,

12X,6SPIN4=F4.2)
WRITE(6,301) GX,GY,GZ,AAX1,AAY1,AAZ1,AAX2,AAY2,AAZ2,AAX3,AAY3,AAZ3,

1AAX4,AAY4,AAZ4
301 FORMAT (1X, 3HGX=, F6.4, 1X3HGY=, F6.4, 1X3HGZ=, F6.4/
1X,5HAAXI=, F10.5, 1X, SHAAYI=, F10.5, 1X, SHAAZI=, F10.5/
21X, SHAAX2=, F10.5, 1X, SHAAY2=, F10.5, 1X, SHAAZ2=, F10.5/
31X, SHAAX3=, F10.5, 1X, SHAAY3=, F10.5, 1X, SHAAZ3=, F10.5/
41X, SHAAX4=, F10.5, 1X, SHAAY4=, F10.5, 1X, SHAAZ4=, F10.5)
WRITE(6, 302) WWX, WViY, WWZ, ALPHA
302 FORMAT (1X, 4HWWX=, F4.1, 1X, 4HWY=, F4.1, 1X, 4HWZ=, F4.1, 1X, 5HALPH=, F1)

WRITE(6, 304) { (INT1(I), I=1, NSP1), (INT2(J), J=1, NSP2), 
1(1, INT3(K), K=1, NSP3), (INT4(LM), LM=1, NSP4) }
304 FORMAT (2014/2014)
GXX=GX*GX
GYY=GY*GY
GZZ=GZ*GZ
WSO=1.0000
AX1=AAX1*100.0+0.5
AY1=AAY1*100.0+0.5
AZ1=AAZ1*100.0+0.5
AX2=AAX2*100.0+0.5
AY2=AAY2*100.0+0.5
AZ2=AAZ2*100.0+0.5
AX3=AAX3*100.0+0.5
AY3=AAY3*100.0+0.5
AZ3=AAZ3*100.0+0.5
AX4=AAX4*100.0+0.5
AY4=AAY4*100.0+0.5
AZ4=AAZ4*100.0+0.5
AXX=AX1*AX1
AYY=AY1*AY1
AZZ=AZ1*AZ1
C CX(I) AND CS EQUALS COSINE(THETA)
C SX(I) AND SN EQUALS SINE(THETA)
C CP(I) AND CC EQUALS COSINE(PHI)
C SP(I) AND SS EQUALS SINE(PHI)
C D(I) INTERGRATION FACTORS FOR THETA
C DPHI(I) INTERGRATION FACTORS FOR PHI
DO 108 I=1, NN3
CS=CX(I)
SN=SX(I)
DO 108 M=1, MM3
CC=CP(M)
SS=SP(M)
SN2=SN*SN
CS2=CS*CS
SS2=SS*SS
CC2=CC*CC
402 LX=SN*SN*CC*CC
405 NSS=(CUTOFF*S)/LINT
SS=S*S
WS=W*S
C HH EQUALS PRINCIPAL RESONANCE FIELD FOR AI HYPERFINE INTERACTION
406 DO98 J1=1,NSP1
SPINM=J1-1-SPIN1
HH=HO-ZG*SPINM-CA*(SPN-SPINM**2)-CB*(SPINM**2)
DO98 J2=1,NSP2
KH=HH+ZNG*(SPIN2-J2+1)
DO98 J3=1,NSP3
MH=KH+YNG*(SPIN3-J3+1)
DO98 J4=1,NSP4
LH=MH+CNM*(SPIN4-J4+1)
408 IF(LH.LT.KMIN.OR.LH.GT.KMAX)GO TO 98
NH=(LH-KMIN)/LINT
ZNH=NH-{(LH-KMIN)/LINT)
NI=NH-NSS
NJ=NH+NSS
IF(NJ.LE.0)NJ=1
IF(NJ.GT.KMOT)NJ=KMO
C LINESHAPE OPTION EXERCISED HERE*STAR* EQUALS*1* GAUSSIAN USED
IF(STAR.EQ.1)GO TO 202
C LORENTIZIAN LINESHAPE 1ST DERIVATIVE
C STORE(KL) IS ARRAY POWDER SPECTRUM IS STORED
201 D088KL=Nl,NJ
KK=LH-KMIN-((KL-ZNH)*LINT)
SK=SS+KK*KK
STORE(KL)=STORE(KL)+((S*KK/(SK*SK))*INT1(J1)*INT2(J2)*INT3(J3)*
INT4(J4))
CONTINUE
GO TO 87
C GAUSSIAN LINESHAPE 1ST DERIVATIVE
202 D087KL=Nl,NJ
KK=LH-KMIN-((KL-ZNH)*LINT)
SK={KK*KK)*0.6931471/1SS)
STORE(KL)=STORE(KL)+((S*KK/(SS*SS))*EXP(-SK)*INT1(J1)*INT2(J2)*
INT3(J3)*INT4(J4)*%
CONTINUE
98 CONTINUE
108 CONTINUE
WRITE(6,18)I,M,J1,J2,J3,J4
18 FORMAT(6(2X,13)1
C WEIGHTING COMPUTED SPECTRUM TO MOST INTENSE PEAK
335 PEAK=0
D051N=KLOT,KDOT
PAK=ABS(STORE(N))
IF(PAK.LT.PAK)GOTO 50
GO TO 51
DO 52 N= KLOT*KTOT
X(N-KLOT+1)= ((N-KLOT)*LINT)
Y(N-KLOT+1)= STORE(N)*FACTOR/PEAK
52 CONTINUE
KCMM=KTOT-KLOT
NTOT =KCMM+1
TX1=L
TX2=(LTOT-L)/PL
TY1=FACTOR
TY2=2*FACTOR/PHGT
X(KCMM+2)=0.0
Y(KCMM+2)=TY1
Y(KCMM+3)=TY2
CALL SETSIZ(0.30,0.12,0.15,1.00)
CALL AXIS(0.0,0.0,*INTENSITY*,9,PHGT,90.0,TY1,TY2)
CALL PLOT(0.0,0.5*PHGT,-3)
CALL AXIS(0.0,0.0,*CENTIGAUS*,10,PL,0.0,TX1,TX2)
CALL LINE(X,Y,NTOT,1,0,0)
121 STOP
END
SUBROUTINETHETA(NN,CX,SX,D)
DIMENSION CX(600),SX(600),TETA(600),D(600)
NINT=NN
SINT=1.570796/NINT
GSINT=SINT*0.77459667/2.
J=1
TETA(J)=0.
D(J)=0.22222222
J=J+1
TETA(J)=SINT/2.—SINT*0.28989794/2.
D(J)=0.2497166
J=J+1
TETA(J)=SINT/2.+SINT*0.68989794/2.
D(J)=0.75280612
J=J+1
NNEX=NINT—2
DO 100 I=1,NNEX
TETA(J)=(I+1)*SINT—(SINT/2.+GSINT)
D(J)=0.55555555
J=J+1
TETA(J)=I*SINT+SINT/2.
D(J) = 8888888
J = J + 1
TETA(J) = I*SINT+(SINT/2.*GSINT)
D(J) = 55555555

100 CONTINUE
TETA(J) = 1.5707963-(SINT/2.*SINT*0.28989794/2.)
D(J) = 1.02497166
J = J + 1
TETA(J) = 1.5707963-(SINT/2.-SINT*0.28989794/2.)
D(J) = 0

101 CONTINUE
RETURN
END

SUBROUTINE ORTHRH(MM,CP,SP,DPHI,ALPHA)
DIMENSION CP(600),SP(600),DPHI(600),FI(600)
MINT = MM
RANGE = 3.1415926
IF(ALPHA.EQ.0.0) RANGE = RANGE/2.
SINTP = RANGE/MINT
GSINP = SINTP*0.77459667/2.
J = 1
FI(J) = 0
DPHI(J) = 0.22222222
J = J + 1
FI(J) = SINTP/2.+SINTP/2.*GSINP
DPHI(J) = 1.02497166
J = J + 1
FI(J) = SINTP/2.-SINTP/2.*GSINP
DPHI(J) = 1.02497166
J = J + 1
MINT2 = MINT-2
DO 200 I = 1, MINT2
FI(J) = (I+1)*SINTP-(SINTP/2.*GSINP)
DPHI(J) = 1.02497166
J = J + 1
FI(J) = I*SINTP+SINTP/2.
DPHI(J) = 1.02497166
J = J + 1
FI(J) = I*SINTP+SINTP/2.*GSINP
DPHI(J) = 1.02497166

239
J=J+1
200 CONTINUE
F(J)=RANGE-(SINTP/2.*SINTP*0.68589794/2.)
D PHI(J)=.75280612
J=J+1
F(J)=RANGE-(SINTP/2.-SINTP*0.28589794/2.)
D PHI(J)=1.02497166
J=J+1
F(J)=RANGE
D PHI(J)=22222222
DO 201 MP=1,J
CP(MP)=COS(F(I(MP)))
SP(MP)=SIN(F(I(MP)))
201 CONTINUE
RETURN
END
### EPRPOW DATA FILES

#### CU(PRO)2,DMF,RT
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| 36.0 | 36.0 | 36.0 | 21158 | 21158 | 21158 | 69 | 81.70 | 81.70 | 81.70 |

#### CU(PRO)2,MEDH,RT
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CU IN ZN(PANTH)2

- 248
APPENDIX B

ZFSPLT COMPUTER PROGRAM

Resonance field positions are calculated for $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ coupled spin systems using equations outlined in Section 3.4.
This program calculates resonance positions HX1, HX2, HY1, HY2, HZ1 and HZ2 as a function of zero field splitting parameters, D and E.

Data input consists of GX, GY, GZ, H0 (DPPH field position) and selected values of E (in reciprocal cm).

D is automatically varied from 0 to 3200 gauss.

Nina Albanese, January 23, 1979, University of New Hampshire

```
DIMENSION DP(33), L(33), V(33), X(33), Y(33), Z(33)
REAL GE, GX, GY, GZ, BETA, H0, E
DOUBLE PRECISION FOUT
WRITE(5,7)
07 FORMAT(* OUTPUT FILE NAME: *)
READ(5,8) FOUT
08 FORMAT(A10)
OPEN (UNIT=1, ACCESS=SEGOUT*, FILE=FLUT)
CONTINUE
TYPE 05
05 FORMAT(* ENTER YOUR VALUES OF GX, GY, GZ, H0, AND E*)
READ(5,10) GX, GY, GZ, H0, E
10 FORMAT(5F)
WRITE(5,20) GX, GY, GZ
WRITE(1,20) GX, GY, GZ
20 FORMAT(3X,4HGX= F10.3, 4FGY= F10.3, 4FGZ= F10.3)
WRITE(5,25) H0, E
WRITE(1,25) H0, E
25 FORMAT(3X,4HFO= F10.3, 10HGAUSS E(CM-1)= F10.3)
GE=2.0023
EP=E*GE*BETA
WRITE(5,30)
WRITE(1,30)
30 FORMAT(• DP HX1 HX2 HY1 HY2 HZ1 HZ2•)
DP(1)=0.0
DO 50 I=1,33
U(I)= SQRT(((GE/GX)**2)*((H0-DP(I)+EP)*(H0+2*EP)))
V(I)= SQRT(((GE/GX)**2)*((H0+DP(I)-EP)*(H0-2*EP)))
W(I)= SQRT(((GE/GY)**2)*((H0-DP(I)-EP)*(H0+2*EP)))
X(I)= SQRT(((GE/GY)**2)*((H0+DP(I)+EP)*(H0+2*EP)))
Y(I)= SQRT(((GE/GZ)**2)*((H0-DP(I))**2-(EP**2)))
Z(I)= SQRT(((GE/GZ)**2)*((H0+DP(I))**2-(EP**2)))
WRITE(5,40) DP(I), U(I), V(I), W(I), X(I), Y(I), Z(I)
WRITE(1,40) DP(I), U(I), V(I), W(I), X(I), Y(I), Z(I)
40 FORMAT(7(1X,F6.1))
```
DP(I+1)=DP(I) + 100.0
50 CONTINUE
TYPE 60
60 FORMAT(' TYPE 1 TO RUN ANOTHER SET')
READ(5,*) IND
IF (IND.EQ.1.) GO TO 04
CLOSE (UNIT=1, ACCESS='SEQOUT', FILE=OUT)
STOP
END
FIELD POSITIONS AS FUNCTIONS OF ZERO FIELD SPLITTING PARAMETERS, D AND E.
APPENDIX C

X-RAY POWDER DIFFRACTION DATA
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APPENDIX D

BPEPR COMPUTER PROGRAM

CALCULATION OF BONDING PARAMETERS

The bonding parameters $a^2$, $\beta_1^2$, $\beta^2$, and $\gamma^2$ are calculated using equations outlined in Section 3.3, following an approach suggested by Kivelson and Nieman (28).
CALCULATION OF BONDING PARAMETERS FOR COPPER COMPLEXES WITH TWO NITROGEN AND TWO OXYGEN LIGAND ATOMS

DATA REQUIRED: GX,GY,GZ,AZ,TE,E

A VALUES ARE IN X10,000 CM-1. E IS IN KK.

DOUBLE PRECISION FOUT
WRITE(5,5)
FORMAT(* OUTPUT FILE NAME: * )
READ(5,10) FOUT
10 FORMAT(A10)
OPEN(UNIT=1,ACCESS=’SEGGLT’,FILE=FOUT)
CONTINUE
TYPE 20
FORMAT(* ENTER NAME OF COMPLEX*)
READ(5,25) COMPLEX
25 FORMAT(A20)
TYPE 30
FORMAT(* ENTER VALUES OF GX,GY,GZ*)
READ(5,35) GX,GY,GZ
35 FORMAT(3F)
TYPE 40
FORMAT(* ENTER VALUES OF AZ, E, TN*)
READ(5,35) AZ,E, TN
40 FORMAT(3E)
WRITE(5,50) GX,GY,GZ
WRITE(1,50) GX,GY,GZ
50 FORMAT(3X,4HGX= F6.4,3X,4HGY= F6.4,3X,4HZ= F6.4)
WRITE(5,55) AZ,E, TN
WRITE(1,55) AZ,E, TN
55 FORMAT(3X,4HAZ= F6.2,3X,3HE= F5.2,3X,4HTN= F5.3)
AZC=AZ/10000.0
EC=E*1030.
APAR=AZC
GPAR=GZ
GPER=(GX+GY)/2.0
DGY=GY-2.0023
DGX=GX-2.0023
DGZ=GPAR-2.0023
DGXY=GPER-2.0023
DXY=GX-GY
SJC=828.0
P=0.036
OK=0.43
S=0.0845

CALCULATION OF APPROXIMATE ALPHA-SQUARED (AAS)
AAS=((-APAR/P)-DGZ-((3./7.)*DGXY))/(OK-(4./7.))
AA=AAS**0.5
AAPS = 1.0 - AAS
AAPS = AAPS**0.5
C
CALCULATION OF APPROXIMATE BETA-CONE SQUARED (ABOS)
ABOS = (DGZ*EC)/(8.0*SGC*AAS)
ABO = ABOS**0.5
N = (1-ABUS)**0.5
IF(DXY.EQ.0.0) GO TO 60
C
CALCULATION OF APPROXIMATE BETA SQUARED AND GAMMA SQUARED
C
RHOMBIC CASE
ABRS = (DGY*EC)/(2.0*SGC*AAS)
ABR = ABRS**0.4
AGS = (DGX*EC)/(2.0*SGC*AAS)
AG = AGS**0.5
ABS = ((AG+ABR)/2)**2.
GO TO 65
C
CALCULATION OF APPROXIMATE BETA SQUARED (AXIAL CASE)
60
AB = ABS**0.5
M = (1.0-ABS)**0.5
DO 110 1=1,4
C
CALCULATION OF ZPAR AND ZPER
ZPAR = (AA*(AE0/((AA*AE0)-(AAP*ABG*S)-(0.5*AAP*N*XN)))
ZPER = (AA*(AB))/((AA*AB)-(AAP*ABG*S)-(AAP/2)**(0.5*N*XN)))
WRITE(5,70) ZPAR,ZPER
WRITE(1,70) ZPAR,ZPER
70
FORMAT(* 'Z PARALLEL ',F9.5,* ' Z PERPENDICULAR ',F9.5)
C
RECALCULATION OF ALPHA SQUARED (AS)
AS = ((-APAR/P)-((DGZ*ZPAR)-(3.0/7.0)*DGX*ZPER))/(0.0-(4.0/7.0))
APS = 1.0-AS
AP = APS**0.5
A = AS**0.5
WRITE(5,75) AS,APS
WRITE(1,75) AS,APS
75
FORMAT(* 'ALPHA SQD ',5X,F8.5,* 'ALPHA PRIME SQD ',5X,F8.5)
C
RECALCULATION OF BETA-CONE SQUARED
BXY = (DGZ*EC)/(8.0*SGC*AS)
B = BXY**0.5
WRITE(5,80) BXY
WRITE(1,80) BXY
80
FORMAT(* 'BETA 1 SQUARED ',5X,F8.5)
C
IF(DXY.EQ.0.0) GO TO 95
C
RECALCULATION OF BETA SQUARED AND GAMMA SQUARED (RHOMBIC CASE)
BS = (DGY*EC)/(2.0*SGC*AS)
B = BS**0.5
GS = (DGX*EC)/(2.0*SGC*AS)
G = GS**0.5
ADS = ((B+G)/2)**2.
WRITE(5,85) B,GS
WRITE(1,85) BS,GS
85 FORMAT(' BETA SQUARED ',5X,F8.5,' GAMMA SQUARED ',5X,F8.5)
FORMAT(' ')
GO TO 105
C RECALCULATION OF BETA SQUARED (AXIAL CASE)
95 BS=(DGXY*EC)/(2.*SOC*AS)
BS=BS**0.5
WRITE(5,100) BS
WRITE(1,100) BS
100 FORMAT(' BETA SQUARED ',5X,F8.5)
ABS=BS
105 AAA=A
ABD=BD
AAP=AP
AB=B
N=(1.-ABD**2.)**0.5
M=(1.-AB**2.)**0.5
WRITE(5,90)
WRITE(1,90)
WRITE(1,90)
TYPE 115
115 FORMAT(' TYPE 1 TO RUN ANOTHER SET*)
READ(5,*)IND
IF(IND.EQ.1.)GO TO 15
CLOSE(UNIT=1, ACCESS='SEGOUT', FILE=FOUT)
STOP
END
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