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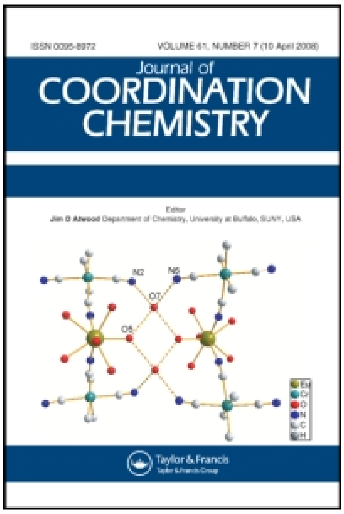

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THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER (II)

IV. N,N-bis-(pyrrole-2-aldehyde)ethylenediimine

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The EPR spectrum of N,N′-bis-(pyrrole-2-aldehyde)ethylenediimino Cu(II), [Cu en(pyal)$_2$] has been investigated in a doped single crystal of the corresponding nickel (II) chelate. The imine and pyrrole nitrogens were found to be chemically inequivalent thus giving rise to unequal coupling constants. The parameters in the doublet spin-Hamiltonian are found to be: $g_z = 2.168 \pm 0.001$, $g_x = 2.042 \pm 0.002$, $g_y = 2.043 \pm 0.002$, $A_z^{Cu} = 197.5 \times 10^{-4}$ cm^{-1}, $A_x^{Cu} = 28.5 \times 10^{-4}$ cm^{-1}, $A_y^{Cu} = 27.3 \times 10^{-4}$ cm^{-1}, imine $A_z^N = 14.1 \times 10^{-4}$ cm^{-1}, $A_x^N = A_y^N = 15.5 \times 10^{-4}$ cm^{-1}, pyrrole $A_z^N = 17.7 \times 10^{-4}$ cm^{-1}, $A_x^N = A_y^N = 15.5 \times 10^{-4}$ cm^{-1}, methine $A_z^H = 7.0 \times 10^{-4}$ cm^{-1}, $A_x^H = A_y^H = 8.2 \times 10^{-4}$ cm^{-1}. These parameters are related to the coefficients of the molecular orbital containing the unpaired electron. Preliminary crystal data for the nickel chelate are also given.

KEY WORDS
EPR spectrum, N,N′-bis-(pyrrole-2-aldehyede)ethylenediimino Cu(II), magnetic parameters, molecular orbitals, ligand field, crystal data.

INTRODUCTION

Transition metal complexes of tetradentate ligands resulting from the 2:1 condensation of salicylaldehyde or β-diketones with diamines have been the subject of many investigations.[1–5] These ligands form planar, neutral complexes of the cis "N_2O_2" type and furnish fields whose approximate symmetry is described by the C_{2v} point group. The related tetradentate Schiff base complexes of the "N_4" type have been somewhat ignored. Only recently have complexes derived from o-aminobenzaldehyde been investigated in any detail.[6–8] There is even a greater dearth of information concerning tetradentate complexes derived from pyrrole-2-aldehyde. This is surprising since they contain the biologically important pyrrole moiety and their ability to form single crystals far exceeds that of the phthalocyanines and the porphyrins.

The condensation product of two moles of pyrrole-2-aldehyde and one mole of ethylenediamine and its complexes of copper(II) and nickel(II) were first reported by Pfieffer[9] *et al.* and later studied in greater detail by Weber and Clarke[10,11] but no EPR data have been presented. Stackelberg[12] attempted to obtain crystal data for the copper complex but his analysis is incomplete. The purpose of this study is to investigate the copper complex by EPR spectroscopy. To obtain the maximum amount of bonding information, this study was carried out on a magnetically dilute sample in order to eliminate dipolar broadening thus enabling the resolution of hyperfine and superhyperfine structure in the spectrum. This was accomplished by doping small amounts of the paramagnetic copper complex into a crystal of the diamagnetic nickel complex.

EXPERIMENTAL

The ligand and the nickel chelate were prepared as described in the literature.[9] Small amounts of Cu(II) were added during the synthesis of the Ni(II) complex

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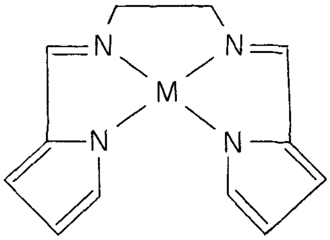

FIGURE 1 Molecular geometry of the complexes where M = Ni(II), Cu(II).

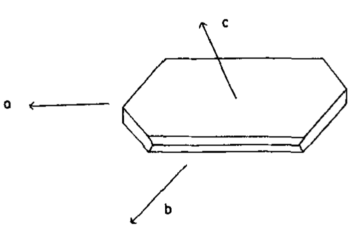

FIGURE 2 Orientation of the crystallographic axes with respect to the external morphology for a single crystal of the nickel complex.

to form the doped compound. Isotopically pure (99.87%) ^{63}Cu(II), as the nitrate, was used in doping to reduce the complexity of the hyperfine splitting. Single crystals of the pure nickel chelate were used to collect x-ray data while Cu-doped (1–3%) crystals of the nickel chelate were used for EPR studies.

The EPR spectrometer and the associated equipment have been previously described.[13] The spectral analysis was simplified by the use of simulated spectra calculated on a Nicolet Nic-80 computer by means of the program "EPRCAL". The data reduction procedure described by Billings and Hathaway[14] employed in our previous studies was modified for use in the present case because we could obtain data in only two orthogonal planes. Since the largest g-value (g_z), obtained from the powdered crystal spectra was observed in one single crystal plane, their method could be modified to accommodate the present system. The modification we have employed is described in the appendix.

Translucent orange crystals of Ni[en(pyal)$_2$] elongated along the a-axis were obtained by slow evaporation of a chloroform solution. Found: C–53.28%, H–4.51%, N–21.10%; Calc: C–53.18%, H–4.46%, N–20.68% with no solvent of crystallization.

Preliminary oscillation and Weissenberg photographs of a crystal showed that it was triclinic. The unit cell parameters[15] were obtained from precession photographs. These are $a = 6.92 \pm 0.02$ Å, $b = 8.83 \pm 0.02$ Å, $c = 10.57 \pm 0.03$ Å, $\alpha = 65.0 \pm 0.5°$, $\beta = 80.8 \pm 0.5°$, $\gamma = 81.2 \pm 0.5°$; space group P_1 or $P_{\bar{1}}$. The density measured by floation in aqueous zinc bromide, 1.55 gcm^{-3}, is in good agreement with the value 1.56 gcm^{-3} calculated for two molecules per unit cell.

The crystallographic axes with respect to the external morphology are shown in Figure 2. A c'-axis was chosen normal to the large face (001) and a b'-axis was chosen normal to the ac' plane. This provides an orthogonal axis system for EPR data collection.

Well resolved spectra were observed in the ab' and ac' planes while in the $b'c'$ plane severe overlapping of the superhyperfine lines as well as line broadening due to the pyrrole protons prevented a detailed analysis. The value for g_z as determined from the powdered crystal spectra was observed in the ac' plane. The maximum value for the copper hyperfine splitting, A_z^{Cu}, was observed when the field was parallel to the g_z direction.

ANALYSIS

The magnetic parameters and the direction cosines were determined by the method outlined in the appendix. These values are collected in Tables I and II.

TABLE I
The Magnetic parameters

$g_z = 2.168 \pm 0.001$

$g_x = 2.042 \pm 0.002$

$g_y = 2.043 \pm 0.002$

$A_z^{\mathrm{Cu}} = 195.1 \pm 0.5$ G
197.5×10^{-4} cm^{-1}

$A_x^{\mathrm{Cu}} = 29.9 \pm 1.0$ G
28.5×10^{-4} cm^{-1}

$A_y^{\mathrm{Cu}} = 28.6 \pm 1.0$ G
27.3×10^{-4} cm^{-1}

imine, $A_z^N = 13.9 \pm 0.5$ G
14.1×10^{-4} cm^{-1}

pyrrole, $A_z^N = 17.5 \pm 0.5$ G
17.7×10^{-4} cm^{-1}

imine, pyrrole, $A_x^N = A_y^N = 15.3 \pm 0.5$ G
14.6×10^{-4} cm^{-1}

methine, $A_z^H = 6.9 \pm 0.5$ G
7.0×10^{-4} cm^{-1}

$A_x^H = A_y^H = 8.6 \pm 0.5$ G
8.2×10^{-4} cm^{-1}

TABLE II
Direction cosines of the g-values with respect to the laboratory axes.

	a	b'	c'
g_x	0.25	0	0.97
g_y	0	1	0
g_z	0.97	0	−0.25

The superhyperfine splitting along g_z consisted of 27 partially overlapped lines. This splitting pattern was first thought to arise from four equivalent nitrogens and the two methine protons since these protons have been known to cause superhyperfine structure in the spectrum of similiar complexes. The spectrum did not yield to such a simple analysis because the lines were unequally spaced. A computer simulation of spectra using different coupling constants for the imine and pyrrole nitrogens accounted for positions of 25 of the 27 lines but the calculated intensities were in poor comparison. Ultimately, a simulation using different nitrogen coupling constants and a methine proton coupling constant of one-half the imine nitrogen value accounted for the missing lines as well as the intensity distribution.

In the molecular plane the superhyperfine structure consisted of nineteen equally spaced lines. This could arise from four equivalent nitrogens and two equivalent protons with a coupling constant of one-half the nitrogen value. Again, the calculated line positions were in agreement but the calculated and experimental intensity ratios were in poor agreement. The observed "extra" lines arising from the protons had intensity ratios less than one-half the expected value. The observed line positions and intensities could be reproduced assuming four equivalent nitrogens and a proton coupling constant of $(A_N)/2 \pm 1G$.

In each case, the final simulated spectrum reproduced the observed line positions to within one gauss. The intensities were in good agreement but overlapping prevented an exact comparison.

BONDING

The molecular geometry of the complex is shown in Figure 2. Assuming $C_{2v}^{(x)}$ point symmetry, the molecular orbital containing the unpaired electron is the antibonding linear combination of the d_{xy} orbital on the copper with ligand sigma orbitals:

$$\psi_{B_2} = \alpha \mid xy \rangle - \alpha'/2 \mid B_2 \rangle \tag{1}$$

The two coefficients are related by the normalization condition

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \tag{2}$$

where S is the overlap integral represented by $2 \langle xy \mid B_2 \rangle$. Here $\mid B_2 \rangle$ is a ligand group orbital given by

$$\mid B_2 \rangle = \mid \sum_{i=1}^{4} c_i \sigma_i \rangle \quad c_i = \pm 1 \tag{3}$$

$$\sigma_i = n(2p)_i \pm (1 - n^2)^{1/2} (2s)_i \tag{4}$$

Complete expressions are available for the ligand hyperfine interaction but we shall deal with only the isotropic part, $1/3\,(A_x^N + A_y^N + A_z^N)$, since correcting for the dipole-dipole contribution requires a knowledge of the copper-nitrogen bond distances and the use of the anisotropic part introduces a large amount of experimental error into the analysis. The isotropic contact term is

$$A_{\text{iso}}^N = 4/3 \pi \gamma_N B_0 B_N \alpha'^2 (1 - n^2) \mid \psi_2 s(\text{o}) \mid^2 \tag{5}$$

where $\mid \psi_2\, s(\text{o}) \mid^2$ is the value of the nitrogen $2s$ function at the nucleus which is estimated[16] to be $33.4 \times 10^{24}\,\text{cm}^{-3}$.

Using the expression,[17]

$$\alpha^2 = 7/4 \left[\frac{\mid A_\parallel^{\text{Cu}} \mid}{P} - \frac{\mid A_{\text{iso}}^{\text{Cu}} \mid}{P} + 2/3 g_\parallel - 5/21 g_\perp - 6/7 \right] \tag{6}$$

setting $P = 0.036\ \text{cm}^{-1}$ and with the spin-Hamiltonian parameters we obtain $\alpha^2 = 0.728$. If it is assumed that the copper nitrogen bond distances are 1.95 Å and that the hybridization of the nitrogen bonding orbitals is sp^2 then $S = 0.088$[18]. The normalization condition then gives $\alpha'^2 = 0.362$. Using equation (5) and setting $n^2 = 0.667$ we calculate $A_{\text{iso}}^N = 16.0 \times 10^{-4}\ \text{cm}^{-1}$, in good agreement with the pyrrole value. The smaller observed isotropic splitting for the imine nitrogens could be due to a p:s ratio on the nitrogen greater than two and/or a copper nitrogen distance greater than 1.95 Å. Since the overlap integral is a function of both the bond distance and the hybridization we hesitate to calculate a coupling constant without knowledge of the bond distance.

The fractional ls electron hole associated with the methine protons is obtained from

$$p_H = \frac{A_{\text{iso}}^H}{a_{\text{H}}} \tag{7}$$

where a_H is the hyperfine splitting constant for the hydrogen atom. Using the value[19] $a_H = 0.0474 \text{ cm}^{-1}$ and obtaining A^H_{iso} using $(A_N)_{/2} + 1G$ as the in-plane methine proton splitting, a value of 0.017 is found. This choice for in-plane proton splitting leads to a ratio of P_H in this complex to the value found for Cu[en(sal)$_2$][20] of 1.13. This is the same as the ratio of α'^2 for the two complexes.

DISCUSSION

If the crystallographic space group is $P_{\bar{1}}$, crystallographic symmetry would demand the occurrence of one magnetic site since the two molecules in the unit cell would be related by an inversion center. This assumption has been critical to the analysis of the superhyperfine splitting. The possibility that the complex superhyperfine pattern partially arises from slightly inequivalent magnetic sites has not been considered. The occurrence of the space group P_1 in a crystal of this chelate seems unlikely and the good agreement between the observed and calculated spectra is good indication that it does not occur here.

The d_{xy} orbital transforms in the molecular point group $C_{2v}^{(x)}$ as the irreducible representation B_2 while the $d_{x^2-y^2}$ and the d_{z^2} orbitals transform as A_1. In this type of copper complex in-plane g-anisotropy is expected to be small, due mainly to the difference in energies of the $d_{xz}{\to}d_{xy}$ and the $d_{yz}{\to}d_{xy}$ transitions.[22] Accordingly, the amount of rhombic character in the g-tensor in our previous studies[13,20,21] of tetradentate complexes of the cis "N_2O_2" type has been found to be small, usually within experimental uncertainty. We therefore expect that we have lost no pertinent information by collecting data in only two planes for the system reported in this study.

The g-values and copper hyperfine splitting values found for this complex are similar to those observed in copper pthalocyanin[23] and copper porphyrins[24]. The imino nitrogen splitting values are similar to those obtained in our previous studies on the cis "N_2O_2" complexes while the pyrrole nitrogen values are reminiscent of those found for copper pthalocyanin.[25]

It is interesting to note that the smaller value of g_z reported[8] for N,N'-bis-(o-aminobenzaldehyde) ethylenediimino Cu(II) should be indicative of greater covalency in that compound. The use of equation (6) and the magnetic parameters give $\alpha^2 = 0.747$ implying less covalency in that compound. As previously observed,[21] $|A^{\text{Cu}}|$ increases with greater covalency rather than decreasing as expected.

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APPENDIX

The data from each of the two planes was fit to the usual equation via a least square analysis.

$$g_e^2 = \alpha_i + \beta_i \cos 2\theta + \gamma_i \sin 2\theta \qquad (8)$$

Here i is the axis of rotation and θ is the rotation angle, not necessarily the angle the magnetic field makes with an axis in the plane. If we take the xz plane to be a principal plane and the xy plane to be another plane of rotation, it follows that $g_{xy}^2 = g_{yz}^2 = 0$ and the remaining g-tensor elements are given by

$$\begin{aligned} g_{xx}^2 &= \alpha_z + \left| (\beta_z^2 + \gamma_z^2)^{1/2} \right| \\ g_{yy}^2 &= \alpha_z - \left| (\beta_z^2 + \gamma_z^2)^{1/2} \right| \\ g_{zz}^2 &= 2\alpha_y - \alpha_z - \left| (\beta_z^2 + \gamma_z^2)^{1/2} \right| \\ g_{xz}^2 &= [\beta_y^2 + \gamma_y^2 - 1/4(g_{zz}^2 - g_{xx}^2)^2]^{1/2} \end{aligned} \qquad (9)$$

The sign of g_{xz}^2 is positive if g_e^2 reaches a maximum between the x and z axes and negative if it reaches a minimum. Our α, β and γ's relate to Billings and Hathaway's[14] a, b and c's as follows: $\alpha = a/2$, $\beta = b$, and $\gamma = c$. We have chosen this convention because a fit of the experimental data to equation (8) gives $\alpha = 1/2(A + B)$ and not $A + B$. Using this convention equations (2) of reference 14 appear without the 1/2 and equations (3) without the 1/4.

If xz is indeed a principal plane, then the three g-values and their directions are determined. It is possible for the g-tensor to be rhombic with only g_z lying in the xz plane. For this case, the average of the two in-plane g-values determined by this method will be the same as the average of the actual two-plane g-values ($g_\perp$). No information would be lost in determining bonding parameters since the usual expressions require only $g_\perp$. If the g-tensor is axially symmetric then each in-plane g-value will still have associated with them a specific direction. Upon diagonalizing the g-tensor, the direction obtained for g_x is where the coordination plane intersects the xz plane and g_y is taken to lie along the y-axis.

Since $g_{xy}^2 = 0$ the expression for the angle of misalignment[25] in the xy plane simplifies to

$$\delta\theta_z = \pm 1/2 \text{ arc tan } |\gamma_z/\beta_z| \qquad (10)$$

The angle of misalignment in the xz plane can be determined from

$$\delta\theta_y = \pm 1/2 \left[\text{arc cos} \left| \frac{(g_{zz}^2 - g_{xx}^2)}{2(\beta_y^2 + \gamma_y^2)^{1/2}} \right| - \text{arc tan } |\gamma_y/\beta_y| \right] \qquad (11)$$

where the signs are those of γ/β.