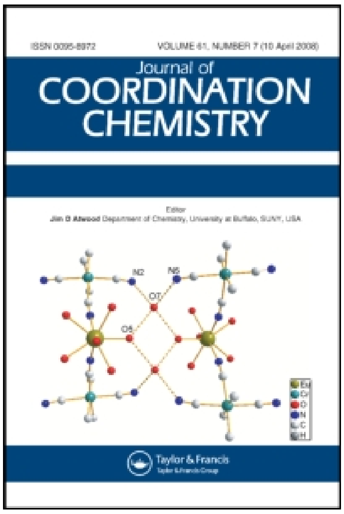

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THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER(II)

IX. N,N′-BIS(2-HYDROXYBENZOPHENONE)ETHYLENEDIIMINE†

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The EPR spectrum of a single crystal of ^{63}Cu(II) doped Ni(II) N,N′-bis(2-hydroxybenzophenone)ethylenediimine was studied at X-band. At most orientations of the crystal in the magnetic field one set of four copper hyperfine lines was observed, indicating that the chelate planes are nearly parallel. When the applied magnetic field was aligned in directions approximately parallel to the molecular planes an unusual ligand superhyperfine splitting of the copper hyperfine components was seen. This splitting pattern was simulated successfully by assuming it to be the result of a combination of anisotropic ligand hyperfine coupling and the presence of two nearly equivalent magnetic sites differing only in the orientations of their in-plane magnetic directions.

The usual doublet spin-Hamiltonian parameters measured for this compound were $g'_x = 2.046 \pm 0.004$, $g'_y = 2.043 \pm 0.004$, $g_z = 2.188 \pm 0.002$, $A'_x = 30.6 \times 10^{-4}$ cm^{-1}, $A'_y = 30.5 \times 10^{-4}$ cm^{-1}, and $A_z = 204.5 \times 10^{-4}$ cm^{-1}.

The in-plane values, g'_x, A'_x, g'_y, A'_y are those measured in directions midway between the two magnetic sites in the crystal.

KEY WORDS: N,N′-bis(2-hydroxybenzophenone)ethylenediimine Cu(II), single crystal, EPR spectrum, Spin Hamiltonian parameters, ligand hyperfine splitting anisotropy.

INTRODUCTION

Over the past several years, the EPR spectra of a series of Cu(II) tetradentate Schiff-base complexes have been studied in this laboratory in an attempt to ascertain the changes in metal-ligand bonding resulting from changes in the ligand structure. Results of nine such studies of compounds in which the immediate Cu(II) environment consists of two cis-nitrogen and two oxygen atoms have been analyzed to show that the isotropic hyperfine constant, χ, is indeed constant for this group of chelates.[1] Analysis of the EPR spectrum of another compound in this series, N,N′-bis(2-hydroxybenzophenone)ethylenediimine copper(II) doped into a single crystal of the corresponding nickel(II) complex is reported here. The structure is shown in Figure 1.

In certain crystal orientations with respect to the external magnetic field, unusual ligand hyperfine splittings are observed and accounted for. The χ value is correlated with those for the other similar Schiff-base chelates.

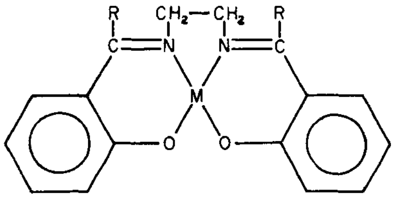

FIGURE 1 N,N′-bis(2-hydroxybenzophenone M(II)) R = C_6H_5.

EXPERIMENTAL

Ligand synthesis N,N′-bis(2-hydroxybenzophenone)ethylenediimine ((phen sal)$_2$en).

To a solution of 0.002 mole of 2-hydroxybenzophenone in methanol was added 6.0 g of a 10% aqueous solution of ethylenediamine (0.01 mole). This mixture was boiled gently for 1/2 hour and allowed to cool slowly. The pale yellow product was recrystallized from methanol (m.p. 169–169.5°C).

Synthesis of complexes 0.05 mole of Ni(II) acetate doped with approximately 1% ^{63}Cu (NO$_3$)$_2$ was dissolved in methanol and added dropwise to a boiling solution of 0.05 mole of ligand in chloroform.

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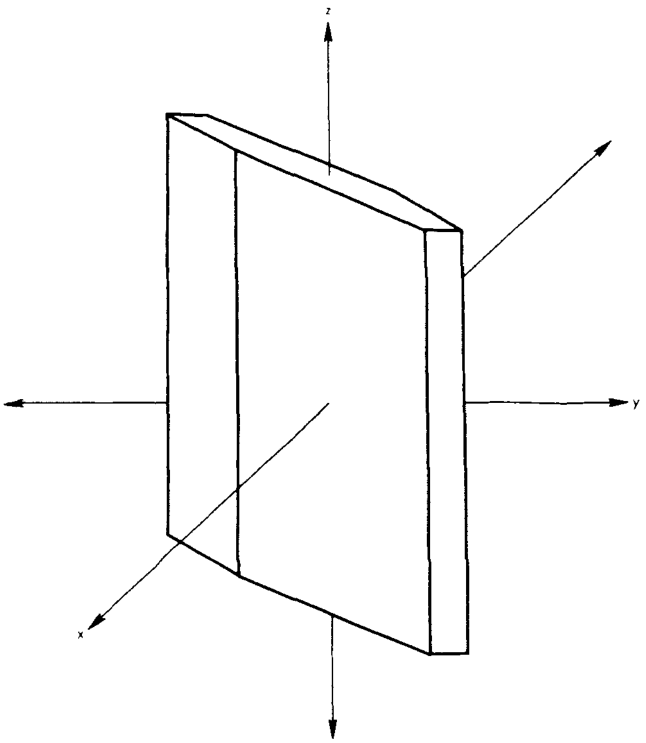

FIGURE 2 Ni(phen sal)$_2$en crystal morphology.

A red product was obtained which was recrystallized from methylene chloride. Single crystals of the compound were grown by slow evaporation from a methylene chloride solution. The crystals were dark red parallelogram shaped plates with a flattened hexagonal cross section. The Cu(II) complex of (phen sal)$_2$ en was synthesized in an analogous manner. Single crystals of this compound are also easily grown from methylene chloride solution.

Figure 2 shows the external morphology of the ^{63}Cu(II) doped Ni(II) (phen sal)$_2$ en crystal and the laboratory axes chosen. EPR spectra were recorded at 5° increments about each of these axes. The method of data collection and data reduction have been described previously.[2]

RESULTS

The parameters of the usual doublet spin-Hamiltonian measured for the single crystal of ^{63}Cu(II) doped Ni(II)(phen sal)$_2$ en are given in Table I. Values of g'_x, g'_y, A'_x, and A'_y are those measured midway between two nearly equivalent magnetic sites in the crystal. Molecular orbital coefficients were calculated assuming local C_{2v} symmetry about the Cu(II) ions.[1,2] The results of these calculations along with a value of χ determined using the methods in Ref. 1 are listed in Table II.

TABLE I
Spin Hamiltonian Parameters (phen sal)$_2$en Cu(II)

$g'_x = 2.046 \pm 0.004$
$g'_y = 2.043 \pm 0.004$
$g_z = 2.188 \pm 0.002$

$A'_x = 32.0 \pm 2.0\ \text{G} = 30.6 \times 10^{-4}\ \text{cm}^{-1}$
$A'_y = 32.0 \pm 2.0\ \text{G} = 30.5 \times 10^{-4}\ \text{cm}^{-1}$
$A_z = 200.2 \pm 1.0\ \text{G} = 204.5 \times 10^{-4}\ \text{cm}^{-1}$

	Direction cosines		
	x	y	z
g'_x	0.981	−0.187	−0.042
g'_y	0.162	0.835	−0.526
g_z	0.134	0.510	0.850

At all orientations of the crystal with respect to the magnetic field one set of four copper hyperfine lines was observed, indicating that all of the chelate planes are essentially parallel. However, at orientations for which the applied field was in the vicinity of the perpendicular magnetic axes an unusual distortion of the 5-line, superhyperfine pattern due to the two equivalent cis-nitrogens of the ligand was observed. An example of this is shown in Figure 3a. It is assumed that these observations result from a combination of an anisotropic ligand hyperfine interaction and the presence of two slightly differing non-equivalent magnetic sites.in the crystal. The anomalous pattern cannot be explained by use of either of these mechanisms alone, but has been simulated using both effects simultaneously, as shown in Figure 3b. This simulation was obtained by taking $A_1^n \cong 12.7$ G, $A_2^n \cong 16.0$ G, $\Delta H_{1/2}$ = 1.75G (first derivative Gaussian lineshape taken out to four half-widths) and a shift of approximately 2.5 G between the two components arising from the non-equivalent magnetic sites.

Due to the poor resolution of the two inequivalent sites in the EPR spectra, only the average of the two sites could be measured. Therefore, the spin Hamiltonian parameters and direction cosines reported in

TABLE II
Molecular Orbital Coefficients and χ

$\alpha^2 = 0.789$
$\alpha'^2 = 0.293$
$\beta^2 = 0.733$
$\chi = -3.932$

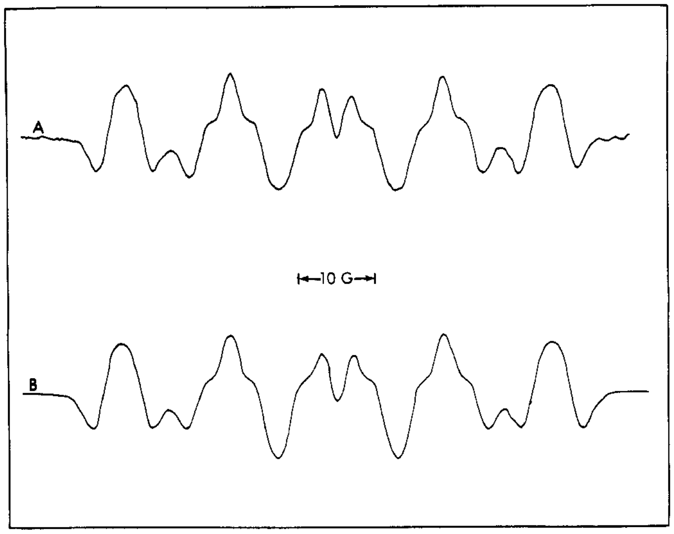

FIGURE 3 Observed (A) and simulated (B) spectra $\Delta M_I = +1/2$ hyperfine line, external magnetic field oriented near *xy* plane.

Table I are not those of the individual complexes, but those corresponding to directions approximately midway between the two sets of molecular magnetic axes. When the applied magnetic field was oriented parallel to the g_z direction in the crystal, the ligand nitrogen superhyperfine splitting pattern is very sharp and the relative intensities of the five components are very close to the expected 1:2:3:2:1 intensity ratios, so the g_z and A_z axes of the two magnetic sites must be very nearly parallel. Thus, the reported values g_z' and A_z' correspond closely to g_z (molecular) and A_z (molecular) respectively. The actual directions of the in-plane magnetic axes of the two sites, however, are rotated by some unknown angles $\pm \theta$ with respect to the measured directions of g_x' and g_y'. This structural feature was also observed in single crystals of Cu(II) doped Ni(II)-(tfacac)$_2$en.[2-4]

The molecular orbital coefficients[2,5] and χ value[1] calculated for Cu(phen sal)$_2$en are given in Table II.

DISCUSSION

The values of the M.O. coefficients are quite similar to those of similar complexes. The value $\chi = -3.932$ is very close to the mean value for ten other Schiff-base complexes in which the immediate Cu(II) environment is the same. The similarity of the M.O. coefficients and the χ-value rule out a solvent adduct, for adducts do affect the value of the bonding parameters.[1]

The linewidth anistropy of the EPR lines observed from a single crystal of the pure Cu(II) complex was examined for possible one-dimensional behavior. The linewidth along the suspected chain direction (the greatest linewidth) appeared to arise from two slightly different magnetic sites. This cannot be confirmed because no crystal structure data is available.

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