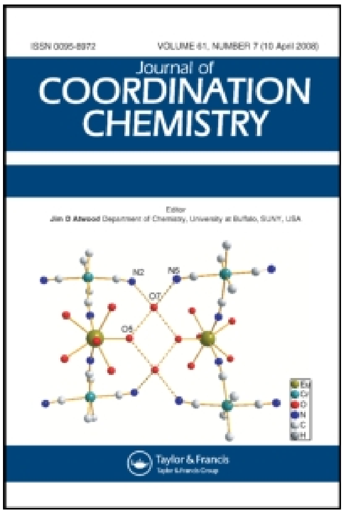

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE EPR SPECTRA OF TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER(II). VII: N, N'-BIS(2-HYDROXYACETOPHENONE)-1,3-PROPANEDUMINE

Michele I. Sculi Ane[ab]; Harry C. Allen Jr.[a]
[a] Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, MA., USA [b] Department of Chemistry, University of New Hampshire, Durham, N.H.

To cite this Article Ane, Michele I. Sculi and Allen Jr., Harry C.(1978) 'THE EPR SPECTRA OF TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER(II). VII: N, N'-BIS(2-HYDROXYACETOPHENONE)-1,3-PROPANEDUMINE', Journal of Coordination Chemistry, 8: 2, 87 — 91

To link to this Article: DOI: 10.1080/00958977808073076

URL: http://dx.doi.org/10.1080/00958977808073076

J. Coord. Chem.
1978, Vol. 8, pp. 87–91

THE EPR SPECTRA OF TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER(II). VII: N,N′-BIS(2-HYDROXYACETOPHENONE)-1,3-PROPANEDUMINE†

MICHELE I. SCULIANE‡ and HARRY C. ALLEN, JR.

Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, MA., USA

(*Received December 20, 1977*)

The EPR spectra of single crystals of the tetrahedrally distorted tetradentate Schiff base complex, N,N′-bis(2-hydroxyacetophenone)-1,3-propanediimine Cu(II) and of its ^{63}Cu(II) doped Ni(II) analogue were studied in an attempt to determine the effects of the tetrahedral distortion on the spin-Hamiltonian parameters and molecular orbital coefficients of the complex. The parameters in the usual doublet spin-Hamiltonian were found to be: Cu(II) complex; $g_x = 2.052 \pm 0.004, g_y = 2.048 \pm 0.004, g_z = 2.225 \pm 0.002$; ^{63}Cu(II) doped Ni(II) complex; $g_x = 2.045 \pm 0.004$, $g_y = 2.043 \pm 0.004, g_z = 2.216 \pm 0.002, A_x = 35.0 \times 10^{-4}$ cm^{-1}, $A_y = 30.2 \times 10^{-4}$ cm^{-1}, $A_z = 190.4 \times 10^{-4}$ cm^{-1}. It was found that although g_z seems to be unusually high, and A_z unusually low, the values of the molecular orbital parameters and of the isotropic contact term fall within the range found for similar compounds which are not tetrahedrally distorted.

KEY WORDS: N,N′-bis(2-hydroxyacetophenone)-1,3-propanediimine Cu(II), EPR spectrum, Spin-Hamiltonian parameters, χ-value, Tetrahedral distortion, one-dimensional magnetic character.

INTRODUCTION

Several tetradentate Schiff-base complexes of Cu(II), in which the immediate environment of the Cu(II) is essentially square planar and consists of N_2O_2 with the nitrogens in cis positions, have been studied,[1] e.g., see Fig. 1. It was found that the molecular orbital coefficients for the compounds in this series are remarkably similar.

Values of:

$$\chi = \frac{4\pi}{s}\left\langle \psi \left| \sum_i \delta(ri) S_{zi} \right| \psi \right\rangle$$

defined by Abragam, Horowitz and Price[2] and postulated to be essentially constant for the first row transition elements also are found to be remarkably constant and do not seem to depend upon ligand substitution or bridging groups.[1] In general, χ has not been found to be very constant even among complexes of the same ion.[3]

Some of the chelates investigated[1,4] have shown unusually high values of g_z and low values of A_z as well as a lowering of the frequency of the ligand field transition, $|xy\rangle \rightarrow |x^2 - y^2\rangle$. Similar effects[5] were observed in tetradentate ligand complexes of Cu(II) in which the immediate Cu(II) environment is N_4. It was postulated that such effects might be due to a tetrahedral distortion[5] of the normally square-planar environment of the Cu(II).

The crystal structure of N,N′-bis(2-hydroxyacetophenone)-1,3-propanediimine Cu(II) [Cu(acetpn)] has been determined by Iida *et al.*[6] They found a considerable tetrahedral distortion of the immediate environment of the Cu(II) ion as evidenced by a dihedral angle of 37° between the N(1)–Cu–O(1) and N(2)–Cu–O(2) planes. This distortion corresponds to a structure approximately midway between square planar (dihedral angle = 0) and tetrahedral (dihedral angle = 90°).

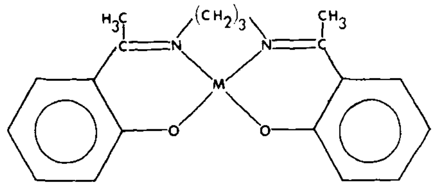

FIGURE 1 Molecular formular of N,N′bis(2-hydroxyacetophenone)-1,3-propanediimine M(II)[M(II)(acetpn)].

---

†Supported by the U.S. Bureau of Mines, Department of Interior under Grant G0166203

‡Present address. Department of Chemistry, University of New Hampshire, Durham, N.H. 03824

Since the structure of the Cu(II) complex is known it seemed appropriate to investigate the EPR and optical spectra to confirm the effect of a tetrahedral distortion on them.

Experimental

In order to obtain data regarding the coupling between the unpaired electron and the copper nucleus, it is necessary to use a magnetically dilute sample. Although no structural data were found for the Ni(II) chelate, the diamagnetic Ni(II) was chosen as the host lattice. The pure copper complex was also synthesized.

Synthesis[8, 9]

Ligand 2-hydroxyacetophenone (Eastman Kodak Co.) and 1,3 diaminopropane (Eastman Organic Chemicals) were reacted in ethanol in a 2:1 molar ratio. The resulting light yellow compound was recrystallized from ethanol.

Cu(II) complex An ethanol solution of copper acetate (Fisher Scientific Company) was added dropwise to boiling ethanol solution of the ligand (1:1 molar ratio). Single crystals of the dark blue complex were grown by slow evaporation of an acetone solution. Cu(acetpn) crystallized as parallelogram-shaped plates with a hexagonal cross section (Fig. 2).

^{63}Cu(II) doped Ni(II) complex A solution of nickel acetate (J. T. Baker Chemical Co.) in ethanol doped with approximately 1% $^{63}Cu(NO_3)_2$ was used in place of the copper acetate in the above procedure. Dark red single crystals in the form of square rods were obtained from an acetone solution by slow evaporation (Fig. 3).

Data Acquisition and Reduction

Descriptions of the instrumentation used in obtaining the EPR data and of the method of data reduction have been previously published[10].

First derivatives of the EPR spectrum were recorded at 10° increments in the three orthogonal planes of the Cu(acetpn) crystal indicated in Figure

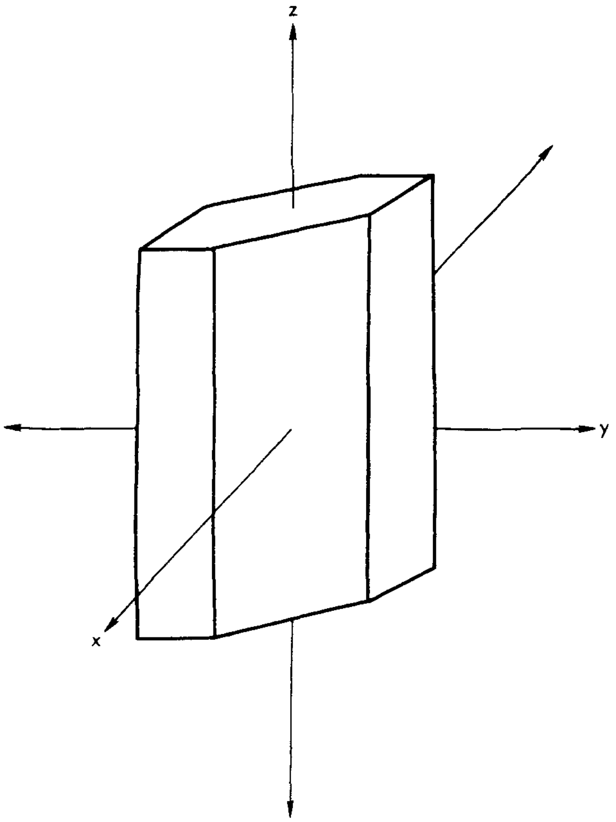

FIGURE 2 Crystal morphology and laboratory axes of Cu(II) (acetpn) single crystal. The crystallographic axes are related to the laboratory axes as follows: $x = b, y = a, c = z$.

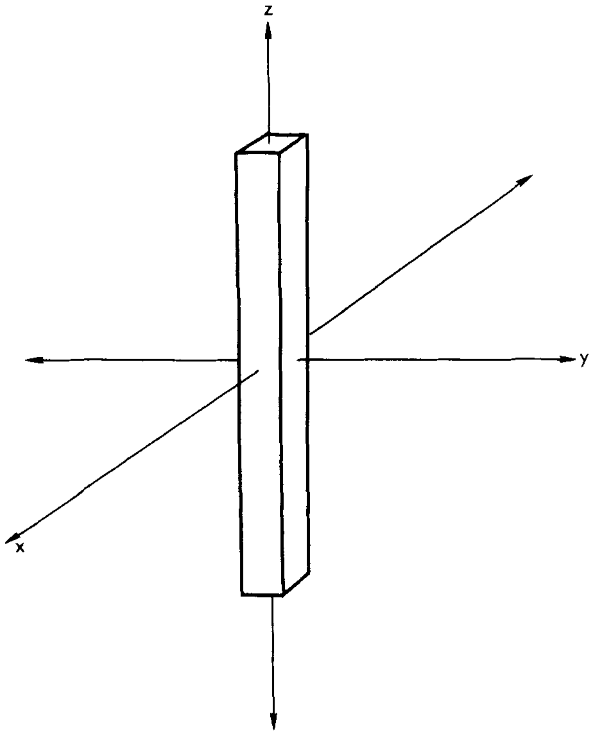

FIGURE 3 Crystal morphology and orientation of laboratory axes for single crystal of ^{63}Cu(II) doped Ni(II) (acetpn).

2. A first derivative presentation was recorded because measurements of the peak-to-peak linewidths were of interest as were the fields at the absorption peaks. In the case of the ^{63}Cu(II) doped crystal the second derivative of the EPR spectrum was recorded at 5° increments in planes perpendicular to the three orthogonal axes indicated in Figure 3. The optical spectrum of the Copper(II) complex was run on a Cary 14 spectrophotometer in both chloroform and acetone solutions. The solvent did not have a measurable effect on the spectrum.

RESULTS

The parameters in the usual doublet spin-Hamiltonian[10] were determined for both the Cu(II)(acetpn) and ^{63}Cu(II) doped Ni(II)(acetpn) crystals. The results are listed in Table I. Direction cosines relating the laboratory axes to the magnetic axes in the ^{63}Cu(II) doped crystal for the two sites measured are given in Table II. Two similar sites are related to these by a rotation of ~90° about the z-axis, reflecting the 4-fold symmetry of the crystal. Values of the molecular orbital coefficients[10] for ^{63}Cu(II) doped Ni(II)(acetpn), calculated assuming an essentially square planar geometry, are listed in Table III. The χ value is also given.

TABLE I
Spin Hamiltonian parameters

^{63}Cu doped Ni(acetpn)	Cu(II)(acetpn)
g_x 2.045 ± 0.004	g_x 2.052 ± 0.004
g_y 2.043 ± 0.004	g_y 2.048 ± 0.004
g_z 2.216 ± 0.002	g_z 2.225 ± 0.004
A_x 36.7 ± 2G = 35.0 x 10^{-4} cm^{-1}	
A_y 31.7 ± 2G = 30.2 x 10^{-4} cm^{-1}	
A_z 184.0 ± 1G = 190.4 x 10^{-4} cm^{-1}	

TABLE II
^{63}Cu(II) doped Ni(II)(acetpn)
direction cosines of sites measured†

	x	y	z
g_x	0.991	−0.036	−0.126
g_y	0.001	0.945	−0.327
g_z	0.131	0.324	0.937
g_x	0.980	0.112	−0.165
g_y	0.141	−0.942	−0.306
g_z	0.121	−0.323	0.939

†Two additional magnetic sites are related to these by a rotation approximately 90° about the z axis.

TABLE III
Molecular orbital coefficients†

α^2	0.771
α'^2	0.311
β^2	0.797
K	0.0124
χ	−3.937

†^{63}Cu(II) doped Ni(II)(acetpn)

EPR and Crystal Structure

Upon examination of the angular dependence of the single crystal EPR spectra of ^{63}Cu(II) doped Ni(II)(acetpn), it becomes evident that there are four distinct magnetically inequivalent sites oriented with their z-axes (perpendicular to molecular planes) lying nearly in the xz and yz planes and ±20° from the z-axis of the crystal (Fig. 3). Each of these sites is split further into two sites at certain orientations of the crystal in the magnetic field. This is probably due to non-alignment of the respective x and y magnetic axes of alternating molecules in the stacks along the z axis.

The crystal structure of the doped Ni(II)(acet)-1,3-pn complex is obviously quite different from that of the pure Cu(II) complex, in which it was found that all of the molecular planes are parallel.[6] In the pure Cu(II)(acetpn) a single EPR line was observed at all orientations of the crystal in the magnetic field, as would be expected from the crystal structure.

It is also noted that these crystals contain linear chains of Cu(II) ions with an intrachain separation of about 5.3 Å and a nearest interchain distance of 9.467 Å.[6] The variation of the linewidth in the yz (ac) plane (see Figure 3), is shown in Figure 4. The linewidth anisotropy is remarkably similar to that observed[11] in N,N′-bis(trifluoroacetylacetone)ethylenediimine Cu(II). The intrachain coupling is weaker than in Cu en(tfhex)$_2$ as indicated by the smaller maximum ΔHpp ~ 90 gauss. A complete analysis of the one-dimensional behavior was not attempted because it was felt that the A-values obtained from the analysis of the spectrum of the magnetically dilute crystal could not safely be transferred for use in the crystal of the pure copper complex due to the difference in crystal structures.

DISCUSSION

The higher g-values and lower frequency of the $|xy\rangle \rightarrow |x^2 - y^2\rangle$ transition are consistent with the

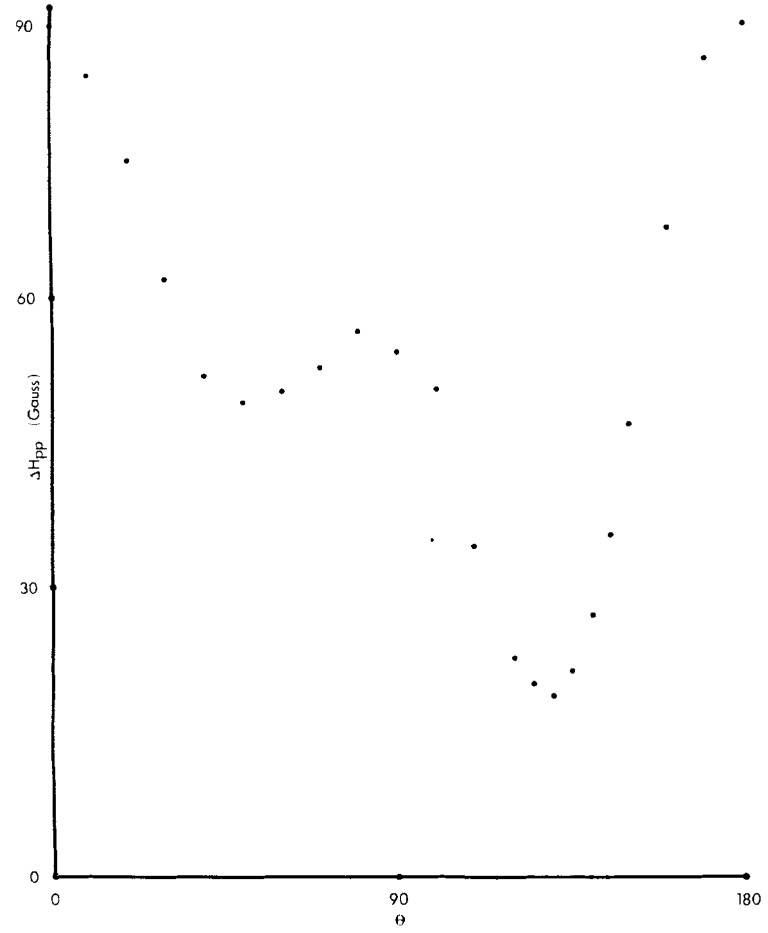

FIGURE 4 Angular dependence of linewidth of 1st derivative EPR signal in single crystal of Cu(II)(acetpn); *yz*(ac) plane.

tetrahedral distortion found in the crystal structure determination. Unfortunately in a magnetically concentrated crystal the principal values of the A-tensor cannot be determined experimentally so there is not sufficient data to calculate the molecular orbital coefficients.

The *g*-values for the copper-doped nickel complex indicate a lesser distortion. This is not surprising since nickel prefers a square planar environment even when the central chelate ring has seven or eight atoms.[7] In the doped crystal, the Cu(II) tends to adopt the environment preferred by the nickel. The magnetic parameters indicate that there is still some distortion. If it is assumed that the distortion is small, so that the usual square planar molecular orbitals are a good approximation, one can then calculate the m.o coefficients and a value for χ. The results of such a calculation are shown in Table III. The method described in reference 1 was used to determine the parameters. The m.o. coefficients are remarkably similar to those found in nine other chelates with the same immediate chemical environment about the Cu(II) ion[1] The χ-value, $\chi = -3.937$ compares favorably with the average value of $\chi = 3.917$ reported for the nine similar complexes.

This result is perhaps not too surprising. Sharnoff has shown that for tetrahedral bonding to the metal ion, the ground state 3d-orbital can mix with the 4p-orbitals.[12] The 4p-orbitals contribute dipolar terms to the A-values which are of opposite sign to the contribution from the 3d orbital. This type of mixing will be present in tetrahedrally distorted, square planar environments and would account for the generally lower A-values observed here. Sharnoff has also shown that the small dipolar terms are due primarily to an admixture of 4p-orbitals rather than a large covalency of the bonds. This is reflected in the similarity of the m.o. coefficients of Cu(acetpn) to those of other complexes with the same immediate chemical environment of the Cu(II) ion.

ACKNOWLEDGMENTS

One of us (MIS) would like to thank the Lever Brothers Foundation for summer support and an equipment grant from the Research Corporation is acknowledged.

REFERENCES

1. H. C. Allen, Jr. and M. I. Scullane, to be published.
2. A. Abragam, J. Horowitz and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A230**, 169 (1955).
3. B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).
4. M. I. Scullane and H. C. Allen, Jr., *J. Coord. Chem.*, in press.
5. G. A. Bowmaker, T. N. Waters and P. E. Wright, J. C. S. Dalton 867 (1975).
6. K. Iida, I. Ooniski, A. Nakahara and Y. Komiyama, *Bull. Chem. Soc., Japan*, **43**, 2347 (1970).
7. J. Weber, *Inorg. Chem.*, **6**, 258 (1967).
8. P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 85 (1933).
9. T. Nakao, N. Nonagase and A. Nakahara, *Bull. Chem. Soc., Japan*, **42**, 452 (1969).
10. R. L. Lancione, H. C. Allen, Jr. and D. R. Sydor, *J. Coord. Chem.*, **4**, 153 (1975).
11. M. I. Scullane and H. C. Allen, Jr., *J. Mag. Res.*, **26**, 119 (1977).
12. M. Sharnoff, *J. Chem. Phys.*, **41**, 2203 (1964); **42**, 3383 (1965).