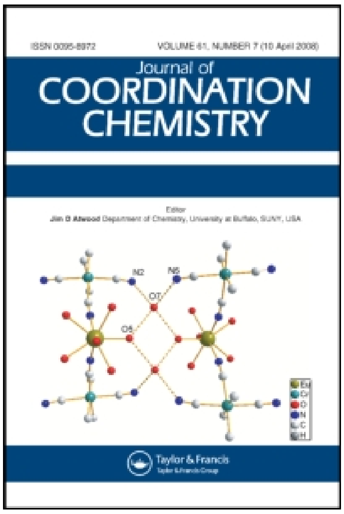

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THE ISOTROPIC HYPERFINE INTERACTION IN SOME TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER (II)

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THE ISOTROPIC HYPERFINE INTERACTION IN SOME TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER (II)[†]

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The isotropic hyperfine constant is investigated for a series of tetradentate Schiff-base complexes of Copper II. In this series the immediate copper environment is essentially square planar and consists of two oxygen and two nitrogen atoms in cis positions. The constancy of χ, which is proportional to the hyperfine constants, indicates that it is quite independent of ligand substitution, depending mainly on the immediate environment of the Cu(II).

KEY WORDS: Tetradentate Schiff-base complexes of Cu(II); isotropic hyperfine interaction; χ-value, N_2O_2 Cu(II) environment.

INTRODUCTION

The isotropic contact term in the hyperfine interaction of paramagnetic ions has been of considerable interest.[1,2] The parameter, χ, as proposed by Abragam, Horowitz and Price,[3]

$$\chi = \frac{4\pi}{S}\left(\psi\,\middle|\,\sum_i \delta(r_i)S_{zi}\,\middle|\,\psi\right), \tag{1}$$

is negative and has been postulated to be of nearly constant magnitude for a large number of compounds of the first transition element series.

McGarvey has made an exhaustive correlation of the χ-values for the first row transition elements making use of data, mainly single crystal data, that are available in the literature. He has shown that the value of χ can vary by as much as 30% depending upon the ligand, host lattice and geometry of the chelate. Over the past several years the EPR spectra of single crystals of several tetradentate Schiff-base complexes of Cu(II) have been studied in this laboratory. In each case, the diamagnetic host lattice has been the corresponding Ni(II) chelate and only the ^{63}Cu isotope was present.[4–9] The data have all been reduced in a consistent manner by the method of Geusic and Brown[10] as modified by Billings and Hathaway.[11] In view of this existing body of data, it seems appropriate to examine the behavior of χ in this series of Cu(II) complexes.

THEORETICAL BACKGROUND

The complexes under consideration generally have a local symmetry about the copper ions that belongs to the point group C_{2V}. The form of the molecular orbitals appropriate to this point group have been given previously[12] and are reported below in order to develop a consistent notation,

$$\begin{aligned}
\psi_{\beta_2} &= \alpha\,|xy\rangle - \alpha'\,|\beta_2\rangle \\
\psi_{A_1}{}^{a} &= \beta\,|x^2-y^2\rangle - (1-\beta^2)^{1/2}\,|A_1{}^{a}\rangle \\
\psi_{A_1}{}^{b} &= \gamma\,|z^2\rangle - (1-\gamma^2)^{1/2}\,|A_1{}^{b}\rangle \\
\psi_{A_2} &= \delta'\,|yz\rangle - (1-\delta'^2)^{1/2}\,|A_2\rangle \\
\psi_{\beta_1} &= \delta''\,|xz\rangle(1-\delta''^2)^{1/2}\,|\beta_1\rangle
\end{aligned} \tag{2}$$

The part of the wave functions represented by $|\beta_2\rangle$, $|A_1{}^a\rangle$ etc. represents the appropriate normalized linear combination of ligand orbitals transforming according to the irreducible representation indicated. The ψ_{β_2} which contains the unpaired electron is subject to the normalization condition;

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1, \tag{3}$$

in which the overlap is explicitly included.[14]

The principal values of the g- and A-tensors in the usual doublet state spin-Hamiltonian are related to the free-ion spin-orbit coupling constant, the electronic

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energy levels and the molecular orbital coefficients through the relations.[2,13,14]

$$(g_z - 2.0023) = -8\rho\,[\alpha\beta - \alpha'\beta S - 2^{-1}\alpha'(1-\beta^2)^{1/2}T(n)] \tag{4a}$$

$$(g_x - 2.0023) = -2\mu\,[\alpha\delta'' - \alpha'\delta'' S - 2^{-1/2}(1-\delta''^2)^{1/2}T(n)] \tag{4b}$$

$$(g_y - 2.0023) = -2\mu'[\alpha\delta' - \alpha'\delta' S - 2^{-1/2}(1-\delta'^2)^{1/2}T(n)], \tag{4c}$$

where

$$\rho = \frac{\lambda_0\alpha\beta}{\Delta_{x^2-y^2}} \qquad \mu = \frac{\lambda_0\alpha\delta''}{\Delta_{xz}} \qquad \mu' = \frac{\lambda_0\alpha\delta'}{\Delta_{yz}}$$

and $T(n)$, an integrand over ligand orbitals, has been defined previously.[14]

For the principal A-values the following relations are found to hold.

$$A_z = -K - \tfrac{4}{7}\alpha^2P + (g_z - 2.0023)PZ_z + \tfrac{3}{14}(g_x - 2.0023)PZ_x + \tfrac{3}{14}(g_y - 2.0023)PZ_y \tag{5}$$

$$A_x = -K + \tfrac{2}{7}\alpha^2P + \tfrac{11}{14}(g_x - 2.0023)PZ_x$$

$$A_y = -K + \tfrac{2}{7}\alpha^2P + \tfrac{11}{14}(g_y - 2.0023)PZ_y,$$

in which

$$Z_z = \frac{\alpha\beta}{[\alpha\beta'' - \alpha'\beta S - 2^{-1}(1-\beta^2)^{1/2}T(n)]}$$

$$Z_x = \frac{\alpha\delta''}{[\alpha\delta'' - \alpha'\delta'' S - 2^{-1/2}\alpha'(1-\delta''^2)^{1/2}T(n)]} \tag{6}$$

$$Z_y = \frac{\alpha\delta'}{[\alpha\delta' - \alpha'\delta' S - 2^{-1/2}(1-\delta'^2)^{1/2}T(n)]};$$

$$P = 2.0023g_N\beta\beta_N(\mathrm{r}^{-3})av \tag{7}$$

In (7), β, β_N are the Bohr magneton and nuclear magneton respectively. K is the isotropic contact term.

In the complexes under consideration, the g- and A-values exhibit approximate axial symmetry, hence a higher molecular symmetry is assumed. This higher symmetry implies that the energies associated with ψ_{A_2}, ψ_{B_1} are essentially the same. Letting $g_x = g_y = g_\perp$ and $A_x = A_y = A_\perp$ and $g_z = g_\parallel$ the following relations among the A_i can be written;

$$A_\parallel - A_\perp = \tfrac{6}{7}\alpha^2P + (g_\parallel - 2.0023)PZ_\parallel - \tfrac{5}{14}(g_\perp - 2.0023)PZ_\perp \tag{8}$$

$$A_\parallel + 2A_\perp = -3K + (g_\parallel - 2.0023)PZ_\parallel + 2(g_\perp - 2.0023)PZ_\perp \tag{9}$$

In the approximation $Z_\parallel = Z_\perp = 1$, Eqn. 9 reduces to

$$(A)_{av} = -K + (g_{av} - 2.0023)P,$$

Thus, as g_{av} increases the value of $(A)_{av}$ will be smaller in absolute magnitude.

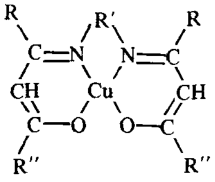
The isotropic contact term, K, is related to χ through the relation,[2]

$$\chi = -\frac{3}{2}\left(\frac{hca_0^3}{2.0023g_N\beta\beta_N}\right)K,$$

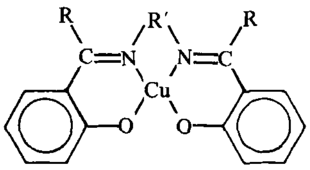
in atomic units. The values for the parameters used in this work are those in general use:[14] i.e., $P = 3.60 \times 10^{-2}$ cm^{-1}, $T(n)_N = 0.330$, $T(n)_0 = 0.220$, $\lambda_0 = 828$ cm^{-1} and $S_N = 0.093$, $S_0 = 0.076$. These values of $T(n)$ and S assume sp^2 hybridization on the ligand bonding atoms. For these chelates with the Cu(II) environment of two nitrogen and two oxygen atoms, the values of $T(n)$ and S were averaged in making the calculations.[14]

Treatment of Data

The complexes considered are summarized in Figure 1. The values for the magnetic parameters in the usual doublet spin-Hamiltonian are collected in Table I. In those cases where the optical spectra were not available in the literature, the spectra were measured



I. R = R'' = CH_3	R' = $-CH_2-CH_2-$	Cu en(acac)$_2$
II. R = CF_3 R'' = CH_3	R' = $-CH_2-CH_2-$	Cu en(tfacac)$_2$
III. R = C_2H_5 R'' = CH_3	R' = $-CH_2-CH_2-$	Cu en(hex)$_2$
IV. R = C_2H_5 R'' = CF_3	R' = $-CH_2-CH_2-$	Cu en(tfhex)$_2$
V. R = C_2H_5 R'' = CF_3	R' = $-CH_2-\underset{\substack{\vert\\ CH_3}}{CH}-$	Cu 1,2-pn(tfhex)$_2$



VI. R = H	R' = phenylene	Cu phen(sal)$_2$
VII. R = CH_3	R' = phenylene	Cu phen(acet)$_2$
VIII. R = H	R' = $-CH_2-CH_2-$	Cu en(sal)$_2$
IX. R = CH_3	R' = $-CH_2-CH_2-$	Cu en(acet)$_2$

FIGURE 1 Formulae for the Chelates studied.

TABLE I
Values for the parameters in the spin-Hamiltonian

Chelate	g_x	g_y	g_z	$A_x \times 10^4$ cm^{-1}	$A_y \times 10^4$ cm^{-1}	$A_z \times 10^4$ cm^{-1}	E(cm^{-1})	Ref.
Cu en(acac)$_2$	2.048	2.047	2.183	31.5	31.1	204.8	18500	4, 19
Cu en(tfacac)$_2$	2.048	2.046	2.192	31.1	28.3	200.8	17400	4, 19
Cu en(hex)$_2$	2.043	2.043	2.185	31.1	25.7	203.3	18400	6
Cu en(tfhex)$_2$	2.048	2.046	2.198	31.5	21.3	196.8	17700	6
Cu 1,2 pn(tfhex)$_2$	2.048	2.047	2.195	32.8	31.9	193.3	14800	8
Cu phen(sal)$_2$	2.049	2.041	2.192	36.4	31.4	201.7	17500	17, 18
Cu phen(acet)$_2$	2.049	2.044	2.209	28.7	24.8	197.4	15400	17
Cu en(sal)$_2$	2.049	2.046	2.192	31.3	29.3	201.0	17900	5, 18
Cu en(acet)$_2$	2.046	2.042	2.188	36.3	31.5	198.6	18000	5

on a Cary 14 spectrophotometer. For these molecules it was generally possible to observe only the lowest energy d–d transition. The higher frequency transitions were masked by strong ligand absorption.

The values for the molecular-orbital coefficients are recalculated for each of the complexes making use of Eqs. 8 and 9. Since the higher energy d–d transitions cannot be observed, it is not possible to calculate a value of δ, the out-of-plane π-bonding coefficient. For those chelates where it has been possible to observe a sufficient number of d–d transitions to enable the calculation of δ^2, its values have turned out to be nearly equal to one.[15] In the calculations made here values of $\delta^2 = 1$ and $\delta^2 = 0.9$ were used. The values of χ determined with these two assumptions differed by less than 2%, therefore the χ-values reported here are those calculated assuming $\delta^2 = 1$.

Initial values for α^2 were calculated from Eq. 8 assuming that $Z_\parallel = Z_\perp = 1$, α'^2 can then be calculated from Eq. 3 and β^2 from Eq. 4a. These values together with the assumption, $\delta^2 = 1$, allow the calculation of an approximation to $Z_\parallel$ and $Z_\perp$. These values of $Z_\parallel$ and $Z_\perp$ enable the calculation of a better approximation to α^2 from Eq. 8. The iteration process is continued until there is no change in the values of the m.o. coefficients. Usually three iterations were sufficient. Values for the isotropic contact term K can be obtained by the use of Eq. 9 and values of χ from Eq. 11. The results of these calculations are summarized in Table II.

TABLE II
Values for the M.O. coefficients and χ

Chelate	α^2	α'^2	β^2	$-\chi$
Cu en(acac)$_2$	0.786	0.295	0.717	3.194
Cu en(tfacac)$_2$	0.784	0.297	0.710	3.915
Cu en(hex)$_2$	0.789	0.292	0.715	3.850
Cu en(tfhex)$_2$	0.789	0.293	0.739	3.824
Cu 1,2 pn(tfhex)$_2$	0.779	0.303	0.628	3.942
Cu phen(sal)$_2$	0.775	0.308	0.726	3.999
Cu phen(acet)$_2$	0.805	0.274	0.667	3.884
Cu en(sal)$_2$	0.782	0.299	0.730	3.933
Cu en(acet)$_2$	0.771	0.311	0.733	4.002

DISCUSSION OF RESULTS

The nine compounds in Table II are complexes in which the immediate Cu(II) environment is two nitrogen and two oxygen atoms with the nitrogens in cis positions. For these complexes the value of χ is amazingly constant. For the nine complexes one finds an average $\chi = 3.918$ with $\sigma = 0.060$. This indicates that the hyperfine contact term is rather insensitive in the ligand substitution. However, Cu en(acet)$_2$ and Cu phen(sal)$_2$ could not be grown from acetone solution because of limited solubility, hence crystals of these complexes were grown from chloroform solution. It is known that chloroform forms an adduct with this type of chelate by hydrogen bonding to a chelate oxygen.[16] This additional bonding may account for the fact that the χ-value for these two chelates is essentially the same and somewhat higher than for the other chelates, although the difference is probably within the accuracy of the calculations.

Preliminary calculations indicate that χ is also constants for series in which the Cu(II) environment consists of four nitrogens. However, there is not an extensive series of chelates treated in a consistent way to test the hypotheses. It does seem that, although constant within the series, the χ-values are significantly lower than for the series treated in this paper.

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