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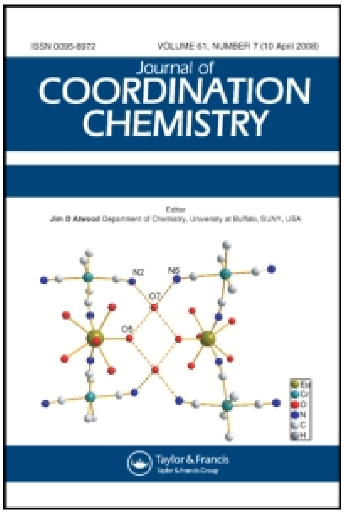

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Lancione, Robert L. , Allen Jr., Harry C. and Sydor, Donald R.(1975) 'THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER (II) I. N, N'-Bis-(acetylacetone) ethylenediimine and N, N'-Bis-(1,1,1-trifluoroacetylacetone) ethylenediimine', Journal of Coordination Chemistry, 4: 3, 153 — 157

To link to this Article: DOI: 10.1080/00958977508075893

URL: http://dx.doi.org/10.1080/00958977508075893

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J. Coord. Chem.
1975, Vol. 4, pp. 153–157

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

I. N,N′-Bis-(acetylacetone) ethylenediimine and N,N′-Bis-(1,1,1-trifluoroacetylacetone) ethylenediimine

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(*Received November 6, 1974*)

KEY WORDS: EPR Spectra, N,N′-bis-(acetylacetone)ethylenediimino Cu(II), N,N′-(1,1,1-trifluoroacetylacetone) ethylenediimino Cu(II), magnetic parameters, molecular orbitals.

The EPR spectrum of N,N′-bis-(acetylacetone)ethylenediimino Cu(II), [Cu-en(acac)$_2$], and N,N′-bis-(1,1,1-trifluoroacetylacetone)ethylenediimino-Cu(II), [Cu-en(tfacac)$_2$], have been studied in doped single crystals of the corresponding Ni(II) chelate. The parameters in the usual doublet spin-Hamiltonian are found to be: Cu[en(acac)$_2$], $g_z = 2.183 \pm 0.003$, $g_x = 2.047 \pm 0.004$, $g_y = 2.048 \pm 0.004$, $A_z = 204.8 \times 10^{-4}\ \text{cm}^{-1}$, $A_x = 31.5 \times 10^{-4}\ \text{cm}^{-1}$, $A_y = 27.1 \times 10^{-4}\ \text{cm}^{-1}$, $A_z{}^N = 12.8 \times 10^{-4}\ \text{cm}^{-1}$ and $A_x{}^N = A_y{}^N = 14.3 \times 10^{-4}\ \text{cm}^{-1}$: Cu[en(tfacac)$_2$], $g_z = 2.192 \pm 0.002$, $g_x = 2.048 \pm 0.004$, $g_y = 2.046 \pm 0.004$, $A_z = 200.8 \times 10^{-4}\ \text{cm}^{-1}$, $A_x = 31.1 \times 10^{-4}\ \text{cm}^{-1}$, $A_y = 28.3 \times 10^{-4}\ \text{cm}^{-1}$, $A_z{}^N = 12.8 \times 10^{-4}\ \text{cm}^{-1}$ and $A_x{}^N = A_y{}^N = 14.6 \times 10^{-4}\ \text{cm}^{-1}$. These parameters are related to coefficients in the molecular orbitals of the complex. It is found that the σ-bonding is quite covalent and there is significant in-plane π-bonding. From the nitrogen hyperfine structure it is determined that the hybridization on the nitrogen is sp^2.

INTRODUCTION

Since the first preparation[1] of the transition metal complexes of tetradentate Schiff bases, there has been considerable interest in their chemistry and structure. These chelates are of interest because they are model compounds for biological systems: in particular the cobalt(II) complexes are synthetic oxygen carriers. However, these chelates are of interest, in their own right, because of their interesting bonding properties.

Considerable work has been done on the optical properties, magnetic susceptibilities and x-ray crystal structure. Only recently has the technique[2–8] of EPR been applied to these complexes. In general the EPR has been studied in dilute solution, frozen solutions that form glasses or polycrystalline samples. One single crystal investigation[2] has been carried out on a copper-doped crystal of N′,N′-bis-(acetylacetone)ethylenediimino nickel(II), [Ni-en-(acac)$_2$]. In this study no rhombic character was detected in the g- or A-tensor. In addition, polycrystalline samples were studied but the spin-Hamiltonian parameters reported for the Cu(II) complex differed between the two samples. The work on this copper complex, Cu[en(acac)$_2$], has been repeated to try to resolve these discrepancies and the EPR spectrum of N,N′bis-(1,1,1-trifluoroacetylacetone)ethylenediimino copper(II), Cu[en-(tfacac)$_2$] doped into a single crystal of the corresponding Ni(II) chelate is reported.

EXPERIMENTAL

The ligands and chelates were prepared as previously described.[9,10] The structural formula is shown in Figure 1. The pure ligands were characterized by their nmr spectrum.[11] From the nmr spectrum it was found that the CF$_3$ groups in Cu[en(tfacac)$_2$] are symmetrically located and at the non-bridged end of the chelate.[12] Single crystals of both chelates were readily grown by the slow evaporation of acetone solutions to which small amounts of water had been added.

The crystals of the [en(acac)$_2$] chelate grew as flat hexagonal crystals, the narrow face of the crystal making an angle of ~17° with a perpendicular to the hexagonal faces. Single crystals of the [en(tfacac)$_2$]

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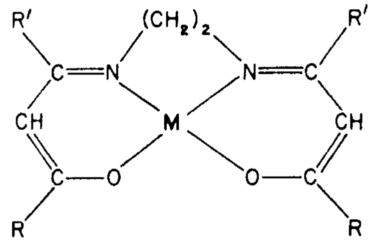

$Cu[en(acac)_2]$ $R = R' = CH_3$

$Cu[en(tfacac)_2]$ $R' = CH_3$ $R = CF_3$

FIGURE 1 Molecular geometry of the complexes.

complex grew as long narrow flat crystals. The EPR spectra were recorded about three mutually perpendicular axes oriented with respect to the crystals as shown in Figure 2.

The EPR spectra were recorded on a Varian E–9 Spectrometer operating at X-band frequencies. Spectra were recorded at angular increments of 5° or 10° depending on the complexity of the spectrum. The magnetic field was measured with a Magnion nmr-type gaussmeter, the frequency being counted by a Hewlett-Packard Model 5245L counter. The klystron frequency was measured with the same counter equipped with a 5255A frequency converter. All measurements were made at room temperature (20°C).

Since the chosen axes of rotation are not necessarily the principal axes of the g-tensor, the data were reduced by the method of Geusic and Brown[13] as modified by Billings and Hathaway[14] to reduce the effects of small crystal misalignments. The determination of the principal A-values required the inclusion of second order terms in order to fit the observed values.[15]

The spectrum of the $[en(acac)_2]$ chelate arose from two magnetically inequivalent sites. Because of the severe overlapping of spectral lines in the high field portion of the spectra, the values of the in-plane A-values are not as accurate as those determined for the $[en(tfacac)_2]$ complex where only one magnetic site was observed. A five line ligand superhyperfine structure was observed in each complex arising from the coupling of the unpaired electron with the nitrogen nuclei of the ligand.

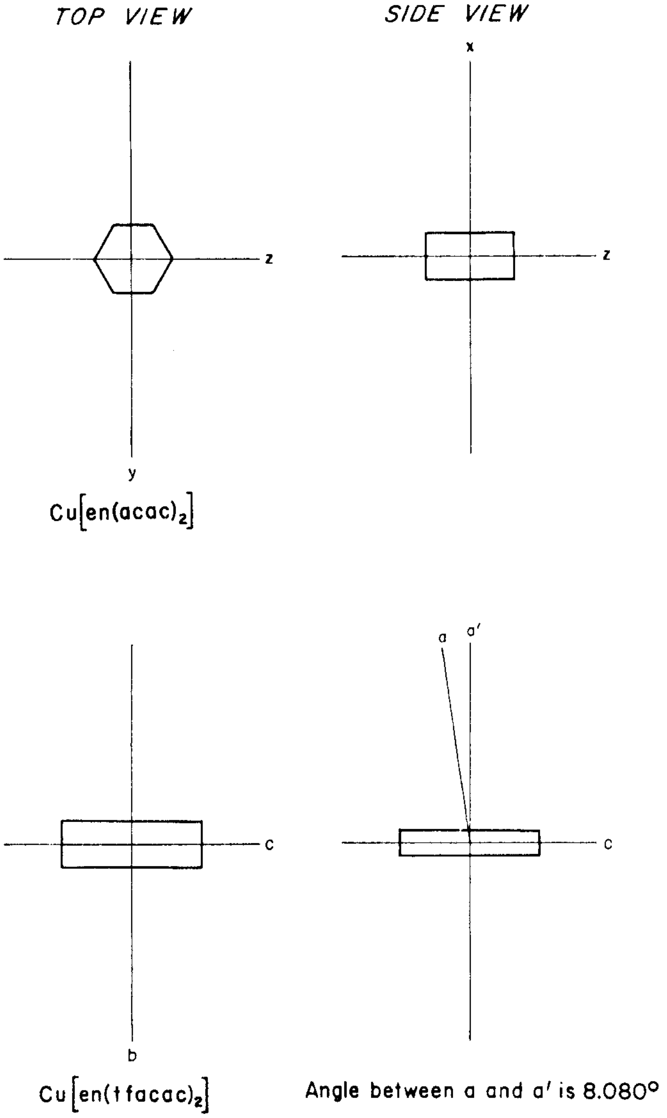

FIGURE 2 Orientation of laboratory axes with respect to the crystal. For $Cu[en(tfacac)_2]$ the crystallographic axes are shown.

The derived values of the magnetic parameters in the usual doublet spin Hamiltonian[13] are collected in Table I. The direction cosines of the magnetic axes with respect to the laboratory axes are also given.

Bonding Parameters

The molecular geometry of the chelates is shown in Figure 1. The molecule is assumed to be planar such that the symmetry of the Cu(II) environment may be described by the point group C_{2v}. The molecular plane is chosen as the xy-plane and the x-axis is chosen as the two-fold rotation axis. With this choice

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TABLE I
Principal values of the *g*- and *A*-tensors

	Cu[en(acac)$_2$]	Cu[en(tfacac)$_2$]
g_z	2.183 ± 0.002	2.192 ± 0.002
g_x	2.047 ± 0.004	2.048 ± 0.004
g_y	2.048 ± 0.004	2.046 ± 0.004
A_z^{Cu}	200.9 ± 1G 204.8 x 10^{-4}cm^{-1}	196.2 ± 1.0G 200.8 x 10^{-4}cm^{-1}
A_x^{Cu}	33.0 + 2G 31.5 x 10^{-4}cm^{-1}	32.5 ± 2G 31.1 x 10^{-4}cm^{-1}
A_y^{Cu}	28.4 ± 2G 27.1 x 10^{-4}cm^{-1}	29.6 ± 2G 28.3 x 10^{-4}cm^{-1}
A_z^N	12.5 + 1.0G 12.8 x 10^{-4}cm^{-1}	12.5 ± 1.0G 12.8 x 10^{-4}cm^{-1}
A_x^N	15.0 ± 1.0G 14.3 x 10^{-4}cm^{-1}	15.3 ± 1.0G 14.6 x 10^{-4}cm^{-1}
A_y^N	15.0 ± 1.0G 14.3 x 10^{-4}cm^{-1}	15.3 ± 1.0G 14.6 x 10^{-4}cm^{-1}
Principal Directions	1, 0, 0 0,0.55, ± 0.83 0, ∓.83 0.55	−0.94, 0, 0.35 0, 1, 0 0.35, 0, 0.94

of axes the ground state molecular orbital[4,16,17,18] is the antibounding linear combination of the d_{xy} orbital on the Cu(II) and the ligand sigma orbitals. It transforms in C_{2v} as the irreducible representation B_2. The molecular orbitals are then,[18]

$$\Psi_{B_2} = \alpha \left| xy > - \frac{\alpha'}{2} \right| B_2 >$$

$$\Psi_{A_1}{}^{a} = \beta \left| x^2 - y^2 > - \frac{1}{2}(1-\beta^2)^{1/2} \right| A_1 >$$

$$\Psi_{A_1}{}^{b} = \gamma \left| z^2 > - \frac{1}{2}(1-\gamma^2)^{1/2} \right| A_1{}^{b} > \qquad (1)$$

$$\Psi_{A_2} = \delta' \left| yz > - \frac{1}{2}(1-\delta'^2)^{1/2} \right| A_2 >$$

$$\Psi_{B_1} = \delta'' \left| xz > - \frac{1}{2}(1-\delta''^2)^{1/2} \right| B_1 >$$

The part of the wave functions represented by $|B_2>|A_2{}^a>$ etc. represents the appropriate linear combination of ligand orbitals transforming as the irreducible representation indicated. The normalization condition on the ground state m.o. requires that

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1, \qquad (2)$$

in which S is the overlap integral between the copper(II) d_{xy} orbital and the ligand σ- oribitals. For Cu–O bonds it has a value[16] of 0.093 assuming sp^2 hybridation on the ligand bonding atom and a Cu–X bond distance of 1.9 Å.

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 energy levels and the coefficients in the molecular orbital through the relations;[16,17]

$$g_z = 2.0023 - \frac{8\lambda}{\Delta E_{x^2-y^2}} \left[\alpha^2\beta^2 - \alpha\alpha'\beta^2 S - \alpha\alpha'\beta(1-\beta^2)^{1/2}\frac{T(n)}{2}\right] \qquad (3a)$$

$$g_x = 2.0023 - \frac{2\lambda}{\Delta E_{xz}} [\alpha^2\delta''^2 - \alpha\alpha' S\delta''^2] \qquad (3b)$$

$$g_y = 2.0023 - \frac{2\lambda}{\Delta E_{yz}} [\alpha^2\delta'^2 - \alpha\alpha' S\delta'^2] \qquad (3c)$$

and

$$A_z = P\left[-\alpha^2\left(\frac{4}{7}+\kappa\right) - 2\lambda\alpha^2\left(\frac{4\beta^2}{\Delta E_{x^2-y^2}} + \frac{3\delta'^2}{14\Delta E_{yz}} + \frac{3\delta''^2}{14\Delta E_{xz}}\right)\right] \qquad (4a)$$

$$A_x = P\left[\alpha^2\left(\frac{2}{7}-\kappa\right) - \frac{22\lambda\alpha^2\delta''^2}{14\Delta E_{xz}}\right] \qquad (4b)$$

$$A_y = P\left[\alpha^2\left(\frac{2}{7}-\kappa\right) - \frac{22\lambda\alpha^2\delta'^2}{14\Delta E_{yz}}\right] \qquad (4c)$$

In these expressions, κ is the Fermi contact term estimated to be 0.43 in the free ion, $T(n)$ is an integral over the ligand functions and is evaluated by using the same assumptions that were used for evaluating the overlap integral,[16] $T(n)_N = 0.333$ and $T(n)_0 = 0.220$. The value of $\lambda = 828$ cm^{-1} is that for the free copper ion. A value of $P = 0.036$ cm^{-1} is the one generally used.

For the two compounds studied here, the in-plane g-values are equal within experimental uncertainty. Thus if it is assumed that the g-tensor is axially symmetric, and neglecting small terms in the expression for the principal g-values, Eq. (4a) may be

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rewritten and solved for α^2 to give,[18]

$$\alpha^2 = \frac{7}{4}\left[\frac{|A_{\|}|}{P} - \frac{|A_i|}{P} + \frac{2}{3}g_{\|} - \frac{5}{21}g_{\perp} - \frac{6}{7}\right] \qquad (5)$$

in which A_i is the isotropic hyperfine coupling constant, determined experimentally as the average value of the observed A-values.

The values of α^2 determined from Eq. (5) were then used in Eq. (2) to determine α'^2. By using[4] $\Delta E_{x^2-y^2} = 18000\ \text{cm}^{-1}$ and the values of α^2, α'^2 and $T(n) = 0.276$, $S = 0.0845$ (Average of Nitrogen and Oxygen values)[4] a value of β^2 may be determined. These values are tabulated for the two chelates in Table II.

Superhyperfine structure was observed from the coupling of the unpaired electron to the two nitrogen nuclei of the ligands. As can be seen in Table I this A_N tensor has axial symmetry with the two in-plane components being larger than the out-of-plane component. In the usual formulation the expression for the isotropic ligand coupling may be written

$$A_i = -\left(\frac{4\pi}{9}\right)\gamma_N\beta_0\beta_N\alpha'^2\ |\Psi_2s(0)|^2 S_z I_z{}^{\text{N}} \qquad (6)$$

where γ_N is the magnetic moment of the nitrogen nucleus in nuclear magnetons and $|\psi_2 s(0)|^2$ is the value of the probability of the 2s orbital of the nitrogen at the nucleus. This latter term has been estimated by Maki and McGarvey[19] from the SCF wave function to be $33.4 \times 10^{24}\ \text{cm}^{-3}$. A_i is the average of the three observed A-values.

If it is assumed that the ligand nitrogen orbitals are of the form $np \mp (1 - n^2)^{1/2}s$, Eq. (6) becomes

$$A_i = -\left(\frac{4\pi}{3}\right)\gamma_N\beta_0\beta_N\alpha'^2(1 - n^2)\ |\Psi_2s(0)|^2 S_z I_z{}^{\text{N}} \qquad (7)$$

This equation together with Eqs. (2) and (5) can be solved for n^2. These values are given in Table II and show good agreement with the value of 0.67 expected for sp^2 hybridization.

The value of n^2 may also be determined by making use of the anisotropy in the A^N tensor. Following Fujimoto and Janeka,[20]

$$A_a = \left(\frac{1}{5}\right)\gamma_N\beta_0\beta_N\alpha'^2 n^2 \langle r^{-3}\rangle_{2p}. \qquad (8)$$

The value of $\langle r^{-3}\rangle_{2p}$ for nitrogen has been calculated to be $21.1 \times 10^{24}\ \text{cm}^{-3}$. From Eqs. (7) and (8) together with the relations[21]

$$A_{\|} = A_i + 2A_a$$
$$A_{\perp} = A_i - A_a$$

a value of $n^2 = 0.647$ for Cu[en(acac)$_2$] and $n^2 = 0.685$ for Cu[en(tfacac)$_2$] is obtained, once again indicating sp^2 hybridization about the nitrogen.

TABLE II
Molecular orbital coefficients

	Cu[en(acac)$_2$]	Cu[en(tfacac)$_2$]
α^2	0.762	0.759
α'^2	0.321 0.311[a]	0.320 0.316[a]
β^2	0.724	0.760
n^2	0.667 0.647[a]	0.667 0.685[a]

[a] From Nitrogen H. F. Splitting.

If the spectroscopic values for the transitions ΔE_{xz} and ΔE_{yz} were known it would be possible to evaluate the parameters δ'^2 and δ''^2. Unfortunately, these transitions are masked in the spectrum by a strong charge transfer band. Thus it is not possible to estimate the amount of out-of-plane π-bonding.

Relationship to Crystal Structure

Crystallographic data for either Ni[en(acac)$_2$] or Ni[en(tfacac)$_2$] do not seem to be found in the literature. The structure of Ni[en(tfacac)$_2$] was made available to us by R. Scaringe and D. J. Hodgson.[22] The unit cell parameters are $a = 11.046$ Å, $b = 17.103$ Å, $c = 7.781$ Å, $\beta = 98.08°$, space group $P2_1/c$ with four molecules per unit cell.

The coordination of the nickel atom is square planar with average Ni–O and Ni–N distances of 1.85 and 1.87 Å respectively. The structure is that of a chain, with a Ni–Ni distance of 4.03 Å, rather than dimeric as reported for similar compounds.[23,24,25]

The plane of the coordination group of all the molecules in the unit cell are parallel. This together with the fact that $g_x \cong g_y$ accounts for the one magnetic site that was observed. In a monoclinic system, one magnetic axis is coincident with the b crystallographic axis and the other two lie in the 010 plane. The direction given by g_x is where the plane of the molecule intersects the 010 plane and g_y is taken to be along b.

From the crystal structure it can be determined that a vector perpendicular to the plane of the molecule has the direction cosines (0.34, −0.05, 0.94) with respect to the a', b, c axes. These compare well with the EPR data which gave the directions (0.35, 0, 0.94) for g_z.

Discussion

The results of this study show that the σ-bonding is quite covalent as evidenced by the value of α. In addition the value of β^2 indicates that there is considerable in-plane π-bonding. The A-values for Cu[en(tfacac)$_2$] are somewhat smaller than in the non-flourinated analog. This is in line with the findings of Kuska and Rogers[18] in their investigation of the isotropic A-values of [Cu(acac)$_2$] and [Cu(tfacac)$_2$] measured in chloroform solutions. This effect arises from the greater electronegativity of the CF$_3$ group.

Our results for Cu[en(acac)$_2$] agree in general with the single crystal values published previously although our g-values in the molecular plane are somewhat larger as are our values for A_x and A_y. The slight anisotropy observed in the in-plane g-values falls within the experimental uncertainty so may not be real.

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ACKNOWLEDGEMENT

One of us (R.L.) would like to thank the Lever Brothers Foundation for partial support during the course of this work.

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