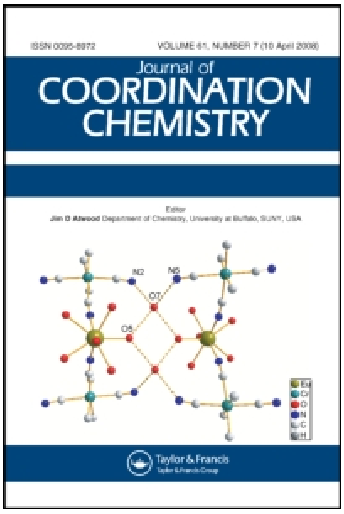

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THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER (II)

III. N,N′-bis-(2,4-hexanedione)ethylenediimine and N,N′-bis-(1,1,1-trifluoro-2,4-hexanedione)ethylenediimine.

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The EPR spectra of N,N′-bis-(2,4-hexanedione)ethylenediimino Cu(II), [Cu en(hex)$_2$], and N,N′-bis-(1,1,1 trifluoro-2,4-hexanedione)ethylenediimino Cu(II), [Cu en (tfhex)$_2$], have been studied in doped single crystals of the corresponding Ni(II) chelate. The parameters in the doublet spin-Hamiltonian are found to be: Cu[en(hex)$_2$], $g_z = 2.185 \pm 0.002$, $g_x = 2.043 \pm 0.004$, $g_y = 2.043 \pm 0.004$, $A_z = 203.3 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_x = 31.1 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_y = 25.7 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_z^N = 13.3 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_x^N = A_y^N = 14.4 \times 10^{-4}\,\mathrm{cm}^{-1}$: Cu[en(tfhex)$_2$], $g_z = 2.198 + 0.002$, $g_x = 2.046 \pm 0.004$, $g_y = 2.046 \pm 0.004$, $A_z = 196.8 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_x = 31.5 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_y = 21.3 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_z^N = 13.1 \times 10^{-4}\,\mathrm{cm}^{-1}$, $A_x^N = A_y^N = 14.6 \times 10^{-4}\,\mathrm{cm}^{-1}$. These parameters are related to the molecular orbital coefficients. The complexes are quite covalent with π-bonding very close in magnitude to σ-bonding. Crystal data for the nickel chelates is also given.

INTRODUCTION

There has been considerable interest in the chemistry and structure of neutral polydentate Schiff base complexes of copper(II). The spectral and magnetic properties of many bidentate complexes have been studied.[1–6] Relatively few tetradentate complexes have received attention from spectroscopists.[7,8]

In previous papers[9,10] (I) a study of the EPR spectra of copper(II) complexes of N,N′-bis-(acetylacetone)ethylenediimine and N,N′-bis-(1,1,1-trifluoroacetylacetone)ethylenediimine and, (II) a study of the EPR spectra of copper (II) complexes of N,N′-bis-(salicylaldehyde)ethylenediimine and 7-methyl-N,N′-bis-(salicylaldehyde)ethylenediimine, doped into single crystals of the corresponding nickel-(II) complexes were reported. In an attempt to elucidate the effect of ligand variation on the bonding environment of the copper(II) ion in tetradentate Schiff base complexes, the study has been extended to include the EPR spectra of copper(II) complexes of (2,4,-hexanedione) ethylenediimine and (1,1,1-trifluoro-2,4-hexanedione)ethylenediimine doped into single crystals of the corresponding nickel(II) complexes.

EXPERIMENTAL

The tetradentate ligands en(hex)$_2$ and en(tfhex)$_2$ were synthesized by combining the diketone with a half-molar portion of ethylenediamine in a small volume of ethanol. The solution was refluxed for one-half hour and the ligand precipitated upon the dropwise addition of water. The product was recrystallized from ethanol. The structure of the ligands was characterized by their nmr-spectra.

The chelates were prepared by the reaction of stoichiometric quantities of the Schiff base with Ni(II) acetate in ethanol. The addition of water precipitated the complex which was recrystallized from acetone. Cu-doping was achieved by adding small amounts of Cu(II) during the synthesis of the Ni(II) chelate. Pure ^{63}Cu(as the nitrate) was used in doping to reduce the complexity of the hyperfine spectra. This was prepared from ^{63}CuO obtained from Oak Ridge National Laboratory.

Single crystals of the pure nickel chelate were used to collect x-ray data, while Cu-doped (1–4%) crystals of the nickel chelate were used for EPR studies. Crystallographic axes with respect to the external morphology are shown in Figure 2. The a′ axis was chosen normal to (100) for Ni[en(tfhex)$_2$] so as to have an orthogonal axis system for EPR data collection.

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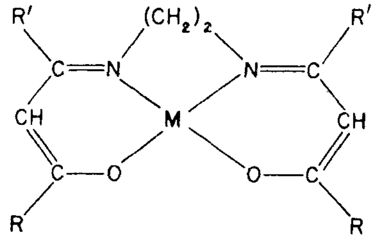

$M[en(hex)_2]$ $R' = CH_2CH_3$ $R = CH_3$

$M[en(tfhex)_2]$ $R' = CF_3$ $R = CH_2CH_3$

FIGURE 1 Molecular geometry of the complexes.

The equipment used in this work and the method used for EPR data reduction have been previously described.[9] As in the previous studies, second order terms[11] were necessary to explain the angular variation of the copper hyperfine splitting. Since the copper hyperfine splitting values reached their maxima and minima at the same orientations as the g-values, their principal axis systems are assumed to be coincident. The principal A^{Cu} values were taken directly from spectra on which the principal g-values were observed.

The EPR spectrum can then be described by the usual spin-Hamiltonian for an electron in a rhombic electric field.

$$\begin{aligned} H = {} & \beta(g_zH_zS_z + g_xH_xS_x + g_yH_yS_y) + A_z^{Cu}S_z\,I_z \\ & + A_x^{Cu}S_xI_x + A_y^{Cu}S_yI_y + A_{\parallel}^{N}S_zI_z \\ & + A_{\perp}^{N}(S_xI_x + S_yI_y) + \text{Higher Terms} \end{aligned}$$

RESULTS

Dark red orthorhombic crystals of $Ni[en(hex)_2]$ elongated along the c axis were obtained by slow evaporation of a 1:1 ethanol/water solution. The unit cell parameters are $a = 10.28 \pm 0.01$ Å, $b = 18.16 \pm 0.01$ Å, $c = 7.82 \pm 0.01$ Å; space group P_{bcn}. The measured density is 1.41 gcm^{-3}. The calculated density with four molecules per unit call is 1.40 gcm^{-3}.

In each plane, two sets of absorptions were observed which merged into a single set when the magnetic field was along the a, b, or c axis. The multiplicity of the space group P_{bcn} is eight and thus the molecule must lie on one of the four fold special positions (c), (b) or (a).[13] The molecule must possess the associated point group symmetry, i.e., an inversion center (b) and (a), or a two fold axis (c). Since an inversion center is not consistent with molecular symmetry, only special position (c) is possible. The two fold molecular symmetry axis lies along the b crystallographic axis. The direction cosines given in Table II, in this case, specifically locate the molecule with respect to the crystallographic axes.

Dark red monoclinic crystals of $Ni[en(tfhex)_2]$ elongated along the c axis were obtained by slow evaporation of an acetone solution. The unit cell parameters are $a = 11.57 \pm 0.01$ Å, $b = 17.82 \pm 0.01$ Å, $c = 8.89 \pm 0.01$ Å and $\beta = 112.1°$.

TABLE I
Magnetic parameters

Single crystal	*$Cu[en(hex)_2]$*	*$Cu[en(tfhex)_2]$*
g_z	2.185 ± 0.002	2.198 ± 0.002
g_x	2.043 ± 0.004	2.048 ± 0.004
g_y	2.043 ± 0.004	2.046 ± 0.004
A_z^{Cu}	199.3 ± 1G 203.3×10^{-4} cm^{-1}	191.8 ± 1G 196.8×10^{-4} cm^{-1}
A_x^{Cu}	32.6 ± 2G 31.1×10^{-4} cm^{-1}	32.9 ± 2G 31.5×10^{-4} cm^{-1}
A_y^{Cu}	26.9 ± 2G 25.7×10^{-4} cm^{-1}	22.3 ± 2G 21.3×10^{-4} cm^{-1}
A_z^{N}	13.0 ± 1G 13.3×10^{-4} cm^{-1}	12.8 ± 1G 13.1×10^{-4} cm^{-1}
$A_x^{N} = A_y^{N}$	15.1 ± 1G 14.4×10^{-4} cm^{-1}	15.3 ± 1G 14.6×10^{-4} cm^{-1}
Powder		
g_z	2.185 ± 0.002	2.198 ± 0.002
A_z^{Cu}	199.8 ± 1G 203.8×10^{-4} cm^{-1}	191.9 ± 1G 196.9×10^{-4} cm^{-1}
A_z^{N}	12.8 ± 1G 13.1×10^{-4} cm^{-1}	12.3 ± 1G 12.6×10^{-4} cm^{-1}

TABLE II
Direction cosines of the principal g-values with respect to the crystallographic axes for $Ni[en(hex)_2]$

	a	b	c
g_x	∓0.96	0	0.27
g_y	0	1	0
g_z	0.27	0	±0.96

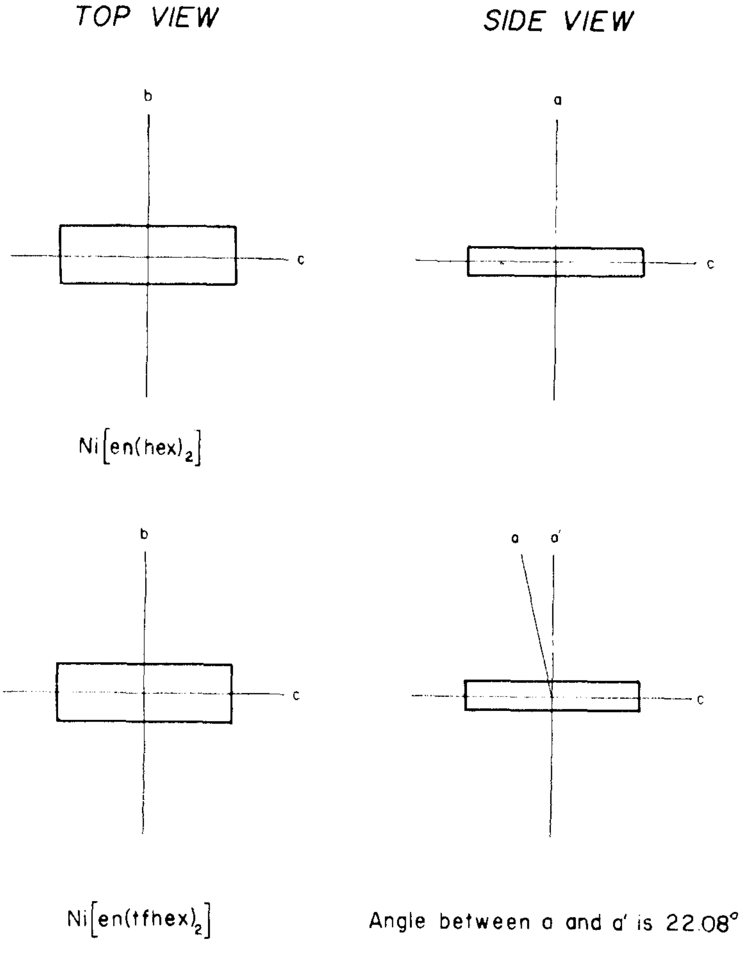

FIGURE 2 Crystallographic axes with respect to the external morphology for Ni[en(hex)$_2$] and Ni[en(tfhex)$_2$].

The space group is $P2_{1/c}$ and there are four molecules per unit cell. The measured density is 1.64 gcm^{-3}, compared with 1.63 gcm^{-3} calculated. Crystals of the corresponding copper chelate were found to be isomorphous.

Only one magnetic site was observed in all directions. The necessary condition for this is that all the coordination planes be parallel. Since the molecule does not occupy any special position, the direction cosines given in Table III locate only the plane of the molecule.[1,2] The direction given for g_x is where the molecular plane intersects the (010) plane and g_y is taken to be along b

TABLE III
Direction cosines of the principal g-values with respect to the crystallographic axes for Ni[en(tfhex)$_2$]

	a'	b	c
g_x	−0.83	0	0.55
g_y	0	1	0
g_z	0.55	0	0.83

In each case, a magnetic site gave rise to four sets of five lines. This is due to nitrogen superhyperfine structure superimposed on the copper hyperfine lines. The relationship between the coefficients in the molecular orbitals and the magnetic parameters are given in complete form in *I*. The assumed symmetry is C_{2v} and the expressions for the in-place antibonding wave functions are:

$$\psi_{B_2} = \alpha \,|\, xy > - \frac{\alpha'}{2} \,|\, B_2 >$$

$$\psi_{A_1} = \beta \,|\, x^2 - y^2 > - \tfrac{1}{2}(1 - \beta^2)^{\frac{1}{2}} |\, A_1 > \qquad (1)$$

Here, $|B_2\rangle$ represents a ligand group orbital made up of s–p hybrid orbitals of proper symmetry to partake in σ-bonding. $|A_1\rangle$ represents a ligand group orbital made up of p orbitals of proper symmetry to partake in in-plane π-bonding.

Values of α^2 are calculated from the approximate formula of Kuska, Rogers and Drullinger,[3]

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

with $P = 0.036\ \text{cm}^{-1}$. The values of β^2 were calculated from the equation:

$$(g_z - 2.0023) = \frac{-8\lambda_0}{\Delta E_{x^2-y^2}} \left[\alpha^2\beta^2 - \alpha\alpha'\beta^2 S - \alpha\alpha'\beta(1-\beta^2)^{1/2}\frac{T_{(\mathrm{N})}}{2}\right] \quad (3)$$

The free Cu(II) ion spin-orbit coupling constant, λ_0, has the value $-828\ \text{cm}^{-1}$ and $T_{(\mathrm{N})}$ is set equal to 0.276. Values of α'^2 were obtained from the expression for the overlap of the ground state:

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \quad (4)$$

where $S = 0.084$ for Schiff base chelates. $\Delta E_{x^2-y^2}$ is taken to be approximately $18{,}000\ \text{cm}^{-1}$.

Ligand nitrogen and oxygen atoms are assumed to contain σ orbitals of the form:

$$\sigma = \eta(2p) + (1-\eta^2)^{1/2}(2s) \quad (5)$$

The value of η^2 is obtained from the isotropic part of the nitrogen hyperfine splitting values through the expression:

$$A_i = -(4\pi/3)\gamma_N\beta_O\beta_N\alpha'^2(1-\eta^2)\,|\psi^2_{2s(0)}| \quad (6)$$

The results are collected in Table IV.

TABLE IV
Molecular orbital coefficients

	Cu[en(hex)$_2$]	*Cu[en(tfhex)$_2$]*
α^2	0.765	0.764
α'^2	0.318	0.323
β^2	0.728	0.782
η^2	0.664	0.671

DISCUSSION

The results of this study show that π-bonding is very close in magnitude to σ-bonding. The trends in the g and A values seem to be consistent with the finding of Kuska and Rogers[6] for substituted copper acetylacetonates. For Cu[en(hex)$_2$], the g_z value is smaller than for Cu[en(tfhex)$_2$] indicating greater covalency as expected. Unfortunately, this is not reflected in the values of α^2 calculated from Eq. (2) because $|A^{\mathrm{Cu}}|$ seems to be increasing with greater covalency rather than decreasing as expected. This inconsistency is explained by Zink and Drago[14] who caution against direct comparison of EPR bonding parameters in metal complexes with substituted ligands. They claim the strength of the crystal field varies from one complex to another and is not constant as assumed in the derivation of the equations relating EPR parameters to molecular orbital coefficients. The explanation postulated by Kuska[3] *et. al.*, that this apparent inconsistency is due to a changing fraction of metal 4s character in the ground state should not be valid for the complexes we have studied. The crystal field cannot mix the ground state with the metal 4s orbital under C_{2v}.

The fact that $g_x \cong g_y$ can be viewed as the result of the molecule possessing C_{2v} symmetry. Hitchman[5] *et. al.*, showed that in similar complexes (bidentate Schiff bases) of C_{2h} symmetry, the crystal field could mix the ground state, d_{xy} or $d_{x^2-y^2}$ depending on the coordinate system, with small amounts of d_{z^2}. The amount of rhombic character is proportional to the amount of d_{z^2} mixed in. In single crystal studies of copper complexes of C_{2h} symmetry, significant rhombic character has been observed.[1,2,4] If this is correct, one would expect significant rhombic character in the molecules we have studied, since the ground state solely transforms as B_2 under $C_{2v}^{(x)}$ only if $\Delta E_{yz} \neq \Delta E_{yz}$.

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