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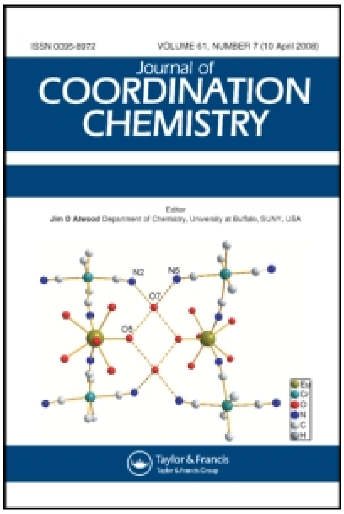

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THE EPR SPECTRA OF TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER(II) VIII. N,N'-BIS(ACETYLPYRROLE)-1,3-PROPANEDIIMINE AND N,N'-BIS(ACETYLPYRROLE)-1,4-BUTANEDIIMINE

Robert L. Lancione[ab]; Harry C. Allen Jr.[a]; James R. Buntaine[ac]
[a] Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, Massachusetts, USA [b] J.B.F. Scientific Corporation, Wilmington, MA [c] Department of Chemistry, Cornell University, Ithaca, New York

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THE EPR SPECTRA OF TETRADENTATE SCHIFF-BASE COMPLEXES OF COPPER(II)†
VIII. N,N′-BIS(ACETYLPYRROLE)-1,3-PROPANEDIIMINE AND N,N′-BIS(ACETYLPYRROLE)-1,4-BUTANEDIIMINE

ROBERT L. LANCIONE,‡ HARRY C. ALLEN, Jr. and JAMES R. BUNTAINE¶

Department of Chemistry, Jeppson Laboratory, Clark University, Worcester, Massachusetts 01610, USA.

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The EPR spectra of N,N′-bis(acetylpyrrole)-1,3-propanediimine [Cu pn(actpy)] and N,N′-bis(acetylpyrrole)-1,4-butanediimine [Cu bn(actpy)] have been observed at x-band frequencies. The parameters in the usual doublet spin-Hamiltonian are: Cu[pn(actpy)$_2$], $g_z = 2.173 \pm 0.001$, $g_x = 2.044 \pm 0.002$, $g_y = 2.043 \pm 0.002$, $A_z^{Cu} = 199.0 \times 10^{-4}\,cm^{-1}$, $A_x^{Cu} = 25.6 \times 10^{-4}\,cm^{-1}$, $A_y^{Cu} = 27.1 \times 10^{-4}\,cm^{-1}$, $A_z^N = 12.8 \times 10^{-4}\,cm^{-1}$, $A_x^N = A_y^N = 15.1 \times 10^{-4}\,cm^{-1}$: Cu[bn(actpy)$_2$], $g_z = 2.189 \pm 0.001$, $g_x = g_y = 2.044 \pm 0.002$, $A_z^{Cu} = 179.9 \times 10^{-4}\,cm^{-1}$, $A_x^{Cu} = 19.9 \times 10^{-4}\,cm^{-1}$, $A_y^{Cu} = 20.6 \times 10^{-4}\,cm^{-1}$, $A_z^N = 11.9 \times 10^{-4}\,cm^{-1}$, $A_x^N = 14.1 \times 10^{-4}\,cm^{-1}$, $A_y^N = 11.9 \times 10^{-4}\,cm^{-1}$. Assuming a square planar configuration about the Cu(II) ions, the molecular orbital coefficients are similar to those found for other tetradentate Schiff-base chelates of Cu(II). However, the g-values, A values and optical spectral data indicate a tetrahedral distortion of the Cu(II) environment in Cu[bn(actpy)$_2$]. The χ-value for this compound also indicates a significantly different isotropic hyperfine interaction from similar chelates.

KEY WORDS: N,N′-bis(acetylpyrrole)-1,3-propanediimine, N,N′-bis(acetylpyrrole)-1,4-butanediime, EPR spectrum, spin-Hamiltonian parameters, molecular orbital coefficients χ-value, tetrahedral distortion.

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INTRODUCTION

Over the past few years a systematic investigation of the structure and bonding in tetradentate Cu(II) complexes has been undertaken. About 10 such chelates have been studied in which the immediate chemical environment of the Cu(II) consists of two nitrogen atoms and two oxygen atoms with the nitrogen atoms cis to each other. It has been found that the magnetic parameters and the m.o. coefficients are quite similar for this group of compounds regardless of the size of the bridge or substitution upon the ligand.[1] In addition, the Abragam, Horowitz and Price[2,3] parameter,

$$\chi = \frac{4\pi}{S} (\Psi|\sum_i \delta(r_i) S_{zi}|\Psi) \qquad (1)$$

is remarkably constant for this series of compounds.

In an attempt to ascertain the effect of modifying the immediate environment of the Cu(II) on the m.o. coefficients and the χ-value, and EPR-optical study of N,N′-bis(pyrrole-2-aldehyde)ethylenediimine Cu(II) [Cu en(pyal)$_2$] was undertaken.[4] (See Figure 1, R = $-(CH_2)_2-$, R′ = H.) The analysis showed that although the coefficients in the σ-antibonding orbital are quite similar to those in the N_2O_2 systems, the in-plane π-bonding seems to be stronger. Further, the value of $\chi = 3.732$ was found in Cu [en(pyal)$_2$] compared to an average of $\chi = 3.917$ for the "N_2O_2" series. This seemed to indicate that the immediate environment of the Cu(II) might have a measurable

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‡Present address: J.B.F. Scientific Corporation, 2 Jewel Drive, Wilmington, MA. 01887.

¶Present Address: Department of Chemistry, Cornell University, Ithaca, New York 14850.

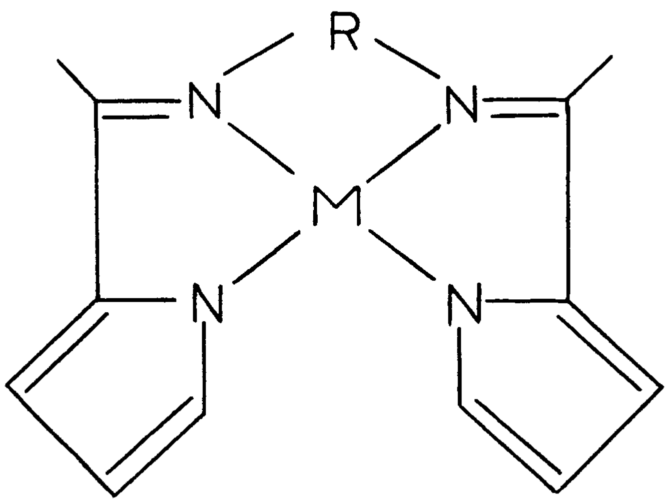

FIGURE 1 Molecular Geometry of the complexes
Cu[pn(actpn)$_2$] R = $-(CH_2)_3-$ R′ = CH_3
Cu[bn(actpn)$_2$] R = $-(CH_2)_4-$ R′ = CH_3

effect on the isotropic hyperfine constant. It was also observed in the spectrum that there were unequal nitrogen hyperfine coupling for the two chemically different kinds of nitrogens bonded to the copper ion. In the two complexes reported on here, the methine protons in Cu[en(pyal)$_2$] have been replaced with methyl groups to reduce the complexity of the spectrum. The bridging groups are 1,3-propanediame and 1,4-butanediamine.

Although we have not observed unequal nitrogen coupling constants, we believe that one of the complexes may be distorted from the usual square planar geometry because of a steric interaction between the methyl groups and the bridge carbons.

Tetradentate Schiff base complexes of copper(II) have been known to deviate from square planar coordination. This can result from dimeric interactions which lead to square pyramidal structures or intramolecular steric interactions which give rise to flattened tetrahedral geometries. These cases are well documented for cis "N_2O_2" type complexes.[5] There are very little data available concerning these types of distortions in tetradentate Schiff-base complexes of the "N_4" type. Weber[6] has investigated nickel(II) complexes derived from pyrrole-2-aldehyde and demonstrated that they remain planar even when the central ring size is seven or eight. The data concerning the corresponding copper complexes are less clear.

In a recent EPR study[7] of polycrystalline N,N′-bis-(o-aminobenzaldehyde)ethylenediimine copper(II) it was postulated that it might be pseudotrahedral, but no crystallographic or single crystal EPR data are available.

In this article the EPR spectra of copper(II) complexes with N,N′-bis-(2-acetylpyrrole)-1,3-propanediimine, [Cu pn(actpy)$_2$] and N,N′-bis-(2-acetylpyrrole)-1,4-butanediimine [Cu bn(actpy)$_2$] are reported. These complexes, R′ = CH_3, R = $-(CH_2)_3-$ and $-(CH_2)_4-$ in Figure 1, are believed to be reported here for the first time. The complexes have been studied as substitutional impurities in single crystals of their corresponding nickel(II) complexes.

EXPERIMENTAL

The complexes were prepared by heating the diamine, 2-acetylpyrrole and the metal acetate, neat, in a 1:2:1 molar ratio for approximately one hour at 130°C and recrystallizing the crude product several times from chloroform. Attempts to isolate the ligands were unsuccessful even using Lewis acid catalysts.[8] The compound 2-acetylpyrrole was prepared by the acylation of pyrrolmagnesium bromide with ethylacetate according to the procedure of Bean.[9]

Single crystals were grown by slow evaporation of chloroform solutions. Isotopically pure ^{63}Cu(II), as

TABLE I
Physical data of the nickel complexes[a]

Compound	°C M.P.[b]	Color	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found
Ni[pn(actpy)$_2$]	313–315	red	57.55	57.34	5.80	5.83	17.90	18.21
Ni[bn(actpy)$_2$]	274–276	purple	58.75	58.39	6.16	6.21	17.13	17.58

[a] Analysis by: Instranal Lab., Inc. Rensselaer, N.Y.
[b] Uncorrected.

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TABLE II
The magnetic parameters

	Cu[pn(actpy)$_2$]	Cu[bn(actpy)$_2$]
g_z	2.173 ± 0.001	2.189 ± 0.001
g_x	2.044 ± 0.002	2.044 ± 0.002
g_y	2.043 ± 0.002	2.044 ± 0.002
A_z^{Cu}	196.2 ± 0.5 G 199.0×10^{-4} cm^{-1}	176.0 ± 0.5 G 179.9×10^{-4} cm^{-1}
A_x^{Cu}	26.8 ± 1 G 25.6×10^{-4} cm^{-1}	19.9 ± 1 G 19.0×10^{-4} cm^{-1}
A_y^{Cu}	28.4 ± 1 G 27.1×10^{-4} cm^{-1}	20.6 ± 1 G 19.7×10^{-4} cm^{-1}
A_z^N	12.6 ± 0.2 G 12.8×10^{-4} cm^{-1}	11.6 ± 0.2 G 11.9×10^{-4} cm^{-1}
A_x^N	15.8 ± 0.5 G 15.1×10^{-4} cm^{-1}	14.8 ± 0.5 G 14.1×10^{-4} cm^{-1}
A_y^N	15.8 ± 0.5 G 15.1×10^{-4} cm^{-1}	12.5 ± 0.5 G 11.9×10^{-4} cm^{-1}
υ_1	18,180 cm^{-1}	16,670 cm^{-1}
υ_2	14,300 cm^{-1}	12,990 cm^{-1}

TABLE III
Direction cosines of the principle g-values with respect to the laboratory axes for Ni[pn(actpy)$_2$]

	x	y	z
g_x	∓0.56	0	0.83
g_y	0	1	0
g_z	0.83	0	±0.56

TABLE IV
Direction cosines of the principle g-values with respect to the laboratory axes for Ni[bn(actpy)$_2$]

	x	y	z
g_x	0.67	0	0.74
g_y	0	1	0
g_z	0.74	0	−0.67

the nitrate, was added (~3 mole percent) during the synthesis of the Ni(II) complexes to form the doped compounds. Analytical data for the undoped nickel complexes are given in Table I. Copper complexes were prepared according to the above procedure and used to collect optical data.

The EPR spectrometer and the method used for data collecting and reduction have been previously described.[10] Optical spectra were recorded on a Cary-14 spectrophotometer in region from 3000Å to 15000Å.

Spectra were recorded for each of the chelates at 5° increments in the planes perpendicular to the axes indicated in Figures 2 and 3. The parameters in the usual doublet spin-Hamiltonian were determined as previously described.[10] The values of these parameters are given in Table II, and the direction cosines relating the principle axes of the g-tensor to the laboratory axes shown in Figures 2 and 3 are given in Table III. The frequencies of the optical transitions are included in Table II.

Molecular orbital coefficients and χ were calculated for both complexes by methods previously described.[1] These values are reported in Table V where they are compared with the previously reported[4] values for Cu[en(pyal)$_2$].

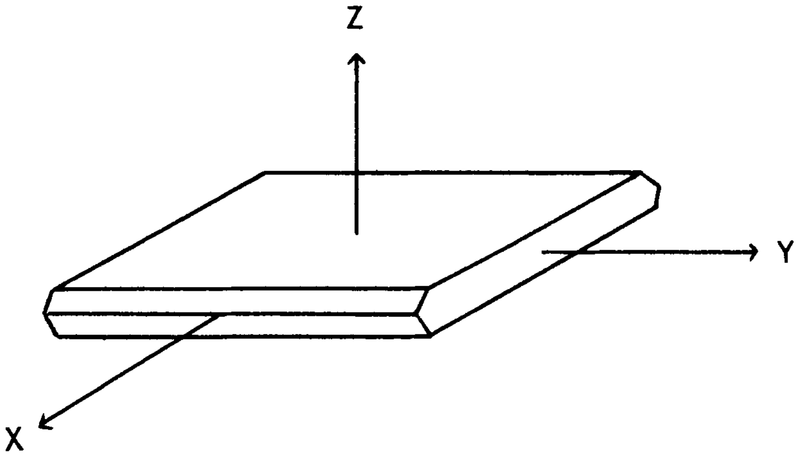

FIGURE 2 Orientation of the laboratory axes with respect to the crystal morphology for Cu[pn(actpy)$_2$].

TABLE V
Molecular orbital coefficients

	Cu[en(pyal)$_2$]	Cu[pn(actpy)$_2$]	Cu[bn(actpy)$_2$]
α^2	0.758	0.775	0.770
α'^2	0.336	0.318	0.322
β^2	0.683	0.695	0.562
$-\chi$	3.732	3.752	3.435

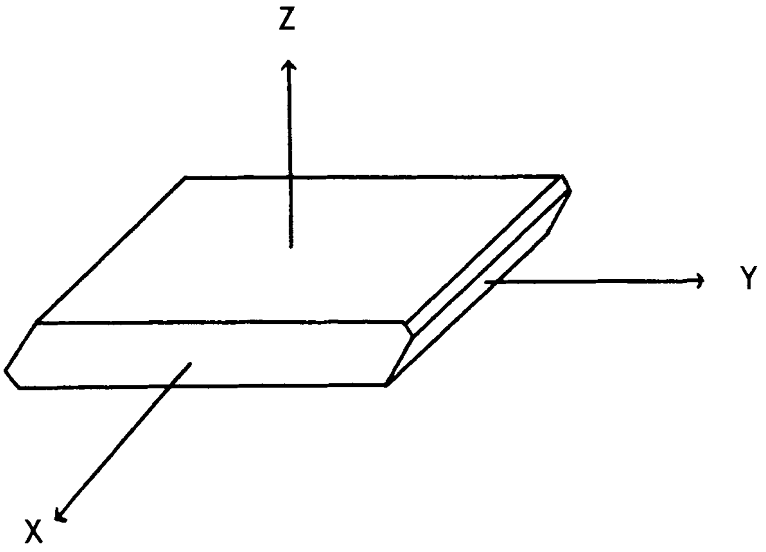

FIGURE 3 Orientation of the laboratory axes with respect to the crystal morphology of Cu[bn(actpy)$_2$].

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DISCUSSION

The values for the coefficients in the antibonding σ-orbital are very similar to those for Cu[en(pyal)$_2$] and are also similar to the values determined for the "N_2O_2" chelates. The coefficients for the in-plane antibonding π-orbital for Cu[en(pyal)$_2$] and Cu[pn(actpy)$_2$] indicate somewhat stronger in-plane π-bonding than is true in the "N_2O_2" chelates. For Cu[bn(actpy)$_2$] the coefficient indicates considerable more π-bonding than in the other "N_4" chelates and the "N_2O_2" chelates. The χ-value for the first two "N_4" chelates, although somewhat lower than the average of the "N_2O_2" chelates, are in essential agreement. However, the χ-value for Cu[bn(actpy)$_2$] is considerable smaller than for the other "N_4" chelates.

This significant deviation of the χ-value is disturbing. While the increase in $\langle g \rangle$ value, decrease in $\langle A \rangle$ value and decrease in the $|xy\rangle \rightarrow |x^2 - y^2\rangle$ transition frequency are all indicative of a tetrahedral distortion of the immediate Cu(II) environment, these symptoms of the immediate Cu(II) environment were also present in 7-methyl-N,N′-bis(salicylidene) ethylenediimine Cu(II) and the χ-value for this "N_2O_2" complex fell near the mean of those for 9 similar complexes.[11] It may be that there is a significantly greater tetrahedral distortion in the Cu[bn(actpy)$_2$] because of steric interference between the long bridge and the methyl group on the acetylpyrrole. In such a case the formalism used to calculate the m.o. coefficients and hence χ is not valid. This hypothesis can only be resolved by a crystal structure determination.

A second possibility is that the molecular structure is a dimer or trimer in which the copper environment is not even close to square planar, although present evidence seems to make this doubtful. Until the structure of the complex is available this inconsistency will remain unresolved.

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