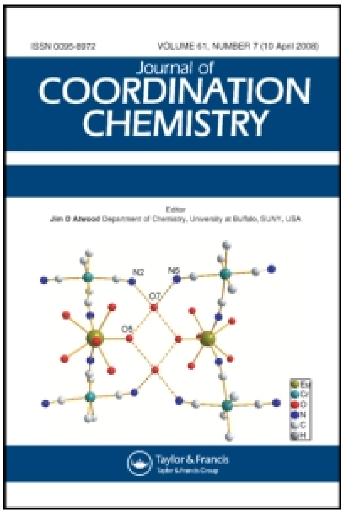

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THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER (II)

II. N,N′-bis(salicylidene)ethylenediimine and 7-methyl-N,N′-bis (salicylidene)ethylenediimine.

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The EPR spectra of single crystals of ^{63}Cu(II) doped N,N′-bis(salicylidene)ethylenediimine Ni(II), [Ni(sal)$_2$en] and 7-methyl-N,N′-bis(salicylidene)ethylenediimine Ni(II), [Ni(7-me sal)$_2$en] have been studied. The usual doublet spin-Hamiltonian parameters for the complexes have been found to be: Cu(II)[(sal)$_2$en]; $g_z = 2.192 \pm 0.002$; $g_x = 2.046 \pm 0.004$; $g_y = 2.049 \pm 0.004$; $A_z = 201.0 \times 10^{-4}$ cm^{-1}; $A_x = 29.3 \times 10^{-4}$ cm^{-1}; $A_y = 31.3 \times 10^{-4}$ cm^{-1}; $A_z^N = 12.6 \times 10^{-4}$ cm^{-1}; $A_x^N = 14.5 \times 10^{-4}$ cm^{-1}; $A_y^N = 15.7 \times 10^{-4}$ cm^{-1}; $A_z^H = 6.3 \times 10^{-4}$ cm^{-1}; $A_x^H = 7.3 \times 10^{-4}$ cm^{-1}, $A_y^H = 7.9 \times 10^{-4}$ cm^{-1}; Cu(II)[(7-me sal)$_2$en]; $g_z = 2.189 \pm 0.002$; $g_x = 2.037 \pm 0.004$; $g_y = 2.046 \pm 0.004$; $A_z = 203.0 \times 10^{-4}$ cm^{-1}; $A_x = 36.9 \times 10^{-4}$ cm^{-1}; $A_y = 22.7 \times 10^{-4}$ cm^{-1}; $A_z^N = 12.6 \times 10^{-4}$ cm^{-1}; $A_x^N = 13.3 \times 10^{-4}$ cm^{-1}; $A_y^N = 14.0 \times 10^{-4}$ cm^{-1}. Values of molecular orbital coefficients calculated for these complexes show that their bonding properties are similar to those of other compounds of this type. There is considerable covalency in the metal-ligand σ-bonds, and significant in-plane pi-bonding is present.

INTRODUCTION

In an earlier paper[1] (I) a study of the EPR spectra of the copper(II) complexes of N,N′-bis(acetylacetone)-ethylenediimine and N,N′-bis(1,1,1-trifluoroacetylacetone)ethylenediimine doped into single crystals of the corresponding nickel(II) complexes was reported. In an effort to elucidate the effect of ligand variation on the bonding environment of the metal ion in these tetradentate Schiff-base complexes, the study has been extended to include an investigation of the EPR spectra of the copper(II) complexes of N,N′-bis(salicylidene)ethylenediimine [(sal)$_2$en] and 7-methyl-N,N′-bis(salicylidene)ethylenediimine [(7-me sal)$_2$en], also doped into single crystals of the corresponding nickel(II) complexes.

Metal complexes of [(sal)$_2$en] and [(7-me sal)$_2$en] were first prepared by Pfeiffer.[2] Since that time these complexes have generated considerable interest as model compounds of biological interest. The structural formulae of the complexes studied here are shown in Figure 1. Since it is possible to make such a large variety of Schiff base ligands, they provide a convenient means for studying the effects of changes in ligand structure on the bonding environment of the metal ion in these complexes.

Much is already known about Ni[(sal)$_2$en], Cu[(sal)$_2$en] and Ni[(7-me sal)$_2$en]. Magnetic susceptibility data are available for all three compounds.[3–6] X-ray crystal structure determinations have been made on Cu[(sal)$_2$en].[7,8] UV and visible spectra of Cu[(sal)$_2$en] and Ni[(sal)$_2$en] in solution have been studied,[9] as well as the polarized single crystal spectrum of Cu[(sal)$_2$en].[10,11] Results of powder and solution EPR spectra of Cu[(sal)$_2$en] have also been published,[12] although values obtained for the g- and A-values were in general smaller than those found in this single crystal study. In this note the EPR spectra of ^{63}Cu doped single crystals of Ni[(sal)$_2$en] and Ni[(7-me sal)$_2$en] are reported and the optical and magnetic data are used to make inferences about the bonding in these complexes.

EXPERIMENTAL

The chelates were prepared by previously described methods.[2] The Ni(II) chelates were prepared with a doping of approximately 1% of ^{63}Cu. The structures of the ligands and the nickel complexes were characterized by their nmr spectra. Single crystals of the ^{63}Cu-doped [(sal)$_2$en] complex were grown by the slow evaporation of an acetone solution. Crystals

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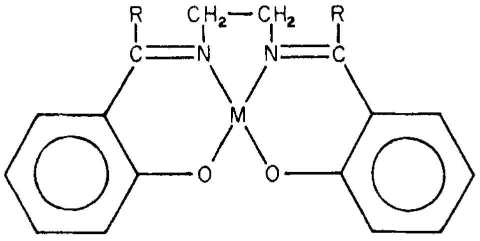

N, N′- bis(salicylaldehyde)ethylenediimine M(II) R=H

7 – methyl – N,N′ – bis(salicylaldehyde)ethylenediimine M(II) R=CH_3

FIGURE 1 Structural formulae of the complexes

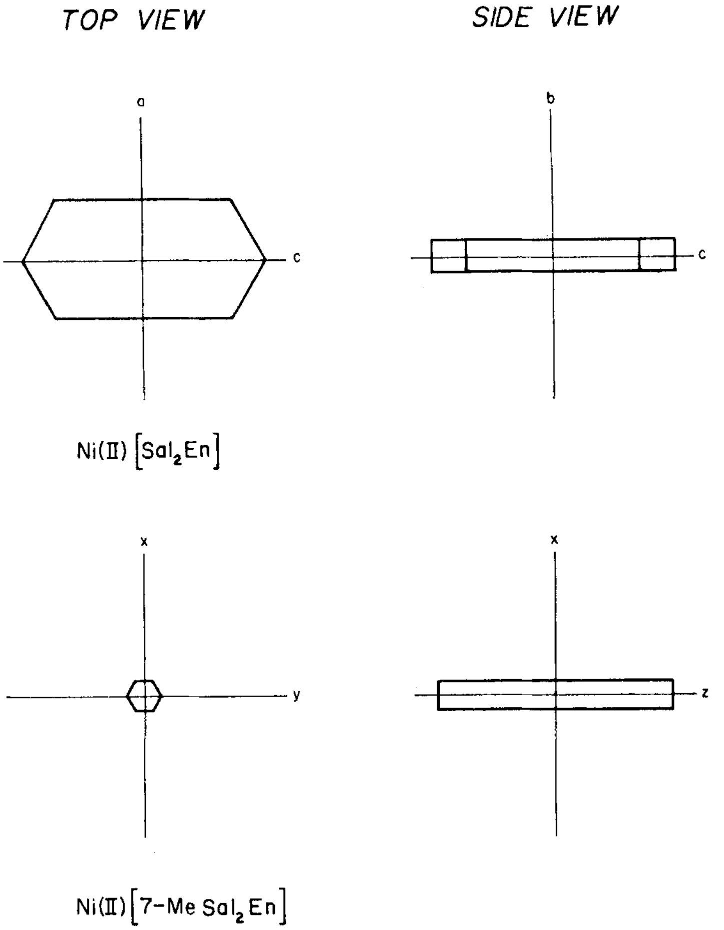

FIGURE 2 Orientation of laboratory axes with respect to the crystals.

of the [(7-me sal)$_2$en] complex were grown from chloroform solutions because of the limited solubility of the complex in acetone. The latter crystals are quite unstable and lose their single crystal character after standing in air for a few days. This seems to be due to the crystals picking up atmospheric water. The deterioration is readily noted since the EPR spectrum becomes that of a polycrystalline sample.

The single crystals of ^{63}Cu doped Ni[(sal)$_2$en] are dark red-orange hexagonal plates. The spectra were obtained as previously described[1] by mounting the crystals along three orthogonal axes as shown in Figure 2. Spectra were recorded at angular increments of 5° as the crystal was rotated about each of the axes. The small angular increments were necessary because of severe overlapping of the spectra at certain angles caused by the presence of two magnetically non-equivalent sites, and a very complicated super-hyperfine splitting. Figure 3 shows a sample spectrum taken in an unusually favorable orientation in which the two magnetic sites are equivalent. The four groups of eleven lines are due to the coupling of the unpaired electron with the copper nucleus ($I = 3/2$). Experience indicates that each of these components should be further split into 5 components, rather than the observed eleven components, through the coupling of the unpaired electron to the two ligand nitrogen atoms, each with $I = 1$. The eleven line pattern is reminiscent of the pattern found by Maki and McGarvey[13] in the EPR spectrum of bis-salicylaldehyde-imine Cu(II). The additional splitting was attributed by them to the protons in positions analogous to those labelled "R" in Figure 1. The relative intensities within the eleven components are the same as they observed. This hypothesis can be tested for our chelate by substituting for that hydrogen another substituent group. In Cu[(7-me sal)$_2$en] this hydrogen is replaced by a methyl group. The single crystals of Ni[(7-me sal)$_2$en] grow as long hexagonal rods. Spectra were recorded at angular increments of 10° about the orthogonal set of axes shown in Figure 2b.

A sample spectrum is shown in Figure 4, in which it is clearly evident that only the expected splitting due to the ligand nitrogen atoms is observed. The spacing between the components is about twice the spacing observed in Cu[(sal)$_2$en]. Thus our situation is quite analogous to that reported by Maki and McGarvey.[13]

Bonding and Magnetic Parameters

The magnetic data could be fit to the usual spin-Hamiltonian for a doublet state.[1] The spin-Hamiltonian parameters derived from the EPR spectra are collected in Table I. The parameters for the two molecules are remarkably similar and the values of g_x and g_y are essentially the same indicating a nearly axial symmetry in the g-tensor. The value of

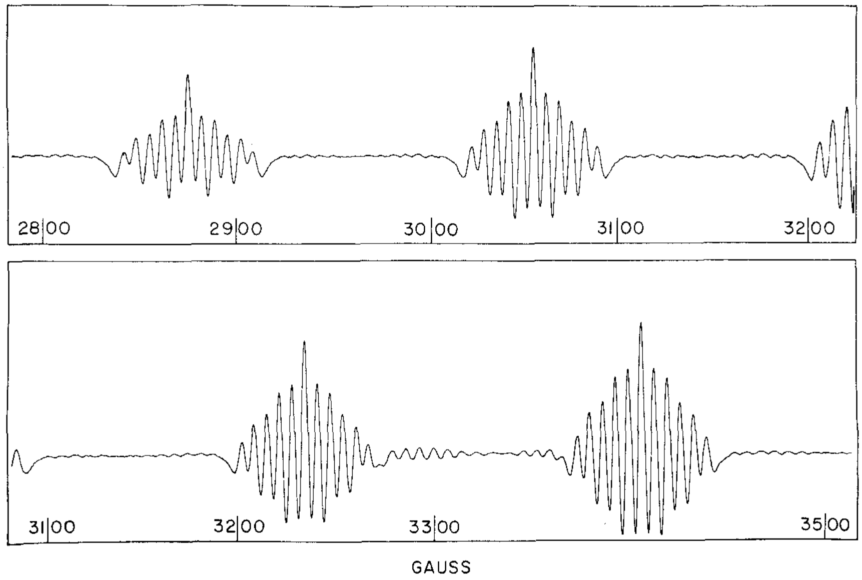

FIGURE 3 Spectrum of ^{63}Cu-doped Ni[(sal)$_2$en] showing the eleven line pattern. Both sites are magnetically equivalent in this orientation.

TABLE I
Spin-Hamiltonian constants

	Cu[(sal)$_2$en]	Cu[(7-me-sal)$_2$en]
g_z	2.192 ± 0,002	2.189 ± 0.002
g_x	2.046 ± 0.004	2.037 ± 0.004
g_y	2.049 ± 0.004	2.046 ± 0.004
A_z	196.7 ± 1 *G* 201.0 x 10^{-4} cm^{-1}	198.6 ± 1 *G* 203.2 x 10^{-4} cm^{-1}
A_x	30.7 ± 2 *G* 29.3 x 10^{-4} cm^{-1}	38.8 ± 2 *G* 36.9 x 10^{-4} cm^{-1}
A_y	32.7 ± 2 *G* 31.3 x 10^{-4} cm^{-1}	23.8 ± 2 *G* 22.7 x 10^{-4} cm^{-1}
A_z^N	12.3 ± 1.0 *G* 12.6 x 10^{-4} cm^{-1}	12.3 ± 1.0 *G* 12.6 x 10^{-4} cm^{-1}
A_x^N	15.2 ± 1.0 *G* 14.5 x 10^{-4} cm^{-1}	14.0 ±1.0 *G* 13.3 x 10^{-4} cm^{-1}
A_y^N	16.5 ± 1.0 *G* 15.7 x 10^{-4} cm^{-1}	14.7 ± 1.0 *G* 14.0 x 10^{-4} cm^{-1}
A_z^H	6.1 ± 1.0 *G* = 6.3 x 10^{-4} cm^{-1}	—
A_x^H	7.6 ± 1.0 *G* = 7.3 x 10^{-4} cm^{-1}	—
A_y^H	8.3 ± 1.0 *G* = 7.9 x 10^{-4} cm^{-1}	—

g_z for Cu(sal$_2$en) is in agreement with the previously reported values obtained from frozen solution and polycrystalline samples.

The small differences in the reported values of A_x and A_y are probably real and reflect the fact that the ligand nitrogen atoms are in cis-positions.

The complexes are treated as belonging to the point group C_{2v} although they may have lower symmetry. The electronic ground state of a d^9 complex belonging to the point group C_{2v} is the antibonding molecular orbital belonging to the irreducible representation B_2. If the x-axis is chosen as the twofold axis of rotation, this is the molecular orbital made up principally of the the d_{xy} orbital on the Cu(II). The explicit forms of the molecular orbitals appropriate to this description are given in I and will not be repeated. The relationships between the coefficients in the molecular orbitals and the magnetic parameters are also given in I. The coefficients of interest here are α, the coefficient of d_{xy} in the B_2 orbital, α', the coefficient of the ligand combination in the B_2 orbital and β, the coefficient of $d_{x^2-y^2}$ in an A_1 molecular orbital.

In the crystal field approximation one would predict, for the unpaired electron in the d_{xy} orbital, that $(g_\parallel - 2) = 4(g_\parallel - 2)$. This relationship holds very well for these two molecules. However, using the spin orbit coupling constant of the free ion, 828 cm^{-1}, and the frequency[10], $E_{x^2-y^2} - E_{xy} \cong 17{,}000$ cm^{-1}, as required by crystal field theory, an orbital reduction factor of about 0.5 is needed to calculate the observed value of g_z. Such an orbital reduction factor has been interpreted as indicating a significant amount of covalency in the σ-bonding and/or significant π-bonding.

The methods for evaluating the molecular orbital parameters and hybridization on the ligand nitrogens from the magnetic and optical data of the molecule are given in detail in I. Unfortunately the d–d spectra of Cu(II) doped into the Ni(II) complexes are not available. However, Ferguson[10] has studied the polarized spectrum of Cu[(sal)$_2$en] in the d–d region. The interpretation of this spectrum has been discussed by Belford and Piper.[11] There seems to be general agreement that the band observed at 17,300 cm^{-1} arises from a transition from the ground state to the molecular orbital consisting mainly of the metal-ion $d_{x^2-y^2}$ orbital. The assignment for a second band observed at 20,800 cm^{-1} is not at all clear. By using the assignment of the 17,300 cm^{-1}

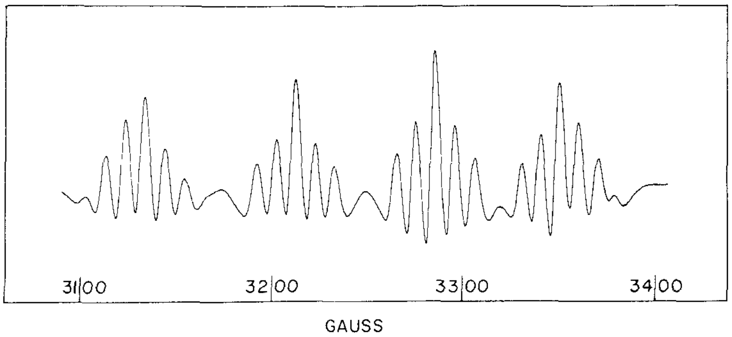

FIGURE 4 Spectrum of ^{63}Cu-doped Ni[(7-me-sal)$_2$en] showing typical 5-line superhyperfine structure. Both sites are magnetically equivalent in this orientation.

band together with the values of the derived magnetic parameters it is possible to calculate the molecular orbital coefficients α^2 and α'^2 for the B_2 molecular orbital (mainly d_{xy}) and the coefficient of $(d_{x^2-y^2})$ in the in-plane A_1 orbital. From the superhyperfine splitting one can calculate the amount of p-character in the bonding orbitals of the ligand nitrogen in both complexes. To calculate values of the molecular orbital parameters in the [(7-me sal)$_2$en] complex, a value of 18,000 cm^{-1} was used for the $E_{xy} \rightarrow E_{x^2-y^2}$ transition[16] The values of the molecular orbital parameters are rather insensitive to the value chosen for this transition. A 20% error in the frequency results in only a 5% error in the m.o. constants.[15] The results of these calculations are collected in Table II. The values of α^2 for the two complexes indicate a significant amount of covalency in the α-bonding, while the values of β^2 indicate a rather strong in-plane π-bonding. The values of n support a picture of essentially sp^2 hybridization on the ligand nitrogen atoms. The expected value of n for sp^2 hybridization is 0.667.

TABLE II
Molecular orbital parameters

	Cu[(sal)$_2$en]	Cu[(7-me-sal)$_2$en]
α^2	0.757	0.764
$(\alpha')^2$	0.327	0.319
β^2	0.764	0.743
$(\alpha')^2$†	0.323	0.309
n	0.673	0.681

†From nitrogen hyperfine splitting

Following Maki and McGarvey[12] a value for the fractional 1s electron hole associated with the proton in the [(sal)$_2$en] complex may be calculated. By comparing the average value of the proton splitting in the chelate (7.2×10^{-4} cm^{-1}) with the hyperfine constant from the proton electron coupling in the hydrogen atom, a value of 0.015 is found. This is slightly higher than found by Maki and McGarvey in bis-salicyaldehyde-iimine Cu(II) but the two values probably agree within experimental uncertainty.

Values of the coefficients in the remaining molecular orbitals cannot be calculated until better spectral information becomes available.

Relationships to Crystal Structure

The crystal structures of both Ni[(sal)$_2$en] and Cu[(sal)$_2$en] have been done.[7,8] The crystals are not isomorphous but the structure of the Ni complex is the important one in this study provided that the Cu(II) is doped into the host lattice substitutionally. The Ni(II) compound is orthorhombic with unit cell parameters $a = 18.818 \pm 0.008$ Å, $b = 26.132 \pm 0.009$ Å and $c = 7.483 \pm 0.003$ Å. The space group is P_{bca} and there are 8 molecules per unit cell.[8]

Ni[(sal)$_2$en] forms centrosymmetric dimers in the crystal with a Ni–Ni distance of 3.21 Å. The Ni–Ni interatomic line makes an angle of 75° with the coordination plane of the molecule. The arrangement of the dimers in the unit cell accounts for the presence of two non-equivalent magnetic sites. The direction cosines of a perpendicular to the molecular plane calculated from the x-ray structure data are in excellent agreement with the direction cosines of the z-direction of the g-tensor.

x-ray	0.46	0.08	± 0.86
magnetic	0.45	0	± 0.89

This agreement indicates that the Cu(II) does, indeed, enter the lattice of the Ni(II) complex substitutionally. No x-ray structures for the Ni(II) or Cu(II) complexes of [(7-me sal)$_2$en] have been found.

DISCUSSION

The values for the molecular orbital parameters found for the two complexes reported here are very nearly the same. Further, they are not significantly different from those reported in I for the N,N′-bis(acetylacetone)ethylenediime Cu(II) and N′,N′-bis(1,1,1-trifluoroacetylacetone) Cu(II). The parameters for the four complexes are probably the same within the experimental uncertainty. This fact is unfortunate, for it makes it dangerous to draw any inferences about the differences in the bonding among the four chelates already studied.

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