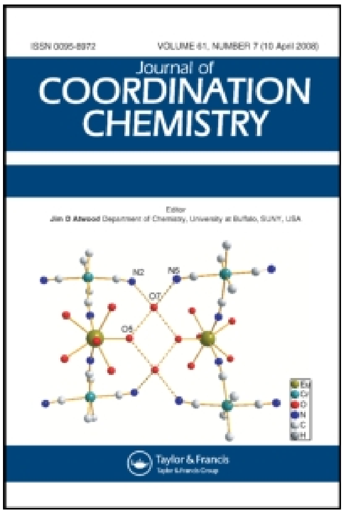

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER II VI, N, N'-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE AND 7-METHYL-N, N'-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE

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To cite this Article Scullane, Michele I. and Allen Jr., Harry C.(1978) 'THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER II VI, N, N'-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE AND 7-METHYL-N, N'-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE', Journal of Coordination Chemistry, 7: 3, 181 — 186

To link to this Article: DOI: 10.1080/00958977808073059

URL: http://dx.doi.org/10.1080/00958977808073059

J. Coord. Chem.
1978, Vol. 7, pp. 181–186

THE EPR SPECTRA OF TETRADENTATE SCHIFF BASE COMPLEXES OF COPPER II VI, N, N′-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE AND 7-METHYL-N, N′-BIS(SALICYLIDENE)-O-PHENYLENEDIIMINE†

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(Received June 6, 1977)

KEY WORDS: N,N′-bis(salicylidene)-o-phenylenediimine Cu(II); 7-methyl N,N′-bis(salicylidene)-o-phenylenediimine Cu(II); EPR spectrum; optical spectra; Spin Hamiltonian parameters; molecular orbital coefficients; Tetrahedral distortion.

The EPR spectra of single crystals of ^{63}Cu(II) doped N,N′-bis(salicylidene)-o-phenylenediimine Ni(II), (Ni(II)(sal)$_2$ phen), and N,N′-bis(7-methyl salicylidene)-o-phenylenediimine Ni(II), (Ni(II)(7-me sal)$_2$ phen) have been studied. The usual doublet spin-Hamiltonian parameters have been found to be: ^{63}Cu(II) doped Ni(II)(sal)$_2$ phen; $g_z = 2.192 \pm 0.002$, $g_x = 2.049 \pm 0.004$, $g_y = 2.041 \pm 0.004$, $A_z = 201.7 \times 10^{-4}$ cm^{-1}, $A_x = 36.4 \times 10^{-4}$ cm^{-1}, $A_y = 31.4 \times 10^{-4}$ cm^{-1}, $A_{\parallel}^{N} = 11.3 \times 10^{-4}$ cm^{-1}, $A_{\perp}^{N} = 14.0 \times 10^{-4}$ cm^{-1}, $A_{\parallel}^{H} = 5.7 \times 10^{-4}$ cm^{-1}, $A_{\perp}^{H} = 7.0 \times 10^{-4}$ cm^{-1}; ^{63}Cu(II) doped Ni(II)(7-me sal)$_2$ phen; $g_z = 2.209 \pm 0.002$, $g_x = 2.049 \pm 0.004$, $g_y = 2.044 \pm 0.004$, $A_z = 197.4 \times 10^{-4}$ cm^{-1}, $A_x = 28.7 \times 10^{-4}$ cm^{-1}, $A_y = 24.8 \times 10^{-4}$ cm^{-1}, $A_{\parallel}^{N} = 10.6 \times 10^{-4}$, $A_{\perp}^{N} = 13.0 \times 10^{-4}$ cm^{-1}. A comparison of the optical transitions and the values of the magnetic parameters for these two complexes indicate that there is a small tetrahedral distortion present in Cu(II)(7-me sal)$_2$ phen.

INTRODUCTION

Results of previous studies of the EPR spectra of ethylenediamine bridged tetradentate Schiff base complexes of Cu(II)[1–3] showed that minor changes in ligand structure have minimal discernable effects on the metal–ligand bonding as evidenced by the similarities in the magnetic parameters and molecular orbital coefficients of the complexes. In order to determine whether the presence of o-phenylenediamine as the bridging amine results in any significant differences in the metal–ligand bonding, the EPR spectra of single crystals of ^{63}Cu(II) doped N,N′-bis(salicylidene)-o-phenylenediimine Ni(II), (Ni(II)(sal)$_2$ phen), and N,N′-bis(7-methyl salicylidene)-o-phenylenediimine, (Ni(II)(7-me sal)$_2$ phen), (Figure 1) have been investigated.

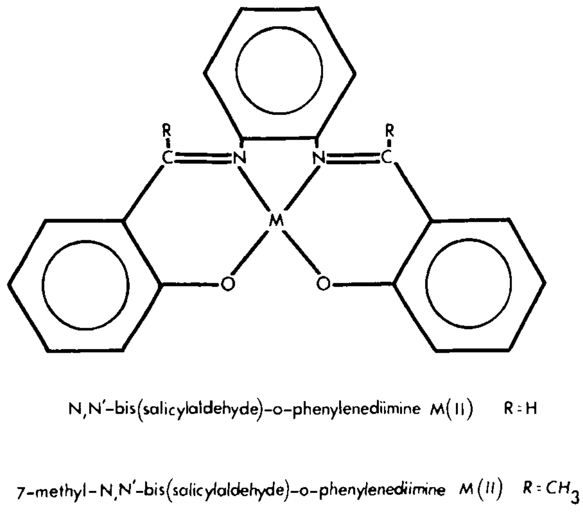

FIGURE 1 Molecular formulae of (sal)$_2$phen M(II) and (7-me sal)$_2$phen M(II).

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†Supported in part by the U.S. Bureau of Mines, Department of Interior under Grant G0166203.

Some kinetic and x-ray structure data are available for the $(sal)_2$ phen complexes,[4-7] but no references to Cu(II)(7-me $sal)_2$phen or Ni(II)(7-me $sal)_2$phen were found in the literature.

EXPERIMENTAL

Ni(II)$(sal)_2$phen was prepared as previously described[4] and doped with ~ 1% of the corresponding ^{63}Cu(II) chelate. Crystals of suitable size could not be grown from any common non-hydrogen bonding solvents. Large dark red single crystals of this complex can be grown from chloroform solution by slow evaporation, however they decompose upon standing. This phenomenon has been observed previously in the Schiff base complexes Cu(II)$(sal)_2$en[8] and Ni(II)(7-me $sal)_2$en,[2] and is apparently due to the loss of chloroform molecules of crystallization. The chloroform adducts of both Ni(II)(7-me $sal)_2$en and Ni(II)$(sal)_2$phen were found to contain one mole of chloroform per mole of complex. No crystal structure information is available for Ni(II)$(sal)_2$phen·$CHCl_3$. The ligand (7-me $sal)_2$phen was obtained by combining 0.01 mole of o-phenylenediamine and 0.02 mole of 2′-hydroxyacetophenone and heating gently on a hot plate for one half hour. When the mixture was cooled slowly, a bright yellow solid (m.p. 99–101°C) formed which was recrystallized from hexane. The structure of the ligand was confirmed by its NMR spectrum.

The metal complexes of (7-me $sal)_2$phen were synthesized by adding dropwise a solution of 0.005 mole of the metal acetate in a minimum amount of methanol to a boiling solution of 0.005 mole of the ligand in 50 ml of chloroform. The resulting mixture was refluxed for about twelve hours. After the solution was cooled, it was mixed with about 100 ml of ether and filtered. The filtrate was left to stand until most of the solvent had evaporated. whereupon a dark green crystalline product was filtered out. Single crystals of the complex were grown by slow evaporation of an acetone solution of the complex.

EPR spectra were obtained as previously described[1] by mounting the crystals along the three orthogonal axes shown in Fig. 2. The data were recorded at 5° increments for ^{63}Cu(II) doped Ni(II)(7-me $sal)_2$phen and at 10° increments for the $(sal)_2$phen complex.

The optical spectra of the copper chelates were recorded on a Cary 14 spectrophotometer in the spectral region of 15000 Å to 3000 Å. Spectra were recorded for solutions of the chelates in chloroform, acetone and methanol. There was no solvent effect on the spectra. The d–d transitions were weak and only the longer wavelength transitions could be observed. Shorter wavelength transitions were masked by strong ligand absorption. The spectrum of Cu(II)$(sal)_2$phen was identical to that previously reported.[9-10] The spectrum of Cu(II)(7-me $sal)_2$phen showed the long wavelength band shifted to 6500 Å.

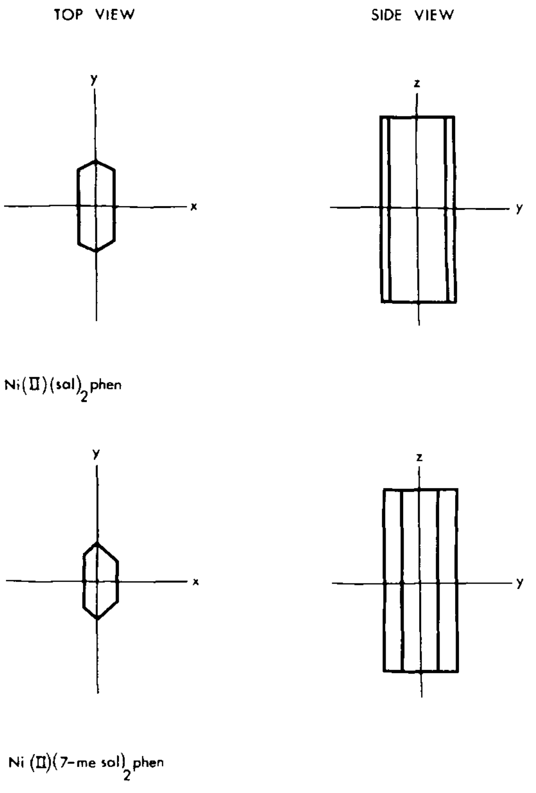

FIGURE 2 Mounting of crystals.

RESULTS

The magnetic data were fit to the usual doublet spin Hamiltonian,[1] with the results given in Table I. Table II contains the direction cosines relating the principal magnetic axes to the laboratory axes for both crystals. Figures 3 and 4 show the orientations of the principal magnetic axes with respect to the crystal morphologies for ^{63}Cu(II) doped Ni(II)$(sal)_2$phen and Ni(II) (7-me $sal)_2$phen respectively. As in the case of Cu(II)$(sal)_2$en each of the four spectral components due to coupling of the unpaired electron with the copper nucleus (I=3/2) in the Cu(II) $(sal)_2$phen was further split into eleven lines due to the coupling of the unpaired electron to the two

TABLE I
Spin Hamiltonian parameters

	Cu(II) doped Ni(II)(sal)$_2$phen	Cu(II) doped Ni(II)(7-me sal)$_2$phen
g_x	2.049 ± 0.004	2.049 ± 0.004
g_y	2.041 ± 0.004	2.044 ± 0.004
g_z	2.192 ± 0.002	2.209 ± 0.002
A_x	38.0 ± 2G = 36.4×10^{-4} cm^{-1}	30.0 ± 2G = 28.7×10^{-4} cm^{-1}
A_y	33.0 ± 2G = 31.4×10^{-4} cm^{-1}	26.0 ± 2G = 24.8×10^{-4} cm^{-1}
A_z	197.1 ± 1G = 201.7×10^{-4} cm^{-1}	191.4 ± 1G = 197.4×10^{-4} cm^{-1}
$A_{\perp}^{N}$	14.3 ± 1G = 14.0×10^{-4} cm^{-1}	13.3 ± 1G = 13.0×10^{-4} cm^{-1}
$A_{\parallel}^{N}$	11.3 ± 1G = 11.3×10^{-4} cm^{-1}	10.8 ± 1G = 10.6×10^{-4} cm^{-1}
$A_{\perp}^{H}$	7.1 ± 1G = 7.0×10^{-4} cm^{-1}	–
$A_{\parallel}^{H}$	5.8 ± 1G = 5.7×10^{-4} cm^{-1}	–

TABLE II
Direction cosines

Site	^{63}Cu(II) doped Ni(II)(sal)$_2$phen				^{63}Cu(II) doped Ni(II)(7-me sal)$_2$phen			
I		g_x	g_y	g_z		g_x	g_y	g_z
	x	0.72	0.62	0.32	x	0.83	0.17	0.52
	y	−0.69	0.70	0.20	y	−0.42	0.82	0.39
	z	−0.10	−0.36	0.93	z	−0.36	−0.55	0.76
II								
	x	0.01	0.93	0.37	x	0.76	0.35	0.55
	y	0.98	−0.07	0.16	y	0.59	−0.73	0.35
	z	−0.18	−0.36	0.92	z	−0.27	−0.59	0.76

nitrogen atoms and the two methine hydrogens on the ligand. The usual five line pattern was observed in the spectrum of Cu(II)(7-me sal)$_2$phen.

The magnetic parameters for the Cu(II)(7-me sal)$_2$-phen show g_z to be considerably larger than the range of values in the three similar complexes, Cu(II)(sal)en, Cu(II)(7-me sal)$_2$en, and Cu(II)(sal)$_2$-phen. Further, the value of A_z is abnormally low, 191 gauss, compared to about 200 gauss. In addition the lowest lying d–d optical transition has been shifted from ~ 18000 cm^{-1} to about 15400 cm^{-1}. Each of these observations is characteristic of a tetrahedral distortion of the Cu(II) environment.[11-16]

Single crystals of ^{63}Cu(II) doped Ni(II)(sal)$_2$phen·CHCl$_3$ contain two inequivalent magnetic sites. The molecular planes corresponding to these sites lie at angles of about 4° relative to one another, and are nearly symmetric with respect to a plane with equation $.420\,x + .907\,y = 0$. If the crystal had been mounted on the face from which the g_x(I) axis protrudes in Figure 3, this symmetry would have been evident, as can be seen by transforming the direction cosines into the appropriate coordinate systems (x', y', z'). A rotation of the axes by $-25°$ around the z axis results in the following direction cosines.

Site I	g_x	g_y	g_z
x'	0.37	0.85	0.37
y'	−0.92	0.38	0.04
z'	−0.10	−0.36	0.93

Site II	g_x	g_y	g_z
x'	0.42	0.81	0.40
y'	0.88	−0.45	−0.01
z'	−0.18	−0.36	0.92

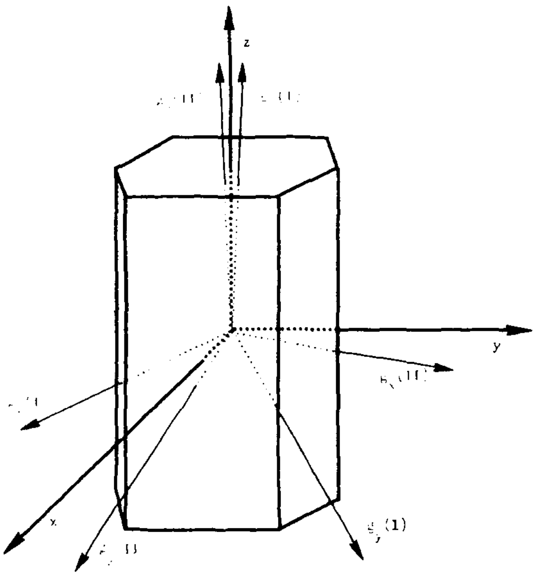

FIGURE 3 Orientation of lab. axes and principal magnetic axes with respect to crystal morphology for ^{63}Cu(II) doped Ni(II) $(sal)_2$ phen·$CHCl_3$.

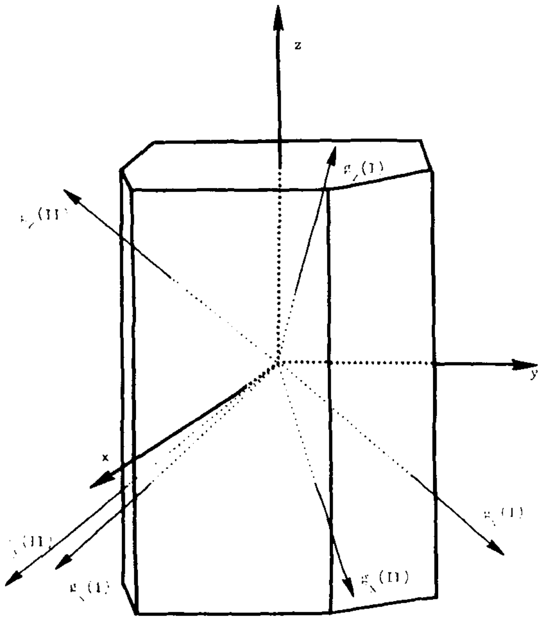

FIGURE 4 Orientation of lab. axes and principal magnetic axes with respect to crystal morphology for ^{63}Cu(II) doped Ni(II) (7-me $sal)_2$ phen.

The two sites are now seen to be nearly symmetric with respect to a reflection in the $x'z'$ plane. These results indicate that the crustal structure of Ni(II)$(sal)_2$phen·$CHCl_3$ is different from those reported for Cu(II)$(sal)_2$phen and Ni(II)$(sal)_2$-phen.[4-5]

In single crystals of ^{63}Cu(II) doped Ni(II)(7-me $sal)_2$phen the molecular planes corresponding to the two magnetic sites lie at angles of about 44° with respect to one another. At some orientations of the crystals, each of these sites can be seen in the EPR spectra to be split into two sites separated by a very small angle, resulting in a total of four inequivalent magnetic sites. The second splitting was so small (max. ~ 5 g), however, that it was necessary to use the average of the two sites in the analysis. In this crystal the molecular planes are oriented symmetrically with respect to the xz crystallographic plane (Figure 4).

MOLECULAR ORBITAL COEFFICIENTS

It is generally assumed that molecules of this type can be treated as belonging to the point group C_{2v}. Since in these molecules the g- and A-tensors are essentially axially symmetric, a higher symmetry will be assumed and the average of the values for nitrogen and oxygen for the integrals $T(N) = 0.276$ and $S =$ 0.0845 will be used. Then, following McGarvey[17] and adopting the notation of Reference 1, we can write,

$$A_{\parallel} - A_{\perp} = \frac{6}{7}\alpha^2 P + (g_{\parallel}-2.0023)PZ_{\parallel} - \frac{5}{14}(g_{\perp}-2.0023)PZ_{\parallel} \tag{1}$$

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

in which

$$Z_{\parallel} = \frac{\alpha\beta}{[\alpha\beta-\alpha'\beta S-2^{-1}\alpha'(1-\beta^2)^{1/2}T(N)]} \tag{3}$$

$$Z_{\perp} = \frac{\alpha\delta}{[\alpha\delta-\alpha'\delta S-2^{-1/2}\alpha'(1-\delta^2)^{1/2}T(N)]} \tag{4}$$

and K is the isotropic contact term. The usual value of $P = 0.0360\ \text{cm}^{-1}$ is used. α and α' are subject to the normalization condition

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \tag{5}$$

Eq. (1, 2, 5) and the usual expressions for the g-values[1] can be used to solve for the molecular orbital coefficients provided the energies for the optical d–d transitions are known as well as the parameters in the spin-Hamiltonian. Unfortunately, for the compounds under study, only the lowest energy d–d transition could be observed and is assigned as the $E_{xy} \rightarrow E_{x^2-y^2}$ transition. This situation prevents the evaluation of the m.o. coefficient, δ, in the out-of-plane π-bonding orbital. In previously studied compounds, for which all necessary d–d transitions can be observed, a value of $\delta^2 \sim 1$ has been determined.[18] In only a few cases has δ^2 been as low as 0.9. Thus, in our initial calculations a value of $\delta^2 = 1$ is assumed.

The m.o. coefficients were obtained by an iteration process. The initial value for α^2 was determined from (1) assuming $Z_{\parallel} = Z_{\perp} = 1$. Initial values of α'^2 and β^2 were determined from (5) and the equation for $g_{\parallel}$. These initial values were used to calculate $Z_{\parallel}$ and $Z_{\perp}$ which were substituted into (1) to determine a new value of α^2. This process was repeated until there was no change in the values of α^2, α'^2 and β^2. Usually only three or four iterations were necessary. The results are presented in Table III where they are compared to the results[2] for Cu(II)(sal)$_2$en and Cu(II)(7-me sal)$_2$en. The values of these coefficients are essentially the same for all the complexes except (7-me sal)$_2$phen. In this complex, the coefficients indicate a weaker σ-bond and a stronger in-plane π-bonding. If a value of $\delta^2 = 0.9$ is assumed, only small changes in the m.o. coefficients result, about 0.05% in α^2 and β^2 and 0.10% in α'^2.

Once the m.o. coefficients are known, values for K, the isotropic contact term can be calculated. This isotropic contact is in proportional to the quantity, χ, defined by Abragam, Horwitz and Pryce[19] and found to be negative and of nearly constant magnitude for the first transition series ions.

$$\chi = -\frac{3}{2}\,\frac{hca_0^3}{2.0023\, g_N \beta_N \beta_e}\,K$$

The values of χ are given in Table 3. The results show that the χ-values are remarkably constant although the value for Cu(II)(7-me sal)$_2$phen is low and falls outside the standard deviation from the mean for the other three compounds and may be lowered by a slight tetrahedral distortion as indicated by the frequency of the optical transition and the values of the spin-Hamiltonian parameters. Alternatively if one considers Cu(7-me sal)$_2$en and Cu(sal)$_2$phen, the two compounds that form chloroform adducts upon crystallization, one finds the χ-values to be the same while the other two complexes that were not crystallized as adducts also have χ-values that are very much alike. In all probability the differences in χ-values lie within the experimental uncertainties.

From the hydrogen splitting observed in the spectrum of Cu(II)(sal)$_2$phen, a value for the fractional 1s electron hole may be calculated by comparing the average value of the proton splitting 6.2×10^{-4} cm^{-1} with the hyperfine constant from the proton-electron coupling in the hydrogen atom. It is found to be 0.013 similar to the value found in Cu(II)(sal)$_2$en.[2]

DISCUSSION

The molecular orbital coefficients for Cu(II)(7-me sal)$_2$phen indicate the bonding in this complex is different from the bonding in the related complexes as do the values of the spin-Hamiltonian parameters and the frequency of the lowest optical transition. The changes in the magnetic parameters and in the optical spectrum are characteristic of a tetrahedrally distorted environment[13] for the Cu(II). Such a reduction in symmetry around the Cu(II) can only lead to a mixing of the metal d_{xy} and p_z orbitals. This should not negate the validity of the value of α^2, for it will still be the coefficient of the σ-orbital on the Cu(II). It should make the overlap between the ligand σ-orbitals and the metal σ-orbital smaller, hence increasing the value of α^2. At the same time it should increase the possible overlap for out-of-plane

TABLE III
Bonding parameters

	^{63}Cu(II) doped Ni(II)			
	(sal)$_2$en	(7-me sal)$_2$en	(sal)$_2$phen	(7-me sal)$_2$phen
α^2	0.782	0.771	0.775	0.805
α'^2	0.299	0.311	0.308	0.274
β^2	0.730	0.733	0.726	0.667
n^2	0.659	0.681	0.666	0.648
χ	−3.93	−4.00	−4.00	−3.89

π-bonding as indicated by the m.o. coefficients. Similar effects have been observed previously. In spite of this distortion from the square planar environment the value of K does not seem to be affected significantly, perhaps because the distortion is small. An x-ray diffraction study would help clear up this matter.

ACKNOWLEDGEMENT

The authors would like to acknowledge support through an equipment grant from the Research Corporation.

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