

ESR Bonding parameter studies of single and mixed ligand complexes of copper(II)

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Abstract. ESR and optical absorption studies are described for a number of copper(II) single and mixed ligand complexes formed with substituted salicylic acids and acetylacetonone. ESR spectra of all these complexes give well-resolved spectra in DMF both at room and liquid nitrogen temperatures. The molecular orbital coefficients are estimated assuming an axial symmetry. A partial covalency is observed in all the single ligand complexes while the in-plane π -bonding is as strong as the σ -bonding in all the mixed ligand complexes. No regular trend is observed in the value of χ (which is proportional to hyperfine constants) with the change in the overall electron withdrawing capacity of the substituent on salicylic acid, either in single ligand or in mixed ligand complexes. However, the χ values for all the complexes (except in the case of *bis*(acetylsalicylato)copper(II) and (acetylacetonato)-(3,5-dinitrosalicylato)copper(II)) are in agreement with the computed value of $\chi = -3.61$ for single crystals of copper-acetylacetonate possessing the same environment of four oxygens around copper(II).

Keywords. ESR studies; bonding parameters; acetylacetonone; salicylic acids; copper(II).

1. Introduction

As part of our current studies on single ligand (Pisipati *et al* 1981, 1984) and mixed ligand (Anjaneyulu *et al* 1983, 1986) complexes of copper(II), we have carried out ESR and optical absorption studies on seven single ligand and seven mixed ligand complexes of copper(II) with acetylacetonone (AA) and substituted salicylic acids (SA) as mixed ligands. In all the complexes the immediate environment of copper(II) is made up of four oxygen atoms in a square planar arrangement, except in the thio complex where the oxygen atom is replaced by a sulphur atom. The studies are undertaken in order to infer the nature of the molecular orbital coefficients, and it is found that these parameters exhibit similar qualitative characteristics for substances with similar environments around the copper(II) atom irrespective of the ligand chemical structure. Such studies on copper complexes, where Cu(II) is surrounded by [4N] (Pisipati *et al* 1981; Lancione *et al* 1976, 1979), [3N, O] (Kwik *et al* 1980), [2N, 2O] (Allen and Scullane 1978; Scullane and Allen 1978) and [N, 3O] (Anjaneyulu *et al* 1983), show consistency in molecular orbital coefficients for a particular type of environment irrespective of substituents on the ligand.

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The Abragam, Horowitz and Pryce parameter ψ (Abragam *et al* 1955) related to the hyperfine contact term K and given by

$$\chi = (4\pi/S_T) \langle \psi | \sum_i \delta(r_i) S_{zi} | \psi \rangle, \quad (1)$$

where χ = the effective field per unpaired electron, S_T = the total spin of the ion $\delta(r_i)$ = the delta function term and S_{zi} = the spin of the i th electron, is found to be remarkably constant for a particular type of environment. McGarvey (1967) carried out extensive calculations on a variety of complexes and concluded that it can vary as much as 30% depending upon the ligand, the host lattice and the geometry of the chelate.

Recently χ values of -3.70 (Pisipati *et al* 1981; Lancione *et al* 1976, 1979), -3.79 (Kwik *et al* 1980), -3.92 (Allen and Scullane 1978, Scullane and Allen 1978) and -3.83 (Anjaneyulu *et al* 1983) for [4N], [3N, O], [2N, 2O] and [3O, N] arrangements respectively, resulting from different types of ligands around copper, are reported. No such systematic studies are carried out for copper complexes with [4O] environment. All the copper compounds studied in the present work possess the [4O] coordination except for the thio complex.

2. Experimental

The preparation and characterisation of all these complexes were reported in our earlier paper (Anjaneyulu and Prabhakara Rao 1986).

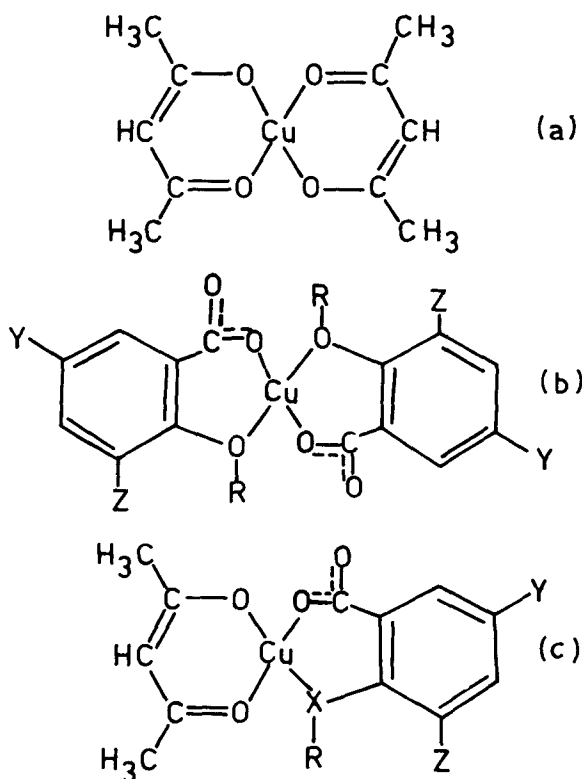


Figure 1. Structural formulae of the complexes.

Table 1. Nomenclature of the structural formulae shown in figure 1.

Figure number	Compound number	Name of the complex	Abbreviation	Substituents			
				Y	Z	R	X
1a	1	<i>Bis</i> (acetylacetonato)-copper(II)	Cu(AA) ₂	—	—	—	—
1b	2	<i>Bis</i> (salicylato)copper(II)	Cu(SA) ₂	H	H	H	—
	3	<i>Bis</i> (5-chlorosalicylato)-copper(II)	Cu(Cl-SA) ₂	Cl	H	H	—
	4	<i>Bis</i> (3,5-dibromosalicylato)-copper(II)	Cu(2Br-SA) ₂	Br	Br	H	—
	5	<i>Bis</i> (3,5-diiodosalicylato)-copper(II)	Cu(2I-SA) ₂	I	I	H	—
	6	<i>Bis</i> (3,5-dinitrosalicylato)-copper(II)	Cu(2NO ₂ -SA) ₂	NO ₂	NO ₂	H	—
	7	<i>Bis</i> (acetylsalicylato)-copper(II)	Cu(Acetyl-SA) ₂	H	H	COCH ₃	—
	1c	8	(Acetylacetonato) (salicylato)copper(II)	Cu(AA) (SA)	H	H	H
9		(Acetylacetonato)5-chlorosalicylato)copper(II)	Cu(AA) (Cl-SA)	Cl	H	H	O
10		(Acetylacetonato) (3,5-diiodosalicylato)-copper(II)	Cu(AA) (2I-SA)	I	I	H	O
11		(Acetylacetonato) (5-nitrosalicylato)copper(II)	Cu(AA) (NO ₂ -SA)	NO ₂	H	H	O
12		(Acetylacetonato) (3,5-dinitrosalicylato)copper(II)	Cu(AA) (2NO ₂ -SA)	NO ₂	NO ₂	H	O
13		(Acetylacetonato) (thio-salicylato)copper(II)	Cu(AA) (thio-SA)	H	H	H	S
14		(Acetylacetonato) (acetylsalicylato)copper(II)	Cu(AA) (acetyl-SA)	H	H	COCH ₃	O

The ESR spectra were recorded in dimethyl formamide (DMF) solution at room (RT) and liquid nitrogen temperatures (LNT) using a varian E4-X-band ESR spectrometer. The optical absorption spectra were recorded in solution using Beckman DK-2 ratio recording spectrophotometer. The molecular orbital coefficients are evaluated by an iterative procedure. The structural formulae of the complexes are shown in figure 1 and their nomenclature given in table 1.

3. Results and discussion

In all these single ligand and mixed ligand complexes the crystal field symmetry of the copper ion may be taken as distorted tetragonal arising out of four oxygen atoms forming a distorted square planar configuration (except in the thio complex where one sulphur atom replaces an oxygen atom) with the possibility of the solvent molecules (DMF) occupying the long axial position, finally giving a distorted octahedral geometry.

Electronic and ESR spectra of copper complexes with square planar and octahedral geometry can be easily understood using ligand field splitting of the energy levels (Reedijk 1981). Such a distortion will be small for strongly coordinating axial ligands and will increase when the coordinating power of the axial ligands decreases, resulting in the observation of only one overlapping band. However, Gersmann and Swalen (1962) reported three $d-d$ transitions for Cu (AA)₂ in a frozen solution for which the solvent was a mixture of chloroform and toluene. In the present work all these complexes exhibited only a broad asymmetric band in solution (DMF) in between 15,000–16,000 cm⁻¹ at room temperature (table 2) indicating that more than one transition is buried under each of the absorption envelopes and the solvent molecules may be weakly coordinating in the long axial positions.

Well-resolved ESR spectra of transition metal complexes in solution are solvent-dependent. Different authors have proved that a particular solvent or solvent mixture provides the best lattice and gives a well-resolved ESR spectrum at liquid nitrogen temperature, in their studies on single ligand complexes of copper(II)-acetylacetonate (Kuska *et al* 1967; Toy *et al* 1971; Belford and Duan 1978), copper diethyldithiocarbamate and mixed ligand complexes of copper(II) formed with diethyldithiocarbamate and other different ligands (Toy *et al* 1971; Yordanov and Shopov 1976; Tirant and Smith 1980). In the present work the spectra of copper substituted salicylic acids and mixed ligand complexes of

Table 2. Experimental ESR solution data at RT and LNT, with ΔE values.

Compound	Frozen solution data at LNT			Solution data (RT)			
	g_{\parallel}	$A_{\parallel} \times 10^4$ g_1	cm^{-1}	$A_{\perp} \times 10^4$ cm^{-1}	g_0	A_0	ΔE cm^{-1}
Cu(AA) ₂	2.291	2.061	159	15	2.129	64	16,129
Cu(SA) ₂	2.284	2.054	142	19	2.102	54	16,129
Cu(Cl-SA) ₂	2.280	2.051	150	22	2.100	60	16,000
Cu(2Br-SA) ₂	2.292	2.057	147	19	2.110	58	16,129
Cu(2I-SA) ₂	2.292	2.055	147	20	2.105	51	16,129
Cu(2NO ₂ -SA) ₂	2.300	2.061	141	18	2.110	53	16,129
Cu(acetyl-SA) ₂	2.280	2.060	153	25	2.100	55	16,129
Cu(AA) (SA)	2.289	2.064	149	11	2.141	68	15,873
	2.240	2.040	175	16			
Cu(AA) (Cl-SA)	2.299	2.060	149	14	2.145	67	15,873
	2.244	2.050	179	15			
Cu(AA) (2I-SA)	2.295	2.051	149	18	2.146	68	15,675
	2.242	2.048	172	16			
Cu(AA) (NO ₂ -SA)	2.296	2.052	146	19	2.144	68	15,625
	2.234	2.046	174	17			
Cu(AA) (2NO ₂ -SA)	2.300	2.069	144	17	2.146	68	15,675
	2.238	2.060	177	14			
Cu(AA) (thio-SA)	2.295	2.051	140	11	2.150	62	15,150
Cu(AA) (acetyl-SA)	2.276	2.056	149	19	2.145	67	15,675
	2.235	2.048	175	18			

The accuracies in the evaluated values of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} are ± 0.004 , ± 0.006 , $\pm 3 \times 10^{-4}$ and 6×10^{-4} respectively

copper(II) with acetylacetonate and substituted salicylic acids in DMF, were well-resolved both at room and liquid nitrogen temperatures. The spectra of all the copper salicylate complexes are similar both at room and liquid nitrogen temperatures and exhibit four spin-dependent hyperfine lines as expected.

The mixed ligand complexes showed well-resolved spectra both at RT and LNT similar to those observed in the extensively studied copper acetylacetonate systems. All the four parallel and perpendicular lines are visible exhibiting an axial symmetry. The interesting features observed in the spectra are as follows. An unusual feature of the parallel lines splitting *i.e.*, the $m_i = 3/2$ line splits into three while $m_i = 1/2, -1/2, -3/2$ lines split into two lines (Chi-Lin O'Young *et al* 1978), we believe that the splitting of lines is solvent-dependent and it is in accordance with similar data for different copper complexes. The characteristic splitting of $m_i = 3/2$ line is assigned to ^{63}Cu and ^{65}Cu isotopes and it is also found in all the mixed ligand complexes. The splitting due to the solvent effect is observed on the parallel and perpendicular lines in the case of Cu(AA) (2I-SA), Cu(AA) (NO_2 -SA), Cu(AA) (Acetyl-SA), Cu(AA) (Cl-SA) and Cu(AA) (SA). The splitting on the

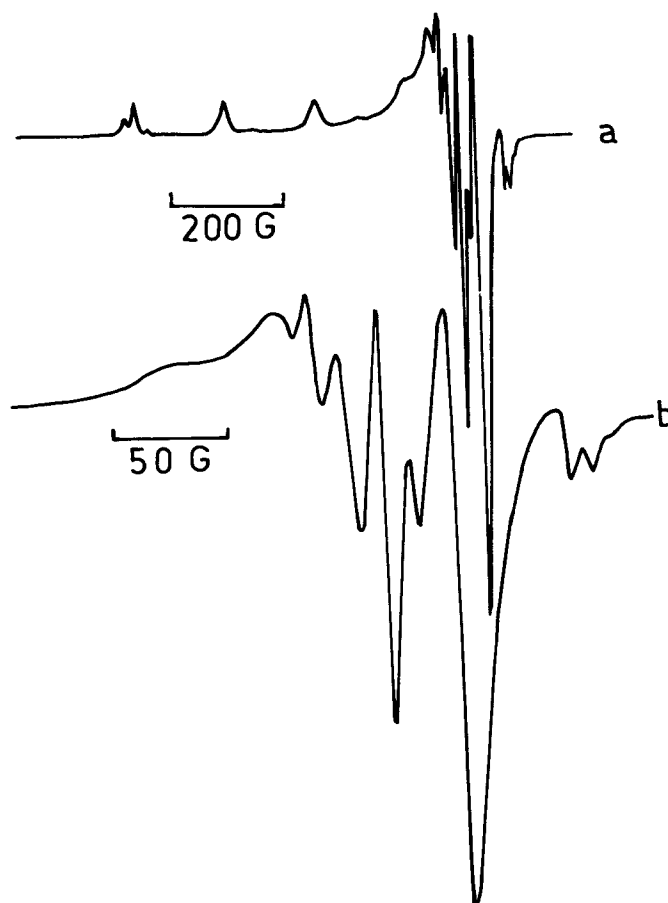


Figure 2. ESR spectra of Cu(AA) (2NO₂-SA) at (a) liquid nitrogen temperature, and (b) resolved perpendicular line at liquid nitrogen temperature.

Table 3. Values of Z_{\parallel} , Z_{\perp} , molecular orbital coefficients and χ .

Compound	Z_{\parallel}	Z_{\perp}	α^2	α'^2	β^2	$-\chi$
Cu(AA) ₂	1.07	1.05	0.77	0.30	0.96	3.53
Cu(SA) ₂	1.06	1.06	0.73	0.35	0.99	3.48
Cu(Cl-SA) ₂	1.07	1.05	0.74	0.33	0.95	3.59
Cu(2Br-SA) ₂	1.06	1.05	0.75	0.33	0.99	3.53
Cu(2I-SA) ₂	1.06	1.05	0.75	0.33	0.99	3.59
Cu(2NO ₂ -SA) ₂	1.06	1.05	0.77	0.31	0.99	3.56
Cu(acetyl-SA) ₂	1.07	1.05	0.74	0.34	0.97	3.76
Cu(AA) (SA)	1.07	1.05	0.78	0.29	0.92	3.47
	1.09	1.05	0.80	0.27	0.75	3.51
Cu(AA) (Cl-SA)	1.06	1.05	0.78	0.29	0.97	3.57
	1.08	1.04	0.82	0.25	0.75	3.61
Cu(AA) (2I-SA)	1.06	1.05	0.75	0.30	0.97	3.53
	1.09	1.05	0.79	0.28	0.77	3.54
Cu(AA) (NO ₂ -SA)	1.07	1.05	0.76	0.32	0.96	3.55
	1.10	1.05	0.78	0.29	0.73	3.54
Cu(AA) (2NO ₂ -SA)	1.07	1.05	0.77	0.30	0.98	3.52
	1.09	1.05	0.81	0.26	0.72	3.70
Cu(AA) (thio-SA)	1.08	1.05	0.76	0.31	0.91	3.32
Cu(AA) (acetyl-SA)	1.08	1.05	0.74	0.33	0.92	3.54
	1.09	1.05	0.79	0.29	0.73	3.57

parallel line only is observed for Cu(AA) (2NO₂-SA) (figure 2). Even such splitting is not observed for Cu(AA) (Thio-SA) on the parallel line.

We believe that the species *I* can be identified as one of the single ligand complexes (either copper acetylacetonate or copper substituted salicylic acids) reported in the present work, while species *II* belongs to the mixed ligand complexes. We cannot identify the exact binary species because the *g* and *A* tensor values are very close for both the copper acetylacetonate and copper substituted salicylic acids. The formation of a single ligand species in solution at liquid nitrogen temperature may be arising out from the partial dissociation of the mixed ligand complexes into single ligand species (Anjaneyulu *et al* 1983). The g_0 , A_0 , ΔE values and the *g* and *A* tensor values at LNT are presented in table 2.

4. Molecular orbital coefficients and χ -parameter

Since the *g* and *A* tensors are essentially axially symmetric the molecular orbital coefficients were calculated taking the values $T(n) = 0.220$ and $S = 0.093$ for oxygen. Following McGarvey (1967) and adopting the notation used in our earlier paper (Pisipati *et al* 1981),

$$A_{\parallel} - A_{\perp} = (6/7)\alpha^2 P + (g_{\parallel} - 2.0023)PZ_{\parallel} - (5/14)(g_{\perp} - 2.0023)PZ_{\perp}, \quad (2)$$

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

in which

$$Z_{\parallel} = (\alpha\beta)/[\alpha\beta - \alpha'\beta S - \alpha'(1 - \beta^2)^{1/2}T(N)/2], \quad (4)$$

$$Z_{\perp} = (\alpha\delta)/[\alpha\delta - \alpha'\delta S - 2\alpha'(1 - \delta^2)^{1/2}T(N)], \quad (5)$$

and K is the isotropic contact term. The usual value of $P = 360 \times 10^{-4} \text{ cm}^{-1}$ is used. α and α' are subjected to the normalisation condition,

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1, \quad (6)$$

Equations (2), (3) and (6) and the usual expressions for the g tensor are taken to solve for the molecular orbital coefficients using the $d-d$ transition energies. For these complexes only the lowest energy $d-d$ transition is observed and is assigned as $E_{xy} - E_{x^2-y^2}$. In view of this δ^2 , the out-of-plane π -bonding coefficient could not be calculated. It is further observed that the value of δ^2 varies from 0.9 to 1.0 and the change in χ value is found to be 2% only. Thus $\delta^2 = 1$ is assumed while calculating the α^2 , α'^2 , β^2 . These coefficients are obtained by the iterative procedure. The initial value of α^2 is determined from (2) assuming $Z_{\parallel} = Z_{\perp} = 1$. Initial values of α'^2 and β^2 are obtained from (6) and the equation for g_{\parallel} respectively (Pisipati *et al* 1981). These three values are used to calculate Z_{\parallel} and Z_{\perp} from (4) and (5), which are substituted in (1) to determine the refined value of α^2 . The α^2 , α'^2 and β^2 values converge after three to four iterations and are presented in table 3. Using the molecular orbital coefficients the isotropic contact term K is evaluated. The isotropic contact term is proportional to the effective field per unpaired electron χ which is given by

$$\chi = (3/2) (hca_0^3/2 \cdot 0023 g_N \beta_N \beta_e) K.$$

The computed values of χ are presented in table 3.

The molecular orbital coefficients, for all the single ligand complexes, are found to exhibit similar qualitative characteristics. The in-plane π -bonding (β^2) is weak compared to the σ -bonding (α^2) for all the single ligand complexes (table 3). It is found that the in-plane π -bonding for the mixed complexes is as strong as that of σ -bonding. The Z_{\parallel} and Z_{\perp} values also showed consistency for all the complexes. The average value of the effective field per unpaired electron $\chi = 3.57$ is in reasonable agreement with the computed value of 3.61 obtained from the reported data of g , A and ΔE values for copper acetylacetonate single crystal possessing [4O] coordination (Kuska *et al* 1967). Furthermore, no regular trend is observed in the magnitude of the parameter χ with increase in overall electron-withdrawing capacity of the substituent in the salicylic acid, either in the single ligand or in the mixed ligand complexes. Previous studies (Scullane and Allen 1978) had indicated that the magnitude of χ is constant and is independent of ligand substitution. In view of the present observations further work is in progress to generalise the effect of electron-withdrawing and -donating groups in the ligand substituent on the magnitude of χ .

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