

Stabilities of mixed ligand complexes of Cu(II) with ligands coordinating through O and N: ESR studies

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Abstract. Mixed ligand complexes of Cu(II) with 8-hydroxy-quinolinate (Hy) as one ligand and acetylacetonate (ac.ac) or salicylaldehyde (Sal) as the second ligand have been prepared in reaction mixtures of $\text{Cu(Hy)}_2 + \text{Cu(ac.ac)}_2$ and $\text{Cu(Hy)}_2 + \text{Cu(Sal)}_2$ in chloroform. Ligand hyperfine structures and the minimum ESR linewidth associated with $m_1 = -3/2$ hyperfine component have been used to detect and identify the mixed ligand complexes. The ligands in these complexes coordinate through O or N. The constants K associated with the ligand exchange equilibria are ~ 2 at -20°C and are close to the value expected from the empirical relation obtained in an earlier work from a study of Cu(II) complexes in which S also participates in the coordination.

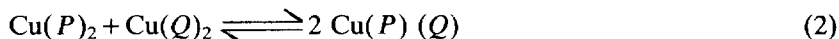
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1. Introduction

The importance of formation of complexes in bioinorganic chemistry is well known (Dennard and Williams 1966; Angelici 1973). In our laboratory, we had attempted to obtain empirical rules for predicting the stabilities of mixed ligand complexes of Cu(II) (Prabhananda 1983) using ESR data. The covalent bonding ability of a bidentate ligand P is reflected in the isotropic g value, g_0 of $\text{Cu}(P)_2$, which is measured from the ESR spectra in liquid solutions. It was noted that the constant K (obtained after dividing by the statistical factor 4),

$$K = [\text{Cu}(P)(Q)]^2 / 4. [\text{Cu}(P)_2] [\text{Cu}(Q)_2] \quad (1)$$

associated with the equilibrium,



was dependent on $|(g_0^P - g_0^Q)|$ where g_0^P and g_0^Q are the g_0 associated with $\text{Cu}(P)_2$ and $\text{Cu}(Q)_2$ respectively. For small values of $|(g_0^P - g_0^Q)|$ K increased with increase in $|(g_0^P - g_0^Q)|$ and was ≥ 1 . However, for large $|(g_0^P - g_0^Q)|$, K became < 1 and decreased with increase in $|(g_0^P - g_0^Q)|$. In the earlier investigations, K was found to be ≥ 1 for small $|(g_0^P - g_0^Q)|$, in the examples where the ligands coordinated through S (Prabhananda 1983). In the present work, we have examined whether

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$K \approx 1$ for small $|(g_{\parallel}^0 - g_{\perp}^0)|$, even when the ligands P and Q coordinate through O or N. Such a coordination is relevant in many biochemical situations.

The Cu(II) complexes with ligands coordinating through O or N have larger magnetic anisotropies, and larger orbital contributions to g than the complexes where the coordination is through S. Therefore, ESR linewidths of these complexes in liquid solutions are larger than those reported in our earlier papers. Furthermore, we are interested in choosing $\text{Cu}(P)_2$ and $\text{Cu}(Q)_2$ such that $|(g_{\parallel}^0 - g_{\perp}^0)|$ is small. These two factors cause considerable overlap of the ESR lines due to the three species [equilibrium (2)]. Thus, the identification of lines and estimation of the concentrations with the help of ESR spectra is in general difficult. However, we can expect this task to become easy if we have resolved ligand hyperfine splittings from one of the ligands and if the isotropic ^{63}Cu hyperfine splitting of $\text{Cu}(P)_2$ and $\text{Cu}(Q)_2$ are substantially different. In this work, we have chosen the ligands, acetylacetonate (ac.ac), salicylaldehyde (Sal) and 8-hydroxyquinoline (Hy) (figure 1) and have studied the formation of $\text{Cu}(\text{ac.ac})(\text{Hy})$ and $\text{Cu}(\text{Sal})(\text{Hy})$.

2. Experimental

The complexes $\text{Cu}(\text{ac.ac})_2$, $\text{Cu}(\text{Sal})_2$ and $\text{Cu}(\text{Hy})_2$ were prepared with acetylacetone (Belford *et al* 1956), salicylaldehyde and 8-hydroxyquinoline (Ugrankar and Prabhananda, to be published) respectively using cupric acetate enriched to $> 90\%$ with ^{63}Cu . Reaction (2) was used to prepare the mixed ligand complexes $\text{Cu}(\text{ac.ac})(\text{Hy})$ and $\text{Cu}(\text{Sal})(\text{Hy})$ in reaction mixtures in chloroform. Degassed solutions were used to eliminate the broadening of ESR lines due to dissolved oxygen. Dilute solutions were used to minimise concentration dependent contributions to linewidths. X-band ESR spectra at different temperatures were obtained using a spectrometer described elsewhere (Prabhananda *et al* 1972). Computer-simulated spectra with Lorentzian line shapes were obtained using a Fortran programme developed earlier (Baratova *et al* 1982). ESR parameters were determined by comparing the observed and simulated spectra.

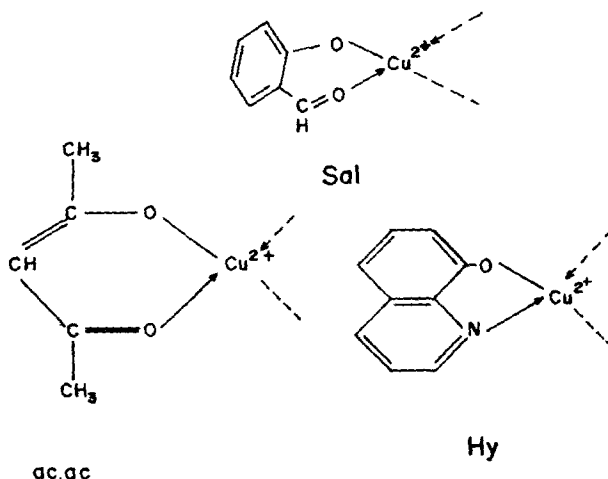


Figure 1. Ligands used in the present study.

3. Results

ESR spectra obtained from reaction mixtures of $\text{Cu}(\text{ac.ac})_2 + \text{Cu}(\text{Hy})_2$ and $\text{Cu}(\text{Sal})_2 + \text{Cu}(\text{Hy})_2$ in chloroform at room temperature (25°C) showed broad overlapping lines, and it was not possible to identify the ESR lines due to any of the separate species. The peak to peak derivative ESR linewidth contribution W due to the tumbling motion of a paramagnetic complex in liquids can be written as (Wilson and Kivelson 1966a; Atkins and Kivelson 1966),

$$W = a/\tau_\theta + b\tau_\theta, \quad (3)$$

when $\omega\tau_\theta \gg 1$ ($\omega = 2\pi \cdot$ microwave frequency). In the above equation, τ_θ is the correlation time associated with reorientational motion. a and b are contributions from the spin-rotational interaction and modulation of g and A , and can be calculated by substituting the ESR parameters in the equations given by Kivelson and coworkers (Atkins and Kivelson 1966; Wilson and Kivelson 1966). τ_θ can be varied by varying the temperature to obtain the minimum linewidth W_m ,

$$W_m = 2(ab)^{1/2}. \quad (4)$$

The ESR parameters associated with $\text{Cu}(P)_2$ or $\text{Cu}(Q)_2$ depend on the choice of the diamagnetic host in which it is studied (Wilson and Kivelson 1966b). Large differences in the A_0 obtained from studies in the solid state and the liquid state are mainly due to small differences in the $4s$ -mixing in the unpaired electron orbital, which depends on the host induced 'deviation from the square-planar structure'. Since our studies are in the liquid state, A_0 obtained in the liquid state is relevant. The anisotropy parameters are much less sensitive to the choice of host. However, it is appropriate to use either the parameters determined from a study of linewidths in liquid solutions (Prabhananda 1979) or the parameters which predict the observed W_m . Table 1 gives the appropriate magnetic parameters of $\text{Cu}(\text{ac.ac})_2$, $\text{Cu}(\text{Sal})_2$ and $\text{Cu}(\text{Hy})_2$ determined in earlier investigations (Maki and McGarvey 1958a; Ugrankar and Prabhananda, to be published). W_m calculated using these parameters (table 1) agree well with the experimentally determined W_m .

In earlier studies, where the ESR spectrum due to the mixed ligand complex could be clearly discerned in frozen solution spectra (Krishnamoorthy and Prabhananda 1980) or in liquid solution spectra (Das and Prabhananda 1983), a procedure for calculating the magnetic anisotropy of mixed ligand complexes was inferred: The principal values of the g tensor and the ^{63}Cu hyperfine tensor A , of $\text{Cu}(P)$ (Q) can be taken to be close to the average of those of $\text{Cu}(P)_2$ and $\text{Cu}(Q)_2$ when the complexes have near-square-planar geometry at the metal ion. Reasonably good estimates of the g_0 and the isotropic part of the ^{63}Cu hyperfine splitting, A_0 , of $\text{Cu}(P)$ (Q) can be obtained by taking the averages of those of $\text{Cu}(P)_2$ and $\text{Cu}(Q)_2$. Better estimates of g_0 and A_0 have been obtained by the procedure described later. The ESR parameters of $\text{Cu}(\text{ac.ac})(\text{Hy})$ and $\text{Cu}(\text{Sal})(\text{Hy})$ calculated by taking the "averages" are also presented in table 1.

The ESR parameters can be substituted in (4) to obtain estimates of W_m . For a near-square-planar $\text{Cu}(\text{ac.ac})_2$, $\text{Cu}(\text{Hy})_2$, $\text{Cu}(\text{ac.ac})(\text{Hy})$ and $\text{Cu}(\text{Sal})(\text{Hy})$ we get $W_m = 11.2$ G, 8.3 G, 9.2 G, and 9.2 G respectively for the high field ^{63}Cu hyperfine component ($m_1 = -3/2$). For a near-square-planar $\text{Cu}(\text{II})$ complex, we expect ligand hyperfine splittings (A_N) in the range 11–15 G from a near ligand

Table 1. ESR Parameters and K^a

Complex	Anisotropic parameters ^b				Isotropic parameters ^c			W_m^d (G)	K
	$g_{ }$	g_{\perp}	$A_{ }$ (G)	A_{\perp} (G)	g_0	A_0 (G)	A_L (G)		
Cu(ac.ac) ₂ ^e	2.266	2.054	151.2	19.8	2.123	76.4	—	11.2	—
Cu(Sal) ₂ ^f	2.264	2.042	168.0	10.0	2.120	59.5	5.5 ^g	10.9	—
Cu(Hy) ₂ ^f	2.252	2.060	186.0	10.0	2.107	87.5	11.8 ^h	8.3	—
Cu(ac.ac)(Hy) ⁱ	2.259	2.057	168.6	14.9	2.114	83.0	11.8 ^h	9.2	2.0
Cu(Sal)(Hy) ⁱ	2.258	2.051	177.0	10.0	2.111	76.2	11.8 ^h 5.5 ^g	9.2	1.9

^a The constant of (1) in chloroform at -20°C ; ^b measured from the ESR spectra obtained in the solid state; ^c measured from the ESR spectra in chloroform solutions at -20°C ; ^d minimum peak to peak derivative ESR width (calculated); ^e single crystal data (Maki and McGarvey 1958a); ^f frozen solution data (Ugrankar and Prabhananda, to be published). Errors in $g_{||}$ and $g_{\perp} \pm 0.005$, errors in $A_{||}$ and $A_{\perp} \pm 5$ G, errors in $A_0 \sim \pm 2$ G; ^g ¹H hyperfine splitting. Error in $A_L \sim \pm 0.2$ G; ^h ¹⁴N hyperfine splitting. Error in $A_L \sim \pm 0.4$ G; ⁱ calculated from the "average" and "equidistant" position as described in the text.

atom ¹⁴N (McGarvey 1966). Since W_m is less than the expected A_N , we may see resolved ligand hyperfine splittings in the high field region, by choosing an appropriate temperature, if Cu(Hy)₂, Cu(ac.ac)(Hy) and Cu(Sal)(Hy) have near-square-planar structure at the metal ion.

Cu(ac.ac)(Hy): Figure 2a shows the ESR spectrum from a reaction mixture of Cu(ac.ac)₂ and Cu(Hy)₂ in chloroform at -20°C . The high field component of the spectrum (which could be assigned to $m_1 = -3/2$ hyperfine transitions), shows sufficiently resolved ligand hyperfine splittings, as expected from linewidth considerations (mentioned above). After identifying the lines due to Cu(Hy)₂ and Cu(ac.ac)₂ from a knowledge of their positions with respect to the DPPH line, we are left with a triplet, with an intensity ratio 1:1:1 in the high field region. The separation between the components of the triplet is 11.8 G.

In Cu(ac.ac)(Hy), we have one coordinating ¹⁴N (figure 1) (nuclear spin = 1). Thus, for Cu(ac.ac)(Hy) we expect a triplet ligand hyperfine structure with an intensity ratio 1:1:1 and hyperfine splitting in the range 11–15 G. Therefore, it is reasonable to assign the above triplet to the ¹⁴N hyperfine structure of the $m_1 = -3/2$ transition associated with Cu(ac.ac)(Hy).

Assuming the above assignment to be correct, we can obtain reasonably good estimates of A_0 (isotropic part of the ⁶³Cu hyperfine constant) associated with Cu(ac.ac)(Hy) by the procedure given below even though lines corresponding to $m_1 = \pm 1/2$ and $3/2$ cannot be distinctly identified due to overlap with other lines. If the g_0 and A_0 associated with Cu(P)(Q) are the "averages" of those associated with Cu(P)₂ and Cu(Q)₂, the magnetic field position of the $m_1 = -3/2$ transition of Cu(P)(Q) will be "equidistant" from those of Cu(P)₂ and Cu(Q)₂ (since the second-order terms are small). Any deviation from this position will be due to the deviations of both g_0 and A_0 of Cu(P)(Q) from the "average" values. In our earlier study (Das and Prabhananda 1983), it has been shown that a correlation exists between the deviations of g_0 and A_0 of Cu(P)(Q) from the "average" values. Such a correlation can be used to determine the corrections that have to be

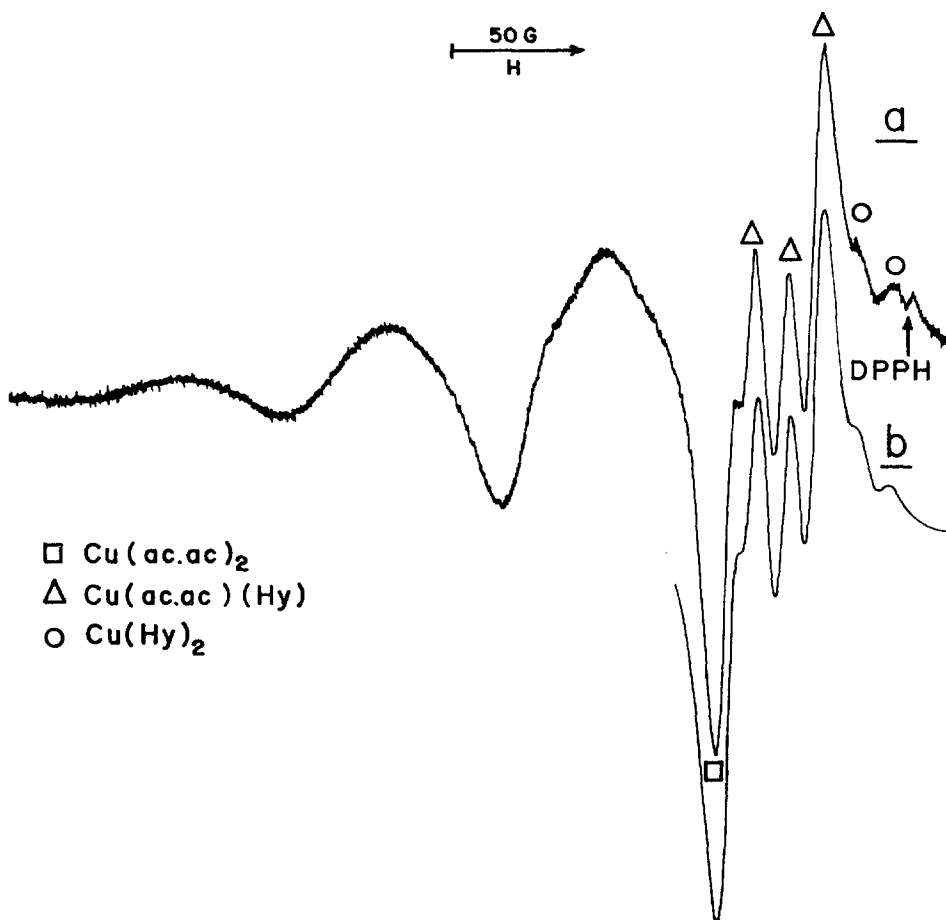


Figure 2. (a) ESR spectrum from a reaction mixture of $\text{Cu}(\text{ac.ac})_2 + \text{Cu}(\text{Hy})_2$ in chloroform at -20°C . (b) Computer-simulated spectrum in the high field region using $[\text{Cu}(\text{ac.ac})_2]:[\text{Cu}(\text{ac.ac})(\text{Hy})]:[\text{Cu}(\text{Hy})_2] = 45:80:18$.

applied to the “average” g_0 and A_0 values, using the deviations from the “equidistant” position. Estimates of g_0 and A_0 obtained by this procedure are included in table 1.

A support for the above assignment of the triplet to $\text{Cu}(\text{ac.ac})(\text{Hy})$ comes from $W_m (= 9.2 \text{ G})$ calculated using the magnetic parameters given in table 1. The calculated W_m agrees well with the experimentally determined $W_m (= 9.3 \text{ G})$. The experimentally determined W_m was obtained comparing the ESR spectra obtained at different temperatures with computer simulated spectra. The computer simulations included ^1H hyperfine splitting, 1.74 G expected from “Hy” on the basis of ENDOR data (Rist and Hyde 1968).

Figure 2b shows the computer simulation which matches the high field region of the spectrum observed at -20°C (figure 2a), and which takes note of the above assignment. The relative concentration estimates used in the simulation give $K = 2.0$ when (1) is used.

Cu(Sal)(Hy): An ESR spectrum obtained from a reaction mixture of $\text{Cu}(\text{Sal})_2 + \text{Cu}(\text{Hy})_2$ in chloroform at -20°C is shown in figure 3a. The high field

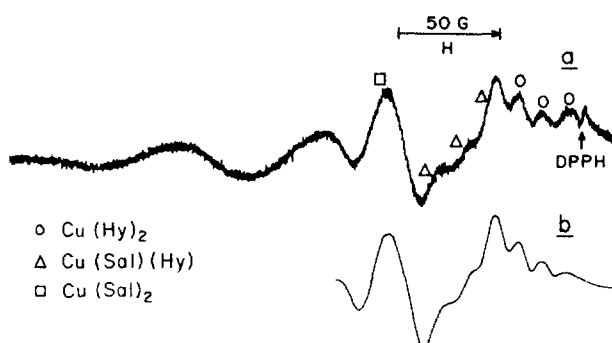


Figure 3. (a) ESR spectrum from a reaction mixture of $\text{Cu}(\text{Sal})_2 + \text{Cu}(\text{Hy})_2$ in chloroform at -20°C . (b) Computer-simulated spectrum in the high field region using $[\text{Cu}(\text{Sal})_2] : [\text{Cu}(\text{Sal})(\text{Hy})] : [\text{Cu}(\text{Hy})_2] = 35 : 65 : 16$.

$m_1 = -3/2$ component of the ESR spectrum from a near-square-planar $\text{Cu}(\text{Sal})(\text{Hy})$ should show ligand hyperfine structure (triplet) due to hyperfine interaction with the ^{14}N of "Hy". This triplet can be identified by a procedure similar to that used in the case of $\text{Cu}(\text{ac.ac})(\text{Hy})$. The ^{14}N hyperfine splitting A_N and A_0 associated with $\text{Cu}(\text{Sal})(\text{Hy})$ are given in table 1. The magnitude of calculated $W_m (= 9.2 \text{ G})$ for $\text{Cu}(\text{Sal})(\text{Hy})$ has a value similar to that of $\text{Cu}(\text{ac.ac})(\text{Hy})$. Nevertheless, the triplet assigned to $\text{Cu}(\text{Sal})(\text{Hy})$ is less resolved, suggesting the presence of additional ligand hyperfine structures. ^1H splittings $\sim 5.5 \text{ G}$ from the ligand "Sal" have been observed in the frozen solution spectrum of $\text{Cu}(\text{Sal})_2$ (Ugrankar and Prabhananda, to be published). Similar ^1H splittings have also been observed in the ESR spectrum of *bis* salicylaldehydeaminato $\text{Cu}(\text{II})$, which is an analogous complex (Maki and McGarvey 1958b). Therefore, in a near-square-planar $\text{Cu}(\text{Sal})(\text{Hy})$, we should have ^1H splitting $\sim 5.5 \text{ G}$ from a proton on "Sal". Inclusion of such a splitting and the ^1H splitting of 1.74 G expected from "Hy" on the basis of ENDOR data (Rist and Hyde 1968) gives the poorly resolved triplet feature in the computer simulations (similar to that observed experimentally) when $W_m = 9.3 \text{ G}$ is used.

Figure 3b shows the computer simulated spectrum which matches the spectrum shown in figure 3a. $K = 1.9$ could be obtained from the relative concentration estimates used in the matching simulation (figure 3b).

4. Discussion

Our assignment of the triplets in the high field region of the ESR spectra to the $m_1 = -3/2$ component of the mixed ligand complexes can be taken to be correct, since (i) the expected ligand hyperfine structures are observed, and (ii) the calculated W_m agree well with the observed W_m . For the two ligand exchange reactions studied in this work K estimated with the help of ESR simulations were ~ 2 .

If A^P , A^Q and A^{PQ} are the ^{63}Cu hyperfine constants of $\text{Cu}(P)_2$, $\text{Cu}(Q)_2$ and $\text{Cu}(P)(Q)$ (in gauss),

$$\delta = A^{PQ} - (A^P + A^Q)/2, \quad (5)$$

is a measure of change in the 4s-mixing on forming the mixed ligand complex (Das and Prabhananda 1983). The free energy change associated with the change in 4s-mixing would depend on the energy of the 4s-orbital. In our previous work (Prabhananda 1983b), it was suggested that the stabilisation of the mixed ligand complex excluding the 4s-mixing factor can be given by,

$$K_0 = K \exp(-f\delta), \quad (6)$$

where f depends on the energy of the 4s-orbital and on temperature. At -20°C ($f = 0.4$) can be obtained following the procedure used earlier (Prabhananda 1983b). Using the ^{63}Cu hyperfine constants given in table 1, we estimate $K_0 = 1.35$ for Cu(ac.ac) (Hy) and $= 0.75$ for Cu(Sal) (Hy). Table 1 also shows that $|(g_{\parallel}^{\beta} - g_{\perp}^{\beta})| = 0.016, 0.013$ in the two situations. Differences in K_0 could have contributions from differences in the π -bonding abilities of the ligands as well (Prabhananda 1983b). In conclusion, we can say that the magnitudes of K and K_0 are ≈ 1 when $|g_{\parallel}^{\beta} - g_{\perp}^{\beta}|$ are small, even when the coordinating ligand atoms are O and N.

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