Stability of mixed ligand complexes of copper(II): ESR studies

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Abstract. Three new mixed ligand complexes of Cu(II) obtained by combining any two of the three ligands, diethyldithiocarbamate, N-benzoyl-N'-diethylthiocarbamide and acetylacetonate have been identified in reaction mixtures using electron spin resonance (ESR), by estimating the equilibrium constant K associated with the ligand exchange reaction. The K values were also determined for fifteen other mixed ligand complexes of Cu(II) reported earlier. The stability of these mixed ligand complexes was correlated with the difference in the strengths of covalent bonding between the metal ion and the two ligands. The bondings involving both the $d_{x^2-y^2}$ and d_{xy} orbitals on the metal were necessary. In addition, the extent of metal 4s-orbital mixed in the unpaired electron orbital contributed to the magnitude of K. The diagrams similar to the ones used in our correlation could be useful in predicting the probable yield of mixed ligand complexes in reaction mixtures.

Keywords. Mixed ligand complex; electron spin resonance; cupric complexes; stability.

1. Introduction

Electron spin resonance (ESR) has been used to study a large number of mixed ligand transition metal complexes. (Dietzch *et al* 1977; Krishnamoorthy and Prabhananda 1978; Baratova *et al* 1982 and references cited therein). In our earlier studies we had shown that mixed ligand complexes are quite useful in inferring the mechanism of spin transfer to ligands. In the present work, we are mainly concerned with the stability of these complexes. A mixed ligand copper(II) complex of two bidentate ligands X and Y can be prepared by an appropriate mixture of $Cu(X)_2$ and $Cu(Y)_2$ in solutions by ligand exchange reactions.

$$Cu(X)_2 + Cu(Y)_2 \rightleftharpoons Cu(X)(Y) + Cu(Y)(X) \tag{1}$$
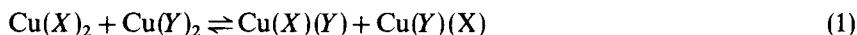
In this reaction, both X and Y coordinate to the metal ion. Even if we can identify two coordinating regions on the metal ion (thereby distinguish $Cu(X)(Y)$ from $Cu(Y)(X)$) there is no reason for X to coordinate preferentially at one of these regions. Thus the concentrations of $Cu(X)(Y)$ and $Cu(Y)(X)$ will be the same. By experiments such as ESR it is not possible to distinguish the mixed ligand complex $Cu(X)(Y)$ from $Cu(Y)(X)$. Therefore, if the measured mixed ligand complex concentration is $[Cu(X)(Y)]_m$, we can write

$$[Cu(X)(Y)] = [Cu(Y)(X)] = [Cu(X)(Y)]_m/2 \tag{2}$$

The equilibrium constant K for reaction (1) can then be written as

$$K = \frac{[Cu(X)(Y)]_m^2}{4.[Cu(X)_2][Cu(Y)_2]} \tag{3}$$

1

(This expression gives the expected value of $K = 1$ if there is no free energy change associated with reaction (1)).

In our previous studies, we had identified the mixed ligand complexes by the ligand hyperfine structures and had determined the equilibrium concentrations of the paramagnetic species in the reaction mixtures by comparing the observed ESR spectra with computer-simulated spectra. These had shown that K depends on the choice of ligands X and Y (Krishnamoorthy and Prabhananda 1978). Dietzch et al (1977) noticed that the mixed ligand complexes formed with maleonitrile dithiolate (MNT) as one of the ligands, had much higher values of K than other mixed ligand complexes studied. Their extended Hückel molecular orbital calculations also indicated such a trend in the values of K. They suggested that when the metal ion forms a four-membered ring with one ligand and a five-membered ring with a second ligand there is considerable energy gain for the mixed ligand complex formation. Such a simple rule is not applicable to the results obtained earlier (Prabhananda et al 1977; Krishnamoorthy and Prabhananda 1978). A better understanding of the stability of mixed ligand complexes can be gained by looking for some sort of correlation between K and ESR determined parameters. This could also help in guessing the probable yield of new mixed ligand complexes in reaction mixtures.

The value of K associated with 18 mixed ligand complexes prepared by various combinations of seven ligands (shown in figure 1) is examined. Equilibrium concentrations determined by computer simulations (Prabhananda et al 1977; Krishnamoorthy and Prabhananda 1978; Krishnamoorthy et al 1978), were used to obtain K in the case
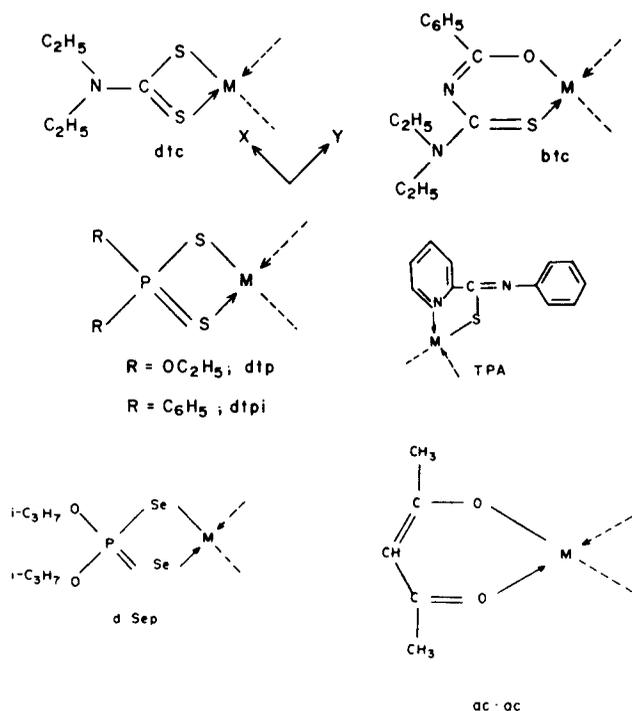

Figure 1. Ligands used in the present study. M is a metal ion to which they coordinate.

of eight complexes. For seven of the complexes we had not simulated the spectra to match the experimental ESR spectra from their reaction mixtures, in our earlier studies (Krishnamoorthy and Prabhananda 1980 and references therein). After determining the equilibrium concentrations of the paramagnetic species in the reaction mixtures the K value associated with these seven complexes was determined by obtaining the computer-simulated spectra and these values agree with the reported spectra.

Three new mixed ligand complexes of copper(II) prepared by the combinations of diethyldithiocarbamate (dtc), N-benzoyl-N'-diethylthiocarbamide (btc) and acetyl-acetonate (ac.ac) have also been reported in the present work. These complexes do not show ligand hyperfine structures. Nevertheless, the spectrum of mixed ligand complex can be identified as follows. In the complex ESR spectra obtained from the reaction mixtures one can easily identify the lines due to species $Cu(X)_2$ and $Cu(Y)_2$ (since their spectra can be obtained separately). The remaining lines could be assigned to the mixed ligand complex. That such an assignment is correct could be confirmed by estimating the concentrations from the observed spectra and plotting $[Cu(X)(Y)]_m^2/[Cu(X)_2]$ against $[Cu(Y)_2]$. From (3) the plot should be a straight line passing through the origin, the slope of which can be used to get an estimate of K. Further confirmation could be obtained if the g_0 value of the mixed ligand complex in liquid solutions can be determined. Our previous studies (Krishnamoorthy and Prabhananda 1980 references cited therein) have shown that g_0 of $Cu(X)(Y)$ is close to the average of those of $Cu(X)_2$ and $Cu(Y)_2$. Such a cross-check has been possible in the case of two new mixed ligand complexes reported in this work. A possible correlation between K and the bonding inferred from ESR parameters is also suggested in this paper.

2. Experimental

The complexes $Cu(dtc)_2$, $Cu(btc)_2$ and $Cu(ac.ac)_2$ which have been used in the preparation of mixed ligand complexes were prepared as described earlier (Krishnamoorthy and Prabhananda 1978, 1980). Reaction mixtures with Cu(dtc)(btc), Cu(btc)(ac.ac) and Cu(dtc)(ac.ac) at different concentrations were obtained according to equation (1), by mixing the chloroform solutions of the complexes in different proportions. Cupric acetate enriched to $> 90\%$ with ^{63}Cu was used in all preparations. X-band ESR spectra of the solutions were recorded at 25°C. Computer-simulated spectra were obtained using a program written earlier (Baratova *et al* 1982).

3. Results

Figure 2 gives the derivative ESR spectra obtained from typical reaction mixtures in the preparation of Cu(dtc)(btc), Cu(dtc)(ac.ac) and Cu(btc)(ac.ac). In the case of Cu(dtc)(btc) (figure 2a) all the four lines corresponding to ^{63}Cu hyperfine components can be seen in the spectrum. The high field components (which are well resolved) can be used to directly estimate the concentrations of the three paramagnetic species, since they are proportional to (peak-to-peak width)^2 × peak-to-peak height of the corresponding derivative lines. The concentrations thus obtained from different reaction mixtures give the expected linear plot (figure 2a') supporting our identification of the spectrum from the mixed ligand complex. The g_0 corresponding to this spectrum (table 1) has the expected value. In figure 2b apart from the lines corresponding to
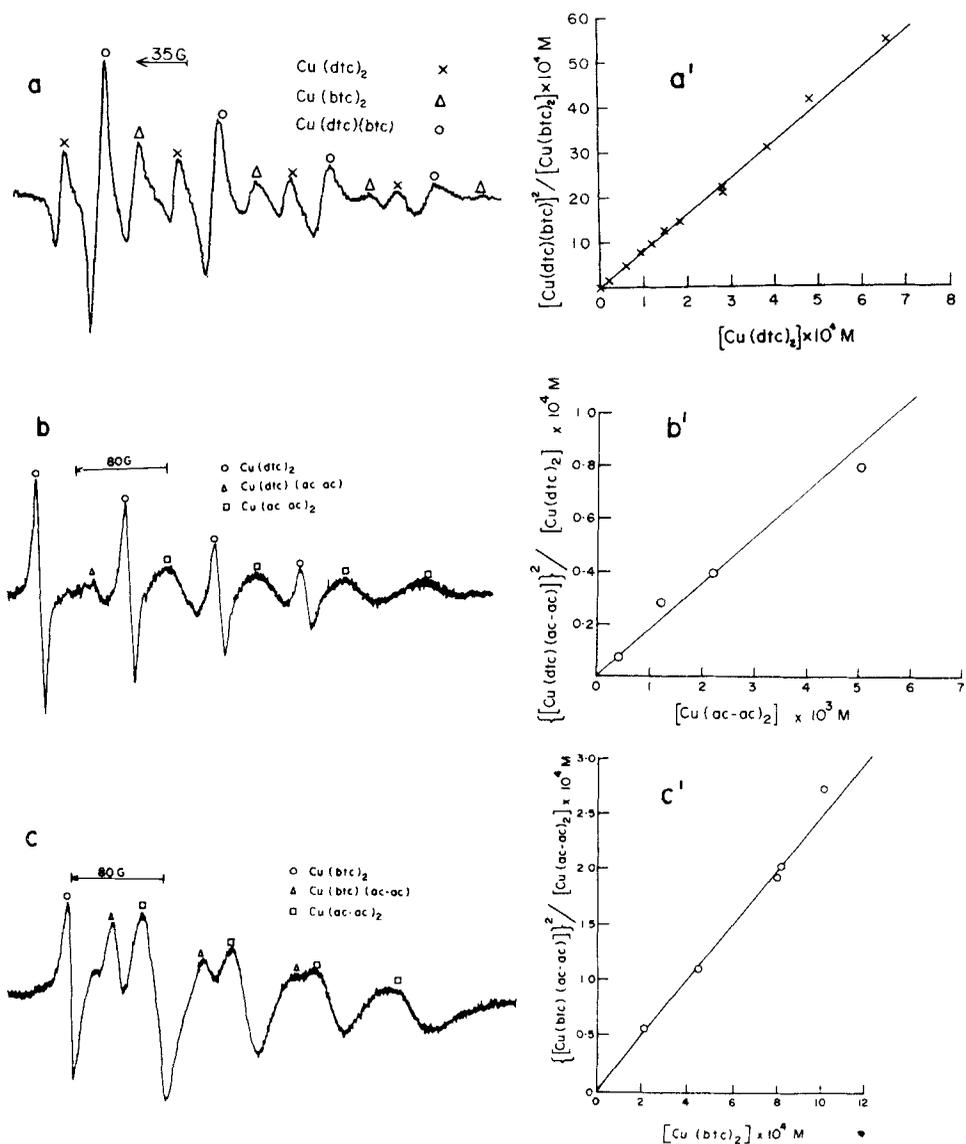
Figure 2. ESR spectra obtained from typical reaction mixtures in the preparations of (a) Cu(dtc)(btc), (b) Cu(dtc)(ac.ac) and (c) Cu(btc)(ac.ac). The plots used in the determination of K of these mixed ligand complexes are (a'), (b') and (c').

Cu(dtc)$_2$ and Cu(ac.ac)$_2$ one extra line is noted which is in the high field region. The estimation of concentrations, assigning this extra line to Cu(dtc)(ac.ac), gives a linear plot (figure 2b') consistent with such an assignment. However, this could not be confirmed from the g_0 measurements since none of the other three hyperfine components (of the spectrum of this complex) could be identified, due to considerable overlap from the spectra due to Cu(dtc)$_2$ and Cu(ac.ac)$_2$. In figure 2c even though there is considerable overlap, the positions of at least three hyperfine components of a

Table 1. ^{63}Cu hyperfine constant A_0 and g_0 determined from the ESR spectra of chloroform solutions at 25°C^a.

Complex	A_0 in G	g_0
Cu(dtc)$_2$	78·0	2·0480
Cu(btc)$_2$	79·6	2·0826
Cu(ac.ac)$_2$	76·2	2·1235
Cu(dtc)(btc)	77·7	2·0650
Cu(btc)(ac.ac)	78·6	2·1046

^{a} The absolute errors in A_0 and g are $\pm 2G$ and ± 0.002 respectively.

spectrum could be determined, apart from those of Cu(btc)$_2$ and Cu(ac.ac)$_2$. These could be assigned to Cu(btc)(ac.ac), since the concentrations estimated (with this assignment) from the spectra of different reaction mixtures (figure 2c′) and the estimated g_0 (table 1) showed the expected behaviour.

Since there is considerable overlap of the lines in the spectra similar to figure 2c, the simple procedures adopted for figures 2(a–b) cannot be used in this case. The concentrations of the three species (C_i, $i = 1$, 3) in the reaction mixtures can be determined by measuring the ESR signal heights $S_0(H_j)$ at three convenient magnetic fields H_j, and solving the simultaneous equations

$$S_0(H_j) = C_1 S_1(H_j) + C_2 S_2(H_j) + C_3 S_3(H_j) \tag{4}$$

$S_1(H_j)$, $S_2(H_j)$ and $S_3(H_j)$ are the signal height at H_j of the three species when their concentrations are unity. These were determined by matching a computer-simulated spectrum with the observed ESR spectrum from one convenient reaction mixture at a particular field region. Procedures used earlier (Prabhananda *et al* 1972a; Krishnamoorthy and Prabhananda 1978) were used in the matching of the spectra and the data plotted in figure 2c′. The K estimated from figures 2(a′–c′) are given in table 2. Figure 3a gives the observed and computer-simulated spectra used to determine $S_1(H_j)$, $S_2(H_j)$ and $S_3(H_j)$ for this system.

It can be seen from figures 2(a′–c′) that the errors in the estimated K for the above three systems are less than 20%. The value of K estimated from analysing one reaction mixture is sufficiently good (with errors of the above order) if it is ensured that (i) an equilibrium has been reached and (ii) the signal height contributions of the three species are good. (Even if the concentration of the complex is small, it is possible to estimate this if the linewidth associated with this complex is small compared to that of the others.) The above procedure has been followed for other systems reported in this paper. However, the estimated K have been cross-checked by comparing the observed and simulated spectra for a second reaction mixture, using the same value of K.

In the spectra of reaction mixtures with Cu(btc)(ac.ac), Cu(TPA)(ac.ac) or Cu(dtc)(dtpi) the lines due to all the three species could be easily distinguished (figures 3a–c) only for the high field ^{63}Cu hyperfine component ($m_I = 3/2$). On the other hand, in Cu(dtc)(dseP), one could identify the lines (figure 3d) only for the low field ^{63}Cu hyperfine component ($m_I = -3/2$). While such identification could be easily made for $m_I = 3/2$ and $m_I = 1/2$ components in the reaction mixtures of Cu(btc)(dtp), this was possible only for the $m_I = 1/2$ component for the mixture with Cu(btc)(dtpi). Thus computer simulations have been carried out to include both these components in these

Table 2. Equilibrium constants K and other relevant parameters associated with the mixed ligand complexes of Cu(II).

Ligands and near neighbours of metal		δ^a in G	K^b	Reference
X	Y			
btc (S, O)	TPA (S, N)	9·0	270·0	K & P 1980^c
dtc (S, S)	dtp (S, S)	0·3	14·0	K & P 1978
dtc (S, S)	TPA (S, N)	5·0	12·8	P et al 1977^c
dtc (S, S)	dtpi (S, S)	0·0	9·6	K & P 1978^c
dtp (S, S)	TPA (S, N)	4·0	3·1	P et al 1977
dtp (S, S)	dtpi (S, S)	0·0	2·2	K & P 1978
dtc (S, S)	btc (S, O)	−1·0	2·0	This work
dtc (S, S)	dSeP (Se, Se)	0·6	1·9	K et al 1978^c
dtpi (S, S)	TPA (S, N)	5·0	1·6	P et al 1977
TPA (S, N)	ac.ac (O, O)	8·4	1·1	K & P 1980^c
dSeP (Se, Se)	dtp (S, S)	0·8	1·1	K et al 1978
dSeP (Se, Se)	dtpi (S, S)	0·8	1·0	K et al 1978
dtpi (S, S)	btc (S, O)	−2·0	0·84	K & P 1978^c
dtp (S, S)	btc (S, O)	−3·2	0·76	K & P 1978^c
dSeP (Se, Se)	btc (S, O)	−2·0	0·5	K et al 1978
dSeP (Se, Se)	TPA (S, N)	1·4	0·4	K et al 1978
btc (S, O)	ac.ac (O, O)	0·7	0·06	This work
dtc (S, S)	ac.ac (O, O)	—	0·005	This work

^{a} δ is a measure of the mixing of metal 4s-orbital in the unpaired electron orbital. See equation (5) in text.
^{b} See text for the discussions on the errors in K. Errors in δ are of $\sim \pm 0.3\,G$.
^{c} Computer simulations carried out in this work.

two systems (figures 4c and 4d). In the spectra obtained from the reaction mixtures containing Cu(btc)(TPA) and Cu(dtc)(TPA), the lines due to Cu(btc)$_2$ and Cu(dtc)$_2$ considerably overlapped with the lines due to other species throughout the spectra. In these two cases, the concentrations of Cu(btc)$_2$ and Cu(dtc)$_2$ were estimated by varying them to get minimum deviation between the observed and calculated line shapes in the high field region. In figures 4a and 4b these small contributions are marked by dotted lines in the simulated spectra. Table 2 gives the K value estimated for these systems and also the K calculated from the equilibrium concentrations used in the simulation of the spectra, for the reaction mixtures containing Cu(dtc)(dtp), Cu(dtp)(dtpi) (Krishnamoorthy and Prabhananda 1978. The concentrations of Cu(dtp)(dtpi) and Cu(dtpi)$_2$ have been erroneously interchanged in figure 3 of this paper), Cu(TPA)(dtp), Cu(TPA)(dtpi) (Prabhananda et al 1977), Cu(dtp)(dSeP), Cu(dtpi)(dSeP), Cu(btc)(dSeP) and Cu(TPA)(dSeP) (Krishnamoorthy et al 1978).

Small deviations between the observed and simulated spectra are noticed in many cases. Departure of the experimental line shape from Lorentzian (especially due to the finite amplitude of field modulation used for detecting the signal), presence of unidentified paramagnetic species in small concentrations are some of the causes for these deviations. However, the K values for different systems cannot be very different from those given in table 2, since K can be used to predict the spectra from other reaction mixtures (of these systems) also, which agree reasonably well with the observed spectra.

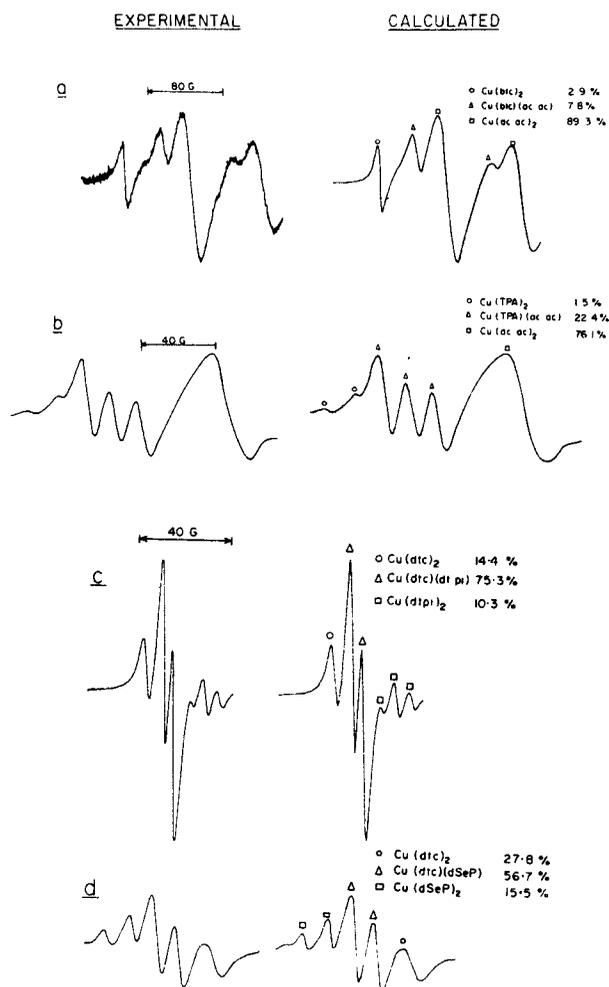Diluting a typical reaction mixture changes the concentration of the three

Figure 3. Experimentally observed and computer simulated ESR spectra for the reaction mixtures containing (a) Cu(btc)(ac.ac), (b) Cu(TPA)(ac.ac), (c) Cu(dtc)(dtpi) in the high field region and (d) Cu(dtc)(dSeP) in the low field region.

paramagnetic species by the same factor. This is expected from (3) and adds confidence to our identification of the reaction as that given by (1). Changing the hydrogen bonding property and the dielectric constant of the solvent (by using methanol) does not affect the estimated K for typical systems. It is therefore clear that the stability of the mixed ligand complex is mainly determined by internal factors.

3.1 *Relative ordering of the ligands on the basis of the strengths of their interaction with copper(II)*

It is natural to expect that K is correlated with the relative strengths of ligand-metal interactions. In previous studies (Krishnamoorthy and Prabhananda 1980), we had placed the ligands in the increasing order of covalent bonding of the metal $d_{x^2-y^2}$
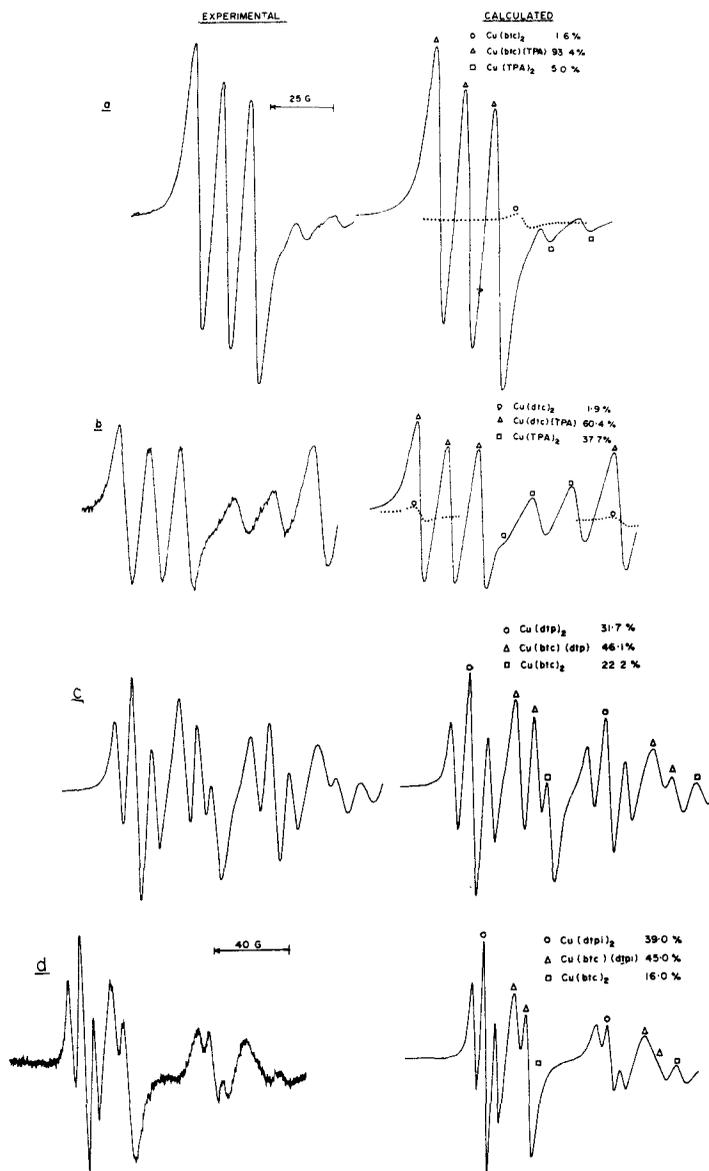
Figure 4. Experimentally observed and computer simulated ESR spectra for the reaction mixtures containing (a) Cu(btc)(TPA), (b) Cu(dtc)(TPA), (c) Cu(btc)(dtp) and (d) Cu(btc)(dtpi) in the high field region. Dotted lines in (a) and (b) correspond to $Cu(btc)_2$ and $Cu(dtc)_2$ components respectively.

orbital with the near neighbours as follows:

$$ac.ac < btc < \text{TPA} < dtp < dtc < dSeP$$

(In our coordinate system the lobes of $d_{x^2-y^2}$ point towards the near neighbours.) In figure 5, the above ordering is along the vertical direction.
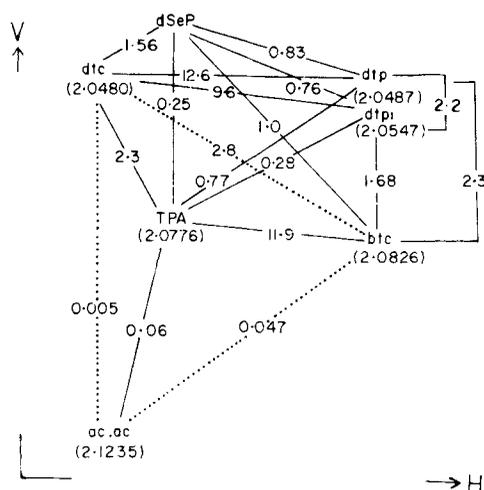
Figure 5. Schematic diagram used in correlating K_0 with the bonding characteristics. The g_0 associated with Cu(L)$_2$ are given within brackets. K_0 associated with Cu(X)(Y) are given between the line connecting X and Y.

If we subtract the contribution of spin-orbit interaction at the ligands from the measured g_0 and designate it by g_0', we note that g_0' differs from g_0 substantially in the case of Cu(dSeP)$_2$ (due to spin orbit interaction on Se). This can be seen in the calculations of Attanasio *et al* (1976). Spin-orbit interaction on the ligands L is quite small for the other complexes Cu(L)$_2$ discussed here. Thus, the g_0 given earlier (Prabhananda 1979; Krishnamoorthy and Prabhananda 1980) can be used as the estimates of g_0' (figure 5). In view of the dependence of g_0 on the interaction of the ligands with the metal $d_{x^2-y^2}$ orbital, we have separated the ligands L along the vertical direction of figure 5, following the pattern seen in the g_0 of Cu(L)$_2$. Attanasio *et al* (1976) show that inclusion of 4d-orbitals of Se is necessary in Cu(dSeP)$_2$ to reproduce the experimentally determined g-tensor by calculations. If the spin-orbit interaction on this ligand orbital is neglected, we get $g_0 \sim 2\cdot046$ (Attanasio *et al* 1976). Therefore dSeP should be placed above dtc. Covalency considerations mentioned above also require dSeP to be placed above dtc in figure 5. Further, we should expect the separation between dtc and dSeP to be more than that between dtp and dtpi, since the coordinating atoms of the two ligands are different in the former case whereas they are all sulphurs in the latter case. This intuitive consideration is used while placing the ligand dSeP in figure 5.

Earlier studies (Prabhananda *et al* 1972b and the later works cited here) had shown that the next neighbour ligand hyperfine splittings observed in the complexes were due to the covalent bonding involving the metal d_{xy} orbital. Studies on the next neighbour hyperfine splittings in mixed ligand complexes (Krishnamoorthy and Prabhananda 1978) had shown that the covalent transfer of electrons in the bonds with stronger bonding ligand increases at the expense of the weaker bonding ligand. This is similar to the observations of Eaton and Phillips (1965). Since these hyperfine interactions are due to configuration interaction mechanism in Cu(II) complexes, the next neighbour hyperfine splittings associated with the stronger bonding ligands actually decrease as a

consequence of increased delocalisation in that bond, as explained earlier (Krishnamoorthy and Prabhananda 1978). Thus the next neighbour hyperfine splittings can be used to arrange the ligands in the increasing order of interaction of the ligand with the metal d_{xy} orbital (see table 2). In figure 5 this interaction increases along the horizontal direction.

The Cu(II) complexes formed by combinations of dtp, dtpi and btc do not show significant changes in the ^{31}P hyperfine splittings. Thus their horizontal coordinates in figure 5 will be similar. The decrease in the ^{31}P hyperfine splitting associated with dtp on forming Cu(dtp)(dSeP) and Cu(TPA)(dSeP) is comparable. Therefore, their horizontal coordinates in figure 5 cannot be much different. Formation of Cu(dtc)(dSeP) decreases the ^{31}P splitting associated with dSeP by a small amount. Thus dSeP (and hence TPA) is placed close to dtc along the horizontal direction. The position of ac.ac along the horizontal direction is not definite, since we have not been able to make observations on Cu(dtp)(ac.ac). However, predictions regarding the relative stabilities of the complexes made later in this paper are not significantly altered by changing the position of ac.ac along the horizontal direction of figure 5.

3.2 *Changes in the metal 4s-mixing*

In our previous work (Krishnamoorthy and Prabhananda 1980) we had noted that if A^X, A^Y and A^{XY} are the ^{63}Cu hyperfine constants of $Cu(X)_2$, $Cu(Y)_2$ and $Cu(X)(Y)$, measured from their ESR spectra in liquid solutions,

$$\delta = A^{XY} - (A^X + A^Y)/2 \neq 0 \tag{5}$$

This non-zero value of δ is due to the change in the mixing of metal 4s orbital in the unpaired electron orbital. The experimentally determined δ are given in table 2.

4. Discussion

The Cu(II) complexes studied are nearly square planar. One can look for correlation between the magnitude of K and the bonding characteristics by referring to figure 5 and table 2. Among the 18 mixed ligand complexes listed in table 2, Cu(btc)(TPA) has the largest value of K (~ 270). Therefore, the characteristics associated with it can be used to find the conditions for stabilisation of the mixed ligand complex. (a) The coordinates of btc and TPA in figure 5 differ substantially along H-direction. But this difference is not much along V-direction. (b) The δ associated with Cu(btc)(TPA) has a large positive value (table 2). The first characteristic feature is the highly stable Cu(dtc)(dtp) (~ 14). It may be reasonable to infer that the smaller value of K for Cu(dtc)(dtp) when compared to that for Cu(btc)(TPA) is to be associated with the differences in the δ values (table 2).

4.1 *Stabilisation associated with change in metal 4s-mixing*

Kuska *et al* (1967) used a value of 0.0975 cm^{-1} for the hyperfine constant associated with a 4s-electron in Cu(II) complexes, based on the calculations of Watson and Freeman (1961). Converting this into magnetic field units and a part of the unpaired electron density with $3d^8\,4s^1$ character ρ gets converted into $3d^9$ character, the hyperfine constant changes by approximately 1000ρ. The δ given in table 2 will correspond to changes in the metal 4s-mixing of the unpaired electron orbital by $\delta/1000$. Using the estimate of energy difference between the configurations $3d^8\,4s^1$ and

$3d^9$ given by Abragam and Pryce (1951), $\sim 70{,}000$ cm^{-1} ($= 8\cdot68$ eV), the above change would correspond to a free energy decrease $\sim 8\cdot68\,\delta/1000$ eV. At room temperature ($kT \sim 1/40$ eV), this would correspond to an increase in the K by a factor exp $(0\cdot347\,\delta)$. For Cu(btc)(TPA), this factor has a value of ~ 22. Thus it is not surprising that K associated with this complex has a large value. K_0 defined by

$$K \exp\left(-0\cdot347\,\delta\right) \tag{6}$$

can be used to discuss the stabilisation of the complex excluding the above factor. The K_0 values thus determined are given in figure 5 on the line connecting the ligands of the mixed ligand complex. For example, $K_0 = 12\cdot6$ is associated with Cu(dtc)(dtp) and $K_0 = 2\cdot8$ with Cu(dtc)(btc).

The mixing of metal 4s-orbital in the unpaired electron orbital (which has $d_{x^2-y^2}$ character on the metal) has been attributed to the mixing of d_{z^2} (which has the correct symmetry to mix with 4s) with $d_{x^2-y^2}$. This could be due to a vibronic mechanism or due to the lower symmetry environment of the metal (Kuska *et al* 1967). Thus in reality we have two contributions to free energy changes associated with a change in the 4s mixing. (i) that associated with a change in configuration from $3d^8\,4s^1$ to $3d^9$ as discussed above; (ii) that associated with the change in vibronic mixing or with change in the symmetry of coordination (to a higher symmetry when there is a reduction in 4s mixing and to a lower symmetry when there is an increase) which could affect the overlap of the metal orbitals with the ligand orbitals. (The reason for such changes on forming the mixed ligand complexes is not clear at present.) The first factor is taken care of by expressing K in terms of K_0 and δ. The importance of the second factor is not yet clear in our system. We can correlate K_0 with bonding characteristics only if we assume that the second factor is negligible.

### 3.3 *Correlation between K_0 and bonding characteristics*

The magnitude of K_0 is mainly determined by the difference in the H-coordinates of the ligands forming the mixed ligand complex, when the difference in the V-coordinates is small (figure 5). This can be seen by comparing the K_0 associated with Cu(dtc)(dtp) and Cu(btc)(TPA). Similarly, a comparison of K_0 associated with Cu(dtc)(TPA) and Cu(btc)(dtp) shows that K_0 is mainly determined by the difference in V-coordinates, when the difference in the H-coordinates is small. From this, we conclude that K_0 is mainly decided by the differences in the bonding characteristics of the two ligands with the metal d_{xy} and $d_{x^2-y^2}$ orbitals.

The terms 'bond energy' or 'bond strength' is used in reference to the covalent bonds involving the ligand orbitals and the metal $d_{x^2-y^2}$ and d_{xy} orbitals. The actual total bond energy could have other contributions also. If V_x and H_x are the coordinates of the ligand X (figure 5) (along the vertical and horizontal directions), $V_x + p.H_x$ is a measure of the strength of the Cu-X bond coming from the covalent bonds involving the metal $d_{x^2-y^2}$ and d_{xy} orbital. (The contributions to strengths are additive in nature. The parameter p takes care of the differences in the scales of V and H axes.) The magnitude of the difference in the strengths of Cu-X and Cu-Y bonds in Cu(X)(Y) is given by

$$D = \left| V_x - V_y + p(H_x - H_y) \right| \tag{7}$$

An intuitive understanding of the dependence of K_0 and D can be gained by

visualising reaction (1) as that involving fictitious diatomic molecules,

$$(A - A) + (B - B) \rightleftharpoons (A - B) + (B - A). \tag{8}$$
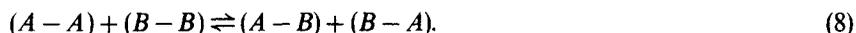
Here, A takes the place of Cu-X bond and B takes the place of Cu-Y bond (see appendix). If this could be done, we can make an analysis similar to that of Pauling (1960) and arrive at the following conclusion (as shown in the appendix). (I) For small D, K_0 increases with D reaching a maximum value corresponding to an 'optimum value' of D. (II) For D greater than this 'optimum', K_0 decreases with increase in D. One can examine 153 pairs ($= 18\,C_2$) of K_0 (figure 5), in an attempt to qualitatively understand the relative magnitudes of K_0 on the basis of this conclusion. Some simple examples of such comparisons are given below.

When $D = 0$, $K_0 = 1$. Thus $K_0 \sim 2$ for Cu(dtp)(dtpi) can be understood on the basis of situation (I). However, when we go from Cu(dtc)(TPA) to Cu(TPA)(ac.ac), K_0 decreases corresponding to situation (II). For Cu(dtc)(dSeP), $V_x - V_y$ and $H_x - H_y$ have the same signs, whereas for Cu(dtp)(dSeP) they have opposite signs. Therefore, D associated with Cu(dtc)(dSeP) is greater than that associated with Cu(dtp)(dSeP). For the case (I), we can expect K_0 to show the same behaviour as D. Experimental observations are consistent with this. A similar situation is encountered in comparing Cu(TPA)(dSeP) and Cu(btc)(dSeP). However, in this case D can be more than the 'optimum' which would then correspond to case II. Thus, it is not surprising that K_0 of Cu(TPA)(dSeP) is less than that of Cu(btc)(dSeP). The above type of correlation of K_0 with D can be seen by comparing several pairs of mixed ligand complexes of our earlier studies. However, the magnitude of K_0 of Cu(btc)(dtpi) and of Cu(TPA)(dtpi) shows small deviations from the expected trend, when we compare them with the K_0 of Cu(btc)(dtp) and Cu(TPA)(dtp) respectively. One could attribute this to the approximations made in the 'assumption' mentioned earlier. Errors in δ which contribute to additional errors in K_0 (when compared to that in K) could also be responsible for such small deviations.

If we are satisfied with the above correlation for the complexes reported earlier the order of magnitude of K_0 could be predicted for the complexes prepared in this work (indicated by dotted lines in figure 5) as follows. From figure 5, we note that a comparison of K_0 of Cu(dtc)(TPA) and Cu(dtc)(btc) will be similar to that of Cu(TPA)(dSeP) and Cu(btc)(dSeP), as discussed above. Thus K_0 of Cu(dtc)(btc) could be greater than 2·3. K_0 of Cu(dtc)(ac.ac) can be much less than that of Cu(TPA)(ac.ac) when a similar comparison between the K_0 associated with Cu(dtc)(TPA) and Cu(TPA)(dSeP) or Cu(TPA)(ac.ac) is made. K_0 associated with Cu(btc)(ac.ac) will be less than that of Cu(TPA)(ac.ac) by anology with a similar situation involving Cu(dtc)(TPA) and Cu(dtp)(TPA). The experimentally determined K_0 are in accordance with the predictions for all the three complexes.

In view of the approximations involved in the assumptions, it is not appropriate to make quantitative predictions of K_0. Nevertheless, our results have shown that diagrams of the type shown in figure 5 could be useful in predicting the relative magnitudes of K_0. Relative stabilities of various mixed ligand complexes could also be guessed, if we take note that certain ligands, such as, TPA favour a reduction in 4s-mixing on forming the mixed ligand complex and the ligands such as btc favour an increase in 4s-mixing (except when in combination with TPA). Our discussion also shows the importance of bonding involving the metal $d_{x^2 - y^2}$ and d_{xy} orbitals in the stabilisation of mixed ligand complex of Cu(II). In addition, changes in 4s-mixing in the unpaired electron orbital also play a significant role.

Acknowledgement

Appendix

The equilibrium constant associated with reaction (8) involving diatomic molecules varies as $\exp(\Delta/RT)$ where

$$\Delta = E_{AB} - (E_{AA} + E_{BB})/2$$

$E_{AA'}$ refers to bond energy of diatomic molecule $(A-A')$. We can also define

$$\Delta' = E_{AB} - (E_{AA} \cdot E_{BB})^{1/2}$$

It is easy to see that

$$P = \Delta' - \Delta = (E_{AA} + E_{BB})/2 - (E_{AA} \cdot E_{BB})^{1/2} \geqslant 0$$

P increases when $|E_{AA} - E_{BB}|$ increases. In the absence of ionic character in the bond $A-B$, $\Delta' = 0$. However, if the electron density of one atom increases at the expense of other, the bond will have an ionic character which requires the inclusion of ionic structures in the valence bond calculations (Pauling 1960 see eqn 3-2). According to Pauling (1960) quantum mechanical calculations support the hypothesis that Δ' increases with increase in the ionic character of the bond which could come from increase in $|E_{AA} - E_{BB}|$. Thus in the expression

$$\Delta = \Delta' - P$$

both Δ' and P increase with increase in $|E_{AA} - E_{BB}|$. Experimental results on halogen halides and alkali metal hydrides cited by Pauling (1960) appear to indicate that for small values of $|E_{AA} - E_{BB}|$ the variation of Δ' dominates and for large values of $|E_{AA} - E_{BB}|$ the variation of P dominates in the expression for Δ. Thus Δ and the equilibrium constant could increase or decrease with $|E_A - E_B|$ depending on its magnitude.

Reaction (1) is visualised as (8) in order to bring out the similarities in our results and those discussed by Pauling (1960). In doing so, we take note of the following equivalences. A takes the place of Cu–X bond and B takes the place of Cu–Y bond. Bond energies of $Cu(X)_2$ and $Cu(Y)_2$ are equivalent to bond energies E_{AA} and E_{BB} of the fictitious diatomic molecules $(A-A)$ and $(B-B)$. Thus, the difference D in the bond strengths of Cu–X and Cu–Y bonds of $Cu(X)(Y)$ is related to $|E_{AA} - E_{BB}|$. The experimental observation that spin density on one ligand (and hence on the bond associated with it) increases at the expense of the other (due to increased delocalisation on the stronger bond) is equivalent to the increase of electron density on one atom at the expense of the other due to the ionic character of the bond $A - B$, when $|E_{AA} - E_{BB}| > 0$. Thus even for reaction (1) one obtains $\Delta = \Delta' - P$, where Δ' and P show the above mentioned behaviour. It is not unreasonable to expect that the variation of Δ and P in our system will be similar to those of diatomic molecules discussed by Pauling (1960). This leads to the conclusion mentioned in this paper.

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