CHAPTER 3

MACROCYCLIC DICOPPER(II) COMPLEXES CONTAINING AZOMETHINE LINKAGES
Synthesis, characterization and electrochemical studies of the binuclear macrocyclic complexes, \( \text{Cu}_2(R,R')L^1(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O} \) (\( \text{R} = \text{R}' = \text{H, Me, Pr, Ph; R = Ph, R}' = \text{Me} \)), have been made. The room temperature magnetic moments of these compounds vary from 0.4 to 0.8 \( \mu_B \). Except for \( \text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O} \), reversible or almost reversible sequential one-electron transfers at two different potentials have been observed in acetonitrile solutions of the other four compounds. In the case with \( \text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O} \), the second couple got obscured due to an adsorption/or secondary electrode reaction phenomenon. However, in DMF only \( \text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O} \) provided a quasi-reversible voltammogram for both the reduction processes. The mixed-valent complexes have considerably greater stabilities in acetonitrile relative to \( \text{Cu}^{II}\text{Cu}^{I}(\text{H,H})L^1 \) in DMF. The potentials of the first reduction step (\( E_1 \)) remain practically invariant throughout the series and are independent of the extent of magnetic interaction in the dicopper(II) complexes. This has been rationalized with a triplet copper(II) reduction model. The potentials of the second reduction step (\( E_2 \)) vary with the substituents, and a linear plot has been obtained for \( E_2 \) vs Hammet \( \sigma^-m \). It has been inferred that in acetonitrile the unpaired electron in the mixed-valent complexes remains localized in one of the copper atoms.
The binuclear macrocyclic complex, Cu$_2$(H,H)L$^1$(ClO$_4$)$_2$·2H$_2$O, 3.1, was first synthesized by Pilkington and Robson$^1$ by condensing 1,3-diaminopropane with 4-methyl-2,6-diformylphenol and Cu(ClO$_4$)$_2$·6H$_2$O. Similar complexes of the type 3.2, and 3.3 were subsequently reported by Okawa and Kida$^2$. X-ray structure determination$^3$ of the chloro analogue, Cu$_2$(H,H)L$^1$Cl$_2$·6H$_2$O, 3.4, revealed that the chloride ions occupy the fifth apical coordination sites; these sites are on opposite sides of the plane of the macrocycle. Variable temperature magnetic moments measured down to 4.2K characterized$^4$ the compound 3.4 by a very strong antiferromagnetic exchange constant, J = -294 cm$^{-1}$. Electron transfer behavior of the compound 3.1, revealed$^5$ that the dicopper(II) complex undergo reduction in successive, quasi-reversible, one-electron steps at -0.52 and -0.91V vs NHE. The mixed-valent [Cu$^{II}$Cu$I$(H,H)L]$^+$ species in dichloromethane exhibited an isotropic seven-line EPR spectrum at the ambient temperature, while an anisotropic pattern with four-lines was observed in frozen solution. Intramolecular electron transfer rate as estimated from the variable temperature EPR spectra was $1.7 \times 10^{10}$ s$^{-1}$ at 298K. The electronic spectra of the dichloromethane solution of the mixed-valent complex showed at least two intravalent transition at 1700 and 1200 nm. X-ray structure
a: R = R' = H,
b: R = R' = Me,
c: R = R' = Pr,
d: R = R' = Ph,
o: R = Ph; R' = Me
determination of \([\text{Cu}^{II}\text{Cu}^{I}(\text{H,H})\text{L}]\text{ClO}_4\cdot 0.5\text{CH}_3\text{OH}\) revealed\(^6\) that the coordination environment of \(\text{Cu}^{II}\) is square planar, but the \(\text{Cu}^{I}\) is statistically distributed in two lattice sites, with one having essentially planar and the other square pyramidal environment.

Apart from the complex \(3.1\), the electrochemical behavior of the complex \(\text{Cu}_2(\text{Me,Me})\text{L}^1(\text{ClO}_4)_2\) was briefly reported by Addison\(^7\), although synthesis and characterization of this compound was not reported. Cyclic voltammetric studies showed that one-electron reduction of the complex in acetonitrile occurs reversibly at -0.74V vs Ag/AgCl. The reduced product showed a four-line EPR spectrum indicating that unlike in \([\text{Cu}^{II}\text{Cu}^{I}(\text{H,H})\text{L}]^+\), the unpaired spin density resides only on one copper atom (\(I = 3/2\)) and is not delocalized over two coppers.

In the preceding chapter we have reported the binuclear complexes of five 4-methyl-2,6-diacyl/benzoylphenols (\(R,R'\))\text{HL}. In this chapter chemistry of the binuclear macrocyclic complexes, \(3.5\), hereafter referred to as \(\text{Cu}_2(R,R')\text{L}^1(\text{ClO}_4)_2\cdot n\text{H}_2\text{O}\), will be reported. The purpose of the present study is to find a correlation between the extent of magnetic interaction and the potentials of electron transfer. We are also interested to see to what extent the stability of the mixed-valent complexes can be regulated by the variation of substituents in the macrocyclic ring, in the light of the fact\(^8\), that in mononuclear macrocyclic
complexes a wide ranging control can be exerted on redox potentials by subtle and cumulative variations in the ligand structure.

**EXPERIMENTAL SECTION**

The materials used were same as described in the Chapter 1. Physical and Electrochemical measurements were carried out in the same way as described in the previous chapter.

**Preparation of complexes, Cu₂(R,R')L¹(ClO₄)₂.nH₂O**

These compounds were obtained in two different ways as outlined in the Scheme 3.1.

**Method I.** The general procedure described here is a modified version of the one reported¹ for the preparation of Cu₂(H,H)L¹(ClO₄)₂.2H₂O. 1,3-Diaminopropane (0.45g, 6 mmol) diluted with methanol (5 mL) was added to a solution of Cu(ClO₄)₂.6H₂O (1.48g, 4 mmol) in methanol (50 mL). The solution was heated to boiling. A second solution of (R,R')HL (4 mmol) in hot ethanol (50 mL) was added to the first in a dropwise condition. The resulting solution was refluxed for 7h. During this period in the cases with (H,H)HL and (Me,Me)HL crystalline copper(II)
complexes began to separate out, while the solution remained clear for the other three ligands. The mixture was cooled to room temperature, filtered, and the filtrate was allowed to evaporate slowly. Additional crops of crystals obtained in the cases with (H,H)HL and (Me,Me)HL were collected by filtration, and washed several times with water, and dried over CaCl₂. In the cases with (Pr,Pr)HL, (Ph,Ph)HL and (Ph,Me)HL needle shaped crystals deposited over a period of 2d. These were collected by filtration, washed with water and finally dried over CaCl₂. 

Cu₂(H₂L)²(ClO₄)₂.2H₂O was recrystallized from water. In order to obtain well-grown crystals, a saturated aqueous solution of the compound in boiling water was made, which was filtered hot, and the filtrate was heated to dissolve some of the precipitated compound. This solution was then cooled to the ambient temperature over a period of 4h. All other compounds were recrystallized from a large volume of boiling methanol. In every case slow cooling and evaporation ensured highly crystalline products.

**Method II.** Cu₂(R,R')L₂(ClO₄)₂.2H₂O (2 mmol) was suspended in dry methanol (75 mL), and a solution of 1,3-diaminopropane (0.30g, 4 mmol) was added. The mixture was boiled under reflux for 5h. During this period Cu₂(R,R')L₂(ClO₄)₂.2H₂O went into solution. The solution was filtered hot and the filtrate was left for crystallization. Over a varying period, depending upon the solubilities of the compounds, crystalline compounds deposited. These were collected by filtration, and recrystallized as described in Method I.
Zn$_2$(Ph,Ph)L$^1$(ClO$_4$)$_2$. To a boiling solution of (Ph,Ph)HL (0.6g, 2 mmol) in ethanol (50 mL), 1,3-diaminopropane (0.15g, 2 mmol) and Zn(ClO$_4$)$_2$.6H$_2$O (0.75g, 2 mmol) were added in succession. The solution was refluxed for 1h, and solvent was removed in a rotary evaporator till solid particles began to separate. At this stage the mixture was cooled to the ambient temperature, and the compound deposited was collected by filtration. The compound was recrystallized from 1:1 ethanol-methanol mixture, and dried over CaCl$_2$.

RESULTS AND DISCUSSION

Synthesis and Characterization

Binuclear macrocyclic complexes, 3.5, were synthesized by template condensation of (i) bis(1,3-diaminopropane) copper(II) with 4-methyl-2,6-diacyl/benzoylphenol, (R,R')HL (method I), (ii) Cu$_2$(R,R')L$_2$(ClO$_4$)$_2$.2H$_2$O with 1,3-diaminopropane (method II). The reaction sequences are shown in Scheme 3.1.

The synthesis according to the method I requires the use of copper(II) perchlorate, 1,3-diaminopropane and (R,R')HL in the molar ratio of 2:3:2. It has been found that the addition of excess of 1,3-diaminopropane over the stoichiometric amount
improves the quality of the products in terms of purity and yield. The yields obtained by both the methods are comparable (80% or better). However, when the method I was modified by using dilute aqueous solutions of copper perchlorate, 1,3-diaminopropane and the sodium salt of \((R,R')\text{HL}\), the major product obtained after boiling the mixture for several hours was \(3.6\), instead of \(3.5\), which formed only in small quantity. The synthesis and chemistry of the complexes of the type \(3.6\) will be discussed in Chapter 4.

![Chemical structure of \(3.6\)](image)

Analytical data of the complexes (Table 3.1) show that all of them, except the diacetyl derivative, were obtained as the dihydrates, \(\text{Cu}_2(R,R')\text{L}(\text{ClO}_4)_2.2\text{H}_2\text{O}\). The diacetyl derivative was devoid of any water molecule. In the case with \(\text{Cu}_2(\text{Ph,Me})\text{L}'(\text{ClO}_4)_2.2\text{H}_2\text{O}\) two isomeric products in which the two methyl/phenyl groups are in syn \((3.7)\) and anti \((3.8)\) positions were expected. However, the products obtained by the methods I and II were identical, and TLC characterized them as an unique compound. We presume that in this compound the two substituents are in the anti position \((3.8)\).
### Table 3.1
Analytical data for the binuclear copper(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>color</th>
<th>% C calcd.</th>
<th>% C found</th>
<th>% H calcd.</th>
<th>% H found</th>
<th>% N calcd.</th>
<th>% N found</th>
<th>% Cu calcd.</th>
<th>% Cu found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂(H,H)L₁(ClO₄)₂.2H₂O</td>
<td>Bright-green</td>
<td>37.69</td>
<td>37.91</td>
<td>3.92</td>
<td>4.01</td>
<td>7.32</td>
<td>7.18</td>
<td>16.63</td>
<td>16.54</td>
</tr>
<tr>
<td>Cu₂(Me,Me)L₁(ClO₄)₂</td>
<td>Brown</td>
<td>42.85</td>
<td>43.16</td>
<td>4.34</td>
<td>4.56</td>
<td>7.14</td>
<td>7.35</td>
<td>15.49</td>
<td>15.62</td>
</tr>
<tr>
<td>Cu₂(Pr,Pr)L₁(ClO₄)₂.2H₂O</td>
<td>Dull-green</td>
<td>46.35</td>
<td>46.82</td>
<td>5.79</td>
<td>5.43</td>
<td>6.00</td>
<td>6.07</td>
<td>13.63</td>
<td>13.81</td>
</tr>
<tr>
<td>Cu₂(Ph,Ph)L₁(ClO₄)₂.2H₂O</td>
<td>Dull-green</td>
<td>53.93</td>
<td>53.82</td>
<td>4.30</td>
<td>4.11</td>
<td>5.24</td>
<td>5.42</td>
<td>11.89</td>
<td>12.01</td>
</tr>
<tr>
<td>Cu₂(Ph,Me)L₁(ClO₄)₂.2H₂O</td>
<td>Dull-green</td>
<td>48.30</td>
<td>48.54</td>
<td>4.44</td>
<td>4.31</td>
<td>5.93</td>
<td>6.13</td>
<td>13.46</td>
<td>13.32</td>
</tr>
</tbody>
</table>
The room temperature magnetic moments of these complexes are shown in Table 3.2. The moments vary from 0.4 to 0.8 $\mu_B$, that of $\text{Cu}_2(\text{Ph,Ph})L^1(\text{ClO}_4)_2\cdot2\text{H}_2\text{O}$ and $\text{Cu}_2(\text{Fr,Fr})L^1(\text{ClO}_4)_2\cdot2\text{H}_2\text{O}$ have the highest and lowest values, respectively. The results show strong antiferromagnetic interaction in these compounds. Determination of the coupling constants ($J$) in these and other binuclear copper(II) complexes described in this dissertation is one of the objectives of this laboratory. At this stage only for $\text{Cu}_2(\text{H,H})L^1\text{Cl}_2\cdot6\text{H}_2\text{O}$, 3.4, the $J$ value (-294 cm$^{-1}$) is known$^4$. It is not known whether the complexes $\text{Cu}_2(R,R')L^1(\text{ClO}_4)_2\cdot\text{nH}_2\text{O}$ have similar structure as 3.4. In any case since the room temperature magnetic moments of $\text{Cu}_2(R,R')L^1(\text{ClO}_4)_2\cdot2\text{H}_2\text{O}$ (0.4 to 0.8$\mu_B$) are comparable to
### Table 3.2

Infrared and electronic spectral data and magnetic moments for the binuclear copper(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>I.R data (^a/cm(^{-1})</th>
<th>UV-Visible (^b)</th>
<th>(\mu) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_2(\text{H,H})L_1) ((\text{ClO}_4))_2\cdot\text{H}_2\text{O} )</td>
<td>1635 (\tilde{\nu}(\text{C\ldots N})) 1610 (\tilde{\nu}(\text{phenyl \ ring})) 1565 (\tilde{\nu}(\text{C\ldots O}))</td>
<td>350(12,000), 600(90), (700\text{sh}(60))</td>
<td>0.74</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{Me,Me})L_1) ((\text{ClO}_4))_2 )</td>
<td>1590 (\tilde{\nu}(\text{phenyl \ ring})) 1610 (\tilde{\nu}(\text{phenyl \ ring})) 1545 (\tilde{\nu}(\text{C\ldots O}))</td>
<td>350(14,200), 580(170)</td>
<td>0.66</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{Pr,Pr})L_1) ((\text{ClO}_4))_2\cdot\text{H}_2\text{O} )</td>
<td>1580 (\tilde{\nu}(\text{phenyl \ ring})) 1610 (\tilde{\nu}(\text{phenyl \ ring})) 1540 (\tilde{\nu}(\text{C\ldots O}))</td>
<td>350(14,500), 590(170)</td>
<td>0.81</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{Ph,Ph})L_1) ((\text{ClO}_4))_2\cdot\text{H}_2\text{O} )</td>
<td>1590 (\tilde{\nu}(\text{phenyl \ ring})) 1610 (\tilde{\nu}(\text{phenyl \ ring})) 1550 (\tilde{\nu}(\text{C\ldots O}))</td>
<td>360(15,800), 580(165)</td>
<td>0.42</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{Ph,Me})L_1) ((\text{ClO}_4))_2\cdot\text{H}_2\text{O} )</td>
<td>1580 (\tilde{\nu}(\text{phenyl \ ring})) 1605 (\tilde{\nu}(\text{phenyl \ ring})) 1540 (\tilde{\nu}(\text{C\ldots O}))</td>
<td>355(14,200), 580(160)</td>
<td>0.70</td>
</tr>
</tbody>
</table>

\(^a\) All strong bands. \(^b\) In MeCN. \(^c\) At 298K.
that of Cu$_2$(H,H)L$^1$Cl$_2$·6H$_2$O (0.9 $\mu_B$). We believe that J values in the compounds will be $\gtrsim$ -290 cm$^{-1}$.

The electronic spectra of the complexes Cu$_2$(R,R')L$^1$ (ClO$_4$)$_2$·nH$_2$O are shown in Figure 3.1. In the UV region (Figure 3.1A) all of them have similar feature (Table 3.2), and show an intense absorption at about 350 nm ($\epsilon$, 10000-15000 M$^{-1}$cm$^{-1}$). This band is also observed in Zn$_2$(Ph,Ph)L$^1$(ClO$_4$)$_2$. 2H$_2$O ($\epsilon$, 8500 M$^{-1}$cm$^{-1}$) and is presumably due to an intra-ligand transition. However, higher molar absorptivity of the dicopper(II) complexes indicate that some charge transfer character is present in the copper complexes. In the visible region (Figure 3.1B) the diformyl complex differs somewhat from the others (Table 3.2). This compound shows a band of relatively weaker intensity at 600 nm and a shoulder at 700 nm, while the others have a broad absorption maximum at ca. 600 nm. The nature of d-d transition(s) in the complexes could not be ascertained from their electronic spectra.

Table 3.3 catalogs the infrared data of all of the copper(II) complexes. In Table 3.2 three strong bands observed in the range 1650 to 1500 cm$^{-1}$ have been compared. It may be noted that the $\nu$ C==N in Cu$_2$(H,H)L$^1$(ClO$_4$)$_2$.2H$_2$O appears at a considerably higher frequency (1635 cm$^{-1}$) relative to rest of the compounds (1585 cm$^{-1}$). The band observed at about 1550 cm$^{-1}$ has been assigned due to $\nu$ C==O. This vibration appears as a
Figure 3.1. Electronic spectra of the complexes $\text{Cu}_2\left(R, R\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$ in acetonitrile.

A: UV region; ---- $\text{Cu}_2\left(H, H\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 6.62x$10^{-5}$M; ---- $\text{Cu}_2\left(\text{Me, Me}\right)\text{L}^2\text{(ClO}_4\text{)}_2$ 4.68x$10^{-5}$M; ---- $\text{Cu}_2\left(\text{Pr, Pr}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 2.7x$10^{-5}$M; ---- $\text{Cu}_2\left(\text{Ph, Ph}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 4.12x$10^{-5}$M; ---- $\text{Cu}_2\left(\text{Ph, Me}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 3.55x$10^{-5}$M.

B: Visible region; ---- $\text{Cu}_2\left(H, H\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 1.65x$10^{-3}$M; ---- $\text{Cu}_2\left(\text{Me, Me}\right)\text{L}^2\text{(ClO}_4\text{)}_2$, 1.20x$10^{-3}$M; ---- $\text{Cu}_2\left(\text{Pr, Pr}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 6.76x$10^{-4}$M; ---- $\text{Cu}_2\left(\text{Ph, Ph}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 1.03x$10^{-4}$M; ---- $\text{Cu}_2\left(\text{Ph, Me}\right)\text{L}^2\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O}$, 8.90x$10^{-6}$.
Table 3.3

Infrared data of the complexes $\text{Cu}_2(R,R')L^1(\text{ClO}_4)_2.n\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Infrared frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{H, H})L^1\text{Cu}_2(\text{ClO}_4)_2.2\text{H}_2\text{O}$</td>
<td>3440(b), 2920(m), 2840(w), 1635(s), 1610(m), 1565(s), 1455(m), 1418(m), 1375(w), 1355(w), 1330(m), 1280(m), 1260(w), 1245(m), 1200(m), 1100(b), 975(w), 945(w), 880(w), 820(s), 865(s), 625(s), 565(w), 520(w), 490(w), 350(w).</td>
</tr>
<tr>
<td>$(\text{Me, Me})L^1\text{Cu}_2(\text{ClO}_4)_2$</td>
<td>3400(b), 2920(w), 2850(w), 1610(s), 1590(s), 1545(s), 1430(s), 1390(w), 1360(m), 1340(m), 1320(w), 1280(s), 1260(s), 1215(s), 1190(w), 1100(b), 1015(w), 980(w), 940(w), 885(m), 825(s), 775(m), 625(s), 545(m), 500(w), 390(w).</td>
</tr>
<tr>
<td>$(\text{Ph, Ph})L^1\text{Cu}_2(\text{ClO}_4)_2.2\text{H}_2\text{O}$</td>
<td>3440(b), 3050(w), 2930(w), 2860(w), 1610(s), 1580(s), 1545(s), 1490(m), 1445(s), 1435(s), 1420(s), 1385(w), 1375(w), 1350(s), 1330(m), 1280(s), 1250(s), 1230(s), 1180(m), 1100(b), 1015(m), 1000(m), 950(w), 930(w), 880(w), 850(w), 830(m), 800(m), 780(s), 715(s), 665(w), 625(s), 600(m), 545(w), 510(m).</td>
</tr>
</tbody>
</table>

contd..
<table>
<thead>
<tr>
<th>Compound</th>
<th>Infrared frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pr,Pr)L²Cu₂(ClO₄)₂.2H₂O</td>
<td>3440(b), 2950(s), 2920(s), 2860(s), 1610(s), 1580(s), 1540(s), 1485(w), 1460(w), 1440(m), 1435(s), 1410(s), 1380(w), 1340(m), 1270(s), 1250(s), 1210(w), 1180(s), 1140(s), 1100(b), 975(w), 925(w), 885(w), 870(w), 810(s), 770(m), 750(w), 680(w), 660(w), 620(s), 550(m), 490(m), 390(w), 300(w).</td>
</tr>
<tr>
<td>(Ph,Me)L²Cu₂(ClO₄)₂.2H₂O</td>
<td>3440(b), 3040(w), 2920(m), 2840(w), 1615(s), 1590(s), 1550(s), 1495(w), 1440(s), 1430(m), 1390(w), 1370(w), 1350(m), 1330(m), 1285(s), 1260(s), 1245(m), 1220(m), 1190(w), 1155(s), 1100(b), 1035(m), 945(w), 890(w), 860(w), 835(m), 800(w), 790(m), 730(s), 630(s), 585(w), 550(w), 510(m), 465(w), 400(w), 345(w), 320(w), 300(w), 270(w).</td>
</tr>
</tbody>
</table>
consequence of delocalization of the double bonds in the chelate rings that has increased the bond order of the phenolic C—O. This band was also observed in the complexes $\text{Cu}_2(R,R')L_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (see Chapter 2). When the C=N bonds in the complexes $\text{Cu}_2(R,R')L_1(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ are reduced no such band is observed (Chapter 6).

Electrochemistry

The cyclic voltammogram of $\text{Zn}_2(H,H)L_1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}_2(\text{Ph},\text{Ph})L_1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in DMF lacked waves at potentials positive of $-1.5V$ showing that the azomethine groups are reduced at more negative potentials. The voltammograms of the copper(II) complexes were carried out in an inert atmosphere using HMDE as the working electrode.

Figure 3.2 shows the cyclic voltammogram of $\text{Cu}_2(H,H)L_1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in DMF solution. When the scanning is made in the potential range $-0.4$ to $-1.3V$ (scan A), stepwise reduction of the dicopper(II) complex to $\text{Cu}^{II} - \text{Cu}^I$ and $\text{Cu}^I - \text{Cu}^I$ species occur. The first reduction step is almost reversible, but the second one is much less reversible in nature. If only the first couple is scanned in the potential range $-0.4$ to $-0.8V$, a highly symmetric voltammogram with the separation in peak potentials ($\Delta E_p$) of $65 \text{ mV}$ is obtained.
Fig. 3.2. Cyclic voltammograms of Cu$_2$(H$_2$)Cl$_3$(ClO$_4$)$_2$. 2H$_2$O in DMF (1.11x10$^{-3}$M).

A: Scanned in the potential range -0.6 to -1.3V at 50 mV/s.

B: Scanned in the potential range -0.4 to -0.8V at 50 mV/s.
The CV of $\text{Cu}_2(H,H)L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in acetonitrile solution is shown in Figure 3.3. The two reduction processes are seen in the cathodic sweep, but in the anodic sweep large consumption of current takes place at a potential where the wave due to the oxidation of $\text{Cu}^\text{I} - \text{Cu}^\text{I} \rightarrow \text{Cu}^\text{II} - \text{Cu}^\text{I}$ should have been observed. However, if the potential scan is reversed at $-0.8\text{V}$, a reversible voltammogram due to $\text{Cu}^\text{II} - \text{Cu}^\text{II} \rightarrow \text{Cu}^\text{II} - \text{Cu}^\text{I}$ is observed. Figure 3.4 shows that $\Delta E_p$ remains invariant (60 mV) with the variation of scan rates for $\text{Cu}_2(H,H)L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in the potential range $-0.3$ to $-0.75\text{ V}$.

The cyclic voltammogram of $\text{Cu}_2(\text{Ph,Me})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in acetonitrile in the potential range $-0.1$ to $-1.5\text{V}$ is shown in Figure 3.5. While the presence of the two redox-couples is evident, yet the abnormality in the potential range $-0.8$ to $-1.1\text{V}$ is noteworthy. On the other hand if the two couples are recorded separately, as shown in Figure 3.6, reversible voltammograms are obtained for each of the couples. In the scanings A and B of figure 3.6 the constancy of the reduction potentials of the two couples at different scanning rates are shown.

The CV of $\text{Cu}_2(\text{Me,Me})L^1(\text{ClO}_4)_2$ and $\text{Cu}_2(\text{Pr,Pr})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in acetonitrile in the full scan range are similar to that of $\text{Cu}_2(\text{Ph,Me})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$. Figures 3.7 and 3.8 show the voltammograms for each of the couples of $[\text{Cu}_2(\text{Me,Me})L]^+$ and $[\text{Cu}_2(\text{Pr,Pr})L]^+$, respectively, at different scan rates. In both
Figure 3.3. Cyclic voltammogram of Cu$_2$(H$_2$)H$_3$(ClO$_4$)$_2$·2H$_2$O in acetonitrile (1.83×10$^{-3}$ M) at 200 mV/s in the potential range -0.3 to -1.1 V.
Figure 3.4. Cyclic voltammogram of $\text{Cu}_2(\text{H}_2\text{HI})_4\text{L}^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in acetonitrile ($1.03\times10^{-3}\mu$) in the potential range $-0.3$ to $-0.75\text{V}$. Scan rates: $50\text{mV/s}$, $100\text{mV/s}$, $200\text{mV/s}$.
Figure 3.5. Cyclic voltammogram of Cu$_2$(Ph$_2$P)$_3$(S$_2$O$_4$)$_2$·2H$_2$O in acetonitrile (0.39±10$^{-4}$ M) at the scan rate of 100 mV/s.
Figure 3.6. Cyclic voltamograms of Cu\textsubscript{2}(H\textsubscript{2}O\textsubscript{2})\textsubscript{2}ClO\textsubscript{4}\textsubscript{2}.2H\textsubscript{2}O in acetonitrile (0.39x10\textsuperscript{-3}M, recorded for Cu\textsuperscript{II}-Cu\textsuperscript{II} \rightarrow Cu\textsuperscript{II} - Cu\textsuperscript{I} (A) and Cu\textsuperscript{II}-Cu\textsuperscript{I} \rightarrow Cu\textsuperscript{I}-Cu\textsuperscript{I} (B) reductions separately at different scan rates. --- 50mV/s; --- 100mV/s; --- 200mV/s; --- 500 mV/s.
Fig. 3-7. Cyclic voltammograms of Cu$_2$(Me$_2$Mo)$_4$Cl$_4$$_2$ in acetonitrile (0.68 x 10^{-3}M) at different scan rates. The two redox couples have been recorded separately (A and B). (1) 50, (2) 100, (3) 200, (4) 300, (5) 400 and (6) 500 mV/s.
Figure 3.8. Cyclic voltammograms of Cu$_2$(Pr,Pz)$_2$ClO$_4$·2H$_2$O in acetonitrile (0.20×10$^{-3}$M) at different scan rates. The two couples have been recorded separately (A and B). —— 50 mV/s; —— 100 mV/s; —— 200 mV/s; —— 500 mV/s
The full range cyclic voltammogram of Cu$_2$(Ph$_2$Ph)$_2$L(ClO$_4$)$_2$.2H$_2$O in acetonitrile is shown in Figure 3.9. In this case almost reversible voltammogram is obtained for both the couples. When the two reduction steps are recorded separately, as shown in Figure 3.10 at different scan rates, the reduction potentials for both the couples remain same as obtained from the full range voltammogram.

From these experiments it is clear that the electron transfer behavior of all five complexes in acetonitrile solutions are similar, that is, one-electron reductions occur at two different potentials for Cu$^{II}$-Cu$^{II}$ and the mixed-valent Cu$^{II}$-Cu$^{I}$ species. However, except for Cu$_2$(Ph$_2$Ph)$_2$L(ClO$_4$)$_2$.2H$_2$O, the voltammograms of the other compounds show complex behavior in the potential range -0.7 to -1.1V. No unusual behavior is observed at potentials more positive of -0.7V or more negative of -1.1V. The exact reason for such abnormality is not understood, precipitation of the reduced species, electrode poisoning, adsorption or secondary electrode reaction might be responsible for this. To avoid precipitation of the mixed-valent we have used fairly dilute solutions for voltammetric experiments. In
Figure 3.9. Full range cyclic voltammogram of $\text{Cu}_2(\text{Ph},\text{Ph})L^4(\text{Cl})\text{O}_4)_2.2\text{H}_2\text{O}$ in acetonitrile ($0.58 \times 10^{-3}$ M) at a scan rate of $50 \text{ mV/s}$.
Figure 3.10. Cyclic voltammograms of \text{Cu}_2\text{(Ph,Ph)TClO}_4\text{.2H}_2\text{O} in acetonitrile (0.58x10^{-3}M) at different scan rates. The two redox couples have been recorded separately (A and B).

--- 50mV/s; --- 100mV/s; --- 200mV/s.
any case except for $\text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ in all other cases highly satisfactory voltammograms for both the couples have been obtained by recording the voltammograms separately. For $\text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ the potentials of the second redox couple could not be determined in acetonitrile solution inspite of our best effort.

Voltammetric measurements have also been carried out for these compounds with their DMF solutions. Only in the case with $\text{Cu}_2(\text{H,H})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$, satisfactory voltammogram (Figure 3.3) has been obtained. For the remaining compounds the quality of the voltammograms was poor and therefore were not investigated further.

The electrochemical results summarized in Table 3.4 show that the $\Delta E_p$ values for both the couples are either 60 mV or slightly greater than this. The ratio of the cathodic and anodic peak currents ($I_p, c/I_p, a$) are almost equal to one. These are in accord with a Nernstian $n=1$ process. The reversible nature of these couples were verified by observing the constancy of $\Delta E_p = 60$ mV with the variation of scan rates. Moreover according to the relation (2.6) for a reversible electron transfer process a linear plot should be obtained for $i_p/c \sqrt{v}$ (where $i_p$ is the peak current, $c$ is the concentration of the reducible species and $v$ is the scan rate). Indeed strictly linear plots have been observed for the couples having $\Delta E_p = 60$ mV and the values of $i_p/c \sqrt{v}$ are shown in Table 3.5.
### Table 3.4

Electrochemical data for the complexes $\text{Cu}_2(R,R')L^1(\text{ClO}_4)_2\cdot n\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^\text{p}_\text{c}$</th>
<th>$E^\text{p}_\text{a}$</th>
<th>$E^\text{a}_1$</th>
<th>$\Delta E^\text{p}$</th>
<th>$I^\text{p,c}/I^\text{p,a}$</th>
<th>$E^\text{p}_\text{c}$</th>
<th>$E^\text{p}_\text{a}$</th>
<th>$E^\text{a}_2$</th>
<th>$\Delta E^\text{p}$</th>
<th>$I^\text{p,c}/I^\text{p,a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}_2(H,H)L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$^{a}$</td>
<td>-0.550</td>
<td>-0.480</td>
<td>-0.515</td>
<td>70</td>
<td>0.97</td>
<td>-0.905</td>
<td>-0.805</td>
<td>-0.855</td>
<td>100</td>
<td>0.92</td>
</tr>
<tr>
<td>$\text{Cu}_2(H,H)L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$^{d}$</td>
<td>-0.495</td>
<td>-0.435</td>
<td>-0.465</td>
<td>60</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cu}_2(\text{Me,Me})L^1(\text{ClO}_4)_2$^{d}$</td>
<td>-0.490</td>
<td>-0.430</td>
<td>-0.460</td>
<td>60</td>
<td>1.02</td>
<td>-1.262</td>
<td>-1.202</td>
<td>-1.232</td>
<td>60</td>
<td>0.98</td>
</tr>
<tr>
<td>$\text{Cu}_2(\text{Pr,Pr})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$^{d}$</td>
<td>-0.500</td>
<td>-0.440</td>
<td>-0.470</td>
<td>60</td>
<td>0.98</td>
<td>-1.280</td>
<td>-1.220</td>
<td>-1.250</td>
<td>60</td>
<td>1.04</td>
</tr>
<tr>
<td>$\text{Cu}_2(\text{Ph,Ph})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$^{d}$</td>
<td>-0.500</td>
<td>-0.435</td>
<td>-0.467</td>
<td>65</td>
<td>0.97</td>
<td>-1.045</td>
<td>-0.985</td>
<td>-1.015</td>
<td>60</td>
<td>0.99</td>
</tr>
<tr>
<td>$\text{Cu}_2(\text{Ph,Me})L^1(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$^{d}$</td>
<td>-0.510</td>
<td>-0.445</td>
<td>-0.478</td>
<td>65</td>
<td>1.02</td>
<td>-1.213</td>
<td>-1.153</td>
<td>-1.183</td>
<td>60</td>
<td>0.98</td>
</tr>
</tbody>
</table>

$^a E^\text{a}_1 = \frac{1}{2}(E^\text{p}_\text{c} + E^\text{p}_\text{a}).$  
$^b \Delta E^\text{p} = E^\text{p}_\text{c} - E^\text{p}_\text{a}. $  
$^c \text{DMF solution.}$  
$^d \text{Acetonitrile solution.}$
### Table 3.5

Electrochemical data for the complexes Cu\(_2\)(R,R')\(L^1\)(ClO\(_4\))\(_2\)\(\cdot\)nH\(_2\)O

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{Cu}^{II}\rightarrow\text{Cu}^{II}) e(-\rightarrow\text{Cu}^{II}\rightarrow\text{Cu}^{I})</th>
<th>(\text{Cu}^{II}\rightarrow\text{Cu}^{I}) e(-\rightarrow\text{Cu}^{I}\rightarrow\text{Cu}^{I})</th>
<th>(E_1 - E_2)</th>
<th>(K_{\text{con}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_2(R,R')L^1(ClO_4)_2\cdot nH_2O)</td>
<td>(&lt; E_1), (E_p = 70\text{ mV}^c)</td>
<td>(&lt; E_2), (E_p = 100\text{ mV}^c)</td>
<td>0.340</td>
<td>5.6 (\times 10^5)</td>
</tr>
<tr>
<td>(\text{Cu}_2(H,H)L^1(ClO_4)_2\cdot 2H_2O)</td>
<td>(-0.515)</td>
<td>(-0.855^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Cu}_2(Me,Me)L^1(ClO_4)_2)</td>
<td>(-0.460)</td>
<td>14.0 ± 0.3</td>
<td>(-1.232)</td>
<td>14.0 ± 0.1</td>
</tr>
<tr>
<td>(\text{Cu}_2(Pr,Pr)L^1(ClO_4)_2\cdot 2H_2O)</td>
<td>(-0.470)</td>
<td>13.5 ± 0.2</td>
<td>(-1.250)</td>
<td>14.5 ± 0.5</td>
</tr>
<tr>
<td>(\text{Cu}_2(Ph,Ph)L^1(ClO_4)_2\cdot 2H_2O)</td>
<td>(-0.467)</td>
<td>(E_p = 65\text{ mV}^c)</td>
<td>(-1.015)</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>(\text{Cu}_2(Ph,Me)L^1(ClO_4)_2\cdot 2H_2O)</td>
<td>(-0.478)</td>
<td>(E_p = 65\text{ mV}^c)</td>
<td>(-1.183)</td>
<td>9.6 ± 0.4</td>
</tr>
</tbody>
</table>

\(^a\) For fully reversible electron-transfer. \(^b\) DMF solution. \(^c\) Quasireversible. 
\(^d\) Acetonitrile solution.
The complexes described in this chapter and those in
the preceding chapter represent two series of compounds having
the chromophores $\text{Cu}_2\text{N}_4\text{O}_2$ and $\text{Cu}_2\text{O}_6$, respectively, in which the
magnetic moments have varied with the change of substituents.
It would be reasonable therefore to ask if there is any corre­
lation between the magnetic properties and electron transfer
behavior in binuclear complexes. No detailed correlation has
yet been obtained due to the paucity of data. However, two
qualitative relations\textsuperscript{10,11} that have been proposed recently may
be tested in the light of our observations. Before this is done
it would be appropriate to discuss these two models.

Model I. Hendrickson et al.\textsuperscript{11} have proposed a qualitative
relation between the magnitude of ground state magnetic exchange
interaction and separation between the two one-electron reduction
waves for binuclear copper(II) complexes. For the d\textsuperscript{9} case,
where the unpaired electron occupies a $d_{x^2-y^2}$ orbital, two
molecular orbitals will form from linear combination of these
two orbitals.

\[
\begin{array}{c}
\text{Metal A} \\
\Phi_2 \\
\Phi_1 \\
\text{Dimer} \\
x^2-y^2 \\
x^2-y^2 \\
\text{Metal B}
\end{array}
\]
\[ \Phi_1 \sim a \ x^2 - y^2 + b \ x^2 - y^2 \]
\[ \Phi_2 \sim a \ x^2 - y^2 - b \ x^2 - y^2 \]

The following many electron configurations arise from these orbitals

\[ \uparrow - \uparrow \downarrow \quad \uparrow \quad \Phi_2 \]
\[ \downarrow \uparrow \quad \downarrow \quad \downarrow \quad \Phi_1 \]

Hoffman et al.\(^{12}\) have shown that \(\xi_1\) and \(\xi_2\), the energies of the two orbitals \(\Phi_1\) and \(\Phi_2\), respectively, are related to the exchange parameter, \(J\), by the relation

\[ E_T - E_S = -2J = -2 K_{ab} + \frac{(\xi_1 - \xi_2)}{J_{aa} - J_{ab}} \]

In this expression, \(J_{ij}\) and \(K_{ij}\) are Coulomb and exchange integrals, respectively. From the above expression it is seen that binuclear complex with the greater antiferromagnetic interaction has the larger \((\xi_1 - \xi_2)\) difference.
Hendrickson et al.\textsuperscript{10} have assumed that in the case of a moderately strong ($J < -300 \text{ cm}^{-1}$) antiferromagnetic interaction there is only a negligible population of the triplet state, and therefore the first electron taken up in the electrode reduction will go into the empty $\phi_2$ orbital. As the orbital $\phi_2$ is displaced to higher energies with increasing ($\epsilon_1 - \epsilon_2$) energy difference, the first reduction wave will occur at a lower potential. This means that the binuclear complex with the greatest antiferromagnetic interaction should have the lowest potential first reduction wave. The addition of the second electron would also occur at the $\phi_2$ orbitals, but the potential for the uptake of the second electron would be different because of electron-electron repulsion. Again this electron-electron repulsion would be greatest with the complex having the greatest antiferromagnetic interaction. In essence, this model proposes that electron transfers occur to the singlet copper(II) and stronger is the antiferromagnetic interaction lower will be the potentials for both the waves.

Model II. According to Gagne et al. in a singlet-triplet system each spin state $S$ have an associated reduction potential $S \Delta E$, and since the singlet represents the more stable ground state, it will have a more negative reduction potential than for the triplet. They then compared the observed potential for the first reduction step of $[\text{Cu}_2(\text{H,H})^+]^{2+}$ having the value of
$J = -293 \text{ cm}^{-1}$ with the calculated redox potential for a hypothetical case when $J=0$. The potential, $E$, for $J = 0$ was calculated from the observed potential, $E_{\text{obsd}} = -0.925 \text{V (vs Fc/Fc}^+)$, and the singlet-triplet separation energy, $^3E - ^1E = 586 \text{ cm}^{-1} = 73 \text{ mV}$. It was assumed that the distribution of spin states at the electrode was constant, and as the triplet ion is reduced, its depleted concentration at the electrode surface is replenished rapidly to maintain spin-state equilibrium. The triplet reduction potential, $^3E$, was calculated from the Nernst equation

$$E_{\text{obsd}} = \frac{3E}{nF} \ln \frac{[3(Cu^{II} - Cu^{II})^{2+}]}{[Cu^{II} - Cu^{I}]}$$

Since $[3(Cu^{II} - Cu^{II})^{2+}]$ is 15% of the total $[Cu^{II} - Cu^{II}]^{2+}$ as obtained from the Boltzmann distribution, therefore, $^3E = -0.876 \text{ V}$, and hence, $^1E = -0.949 \text{ V}$. It can be shown that when $J \rightarrow 0$, as a consequence of the degeneracy in the triplet state, these potentials converge to a value three quarters of the way toward the singlet at $-0.931 \text{ V}$. Thus the difference in the values of potentials observed for $J = -294 \text{ cm}^{-1}$ and calculated for $J = 0$ is only 6 mV. Although not explicitly stated, this model would suggest that in closely related binuclear complexes, the potentials for the addition of the first electron would be independent of the antiferromagnetic interaction.
Table 3.2 shows that the room temperature magnetic moments of the complexes, Cu$_2$(R,R')L$^1$(ClO$_4$)$_2$.2nH$_2$O, have varied considerably (0.4 to 0.8$\mu_B$). The exchange parameters of these complexes are expected to be $\gtrsim -290$ cm$^{-1}$. From Table 3.4 it may be noted that the potentials of the first couple, $E_1$, remain practically invariant ($\simeq -0.47$V) throughout the series. In the case with Cu$_2$(R,R')L(ClO$_4$)$_2$.2H$_2$O also we have found that the redox potentials remain unchanged ($\simeq -0.05$V) albeit the room temperature magnetic moments of these compounds have varied. These observations are consistent with the model II, that is, the triplet copper(II) ion undergoes electrode reduction, and therefore, $E_1$ is independent of the magnitude of $J$.

Since the magnitude of the singlet-triplet separation energy in Cu$^{II}$-Cu$^{II}$ complex has no influence on the energy level of its reduced form, that is, the Cu$^{II}$-Cu$^{+}$ species, therefore, the addition of the second electron should be also independent of $J$. The second electron transfer will be more difficult due to electrostatic reason, and the potential for the addition of the second electron will depend on the nature of the substituents present. Qualitatively, the electron-releasing substituents will shift the potential to a more negative value. This is shown in a plot of Hammet $\sum \sigma_m$ values$^{13}$ against $E_2$ (Figure 3.11). A fairly good linear fit indicates that the electron density on the ligand is transmitted directly to the metal ion.
Figure 3.11. A plot of Hammet \( \sigma_m \) vs \( E_{1/2}^{(2)} \) for the complexes \( \text{Cu}_2(R,R')L^1(C\text{lo}_4)_2\cdot n\text{H}_2\text{O} \).
The conproportionation constant, \( K_{\text{con}} \), for the complexes have been obtained from the following relations

\[
\begin{align*}
\text{Cu}^{\text{II}} - \text{Cu}^{\text{II}} + e^- & \xrightleftharpoons[\text{Cu}^{\text{II}} - \text{Cu}^{\text{I}}]{E_1} \text{Cu}^{\text{II}} - \text{Cu}^{\text{I}} \\
\text{Cu}^{\text{II}} - \text{Cu}^{\text{I}} + e^- & \xrightleftharpoons[\text{Cu}^{\text{I}} - \text{Cu}^{\text{I}}]{E_2} \text{Cu}^{\text{I}} - \text{Cu}^{\text{I}} \\
\text{Cu}^{\text{II}} - \text{Cu}^{\text{II}} + \text{Cu}^{\text{I}} - \text{Cu}^{\text{I}} \xrightarrow[K_{\text{con}}]{ } 2 \text{Cu}^{\text{II}} - \text{Cu}^{\text{I}} 
\end{align*}
\]

\[
K_{\text{con}} = \frac{[\text{Cu}^{\text{II}} - \text{Cu}^{\text{I}}]^2}{[\text{Cu}^{\text{II}} - \text{Cu}^{\text{II}}][\text{Cu}^{\text{I}} - \text{Cu}^{\text{I}}]}
\]

\[
= \exp(nF \Delta E/RT)
\]

where \( \Delta E = E_1 - E_2 \)

Thus a greater value of \( \Delta E \) would indicate greater stability of the mixed-valent species, \( \text{Cu}^{\text{II}} - \text{Cu}^{\text{I}} \), with respect to disproportionation. The values of \( \Delta E \) and \( K_{\text{con}} \) for all of the complexes shown in Table 3.5 reveal that in acetonitrile the mixed-valent complexes, \( \left[ \text{Cu}^{\text{II}} \text{Cu}^{\text{I}}(R, R')L \right]^+ \) are more stable relative to \( \left[ \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(H, H)L \right]^+ \) in DMP.

Some discussion can be made at this stage about the odd-electron delocalization behavior in the mixed-valent complexes. According to the classification made by Robin and Day\(^{14}\) these would belong either to the class I or II, that is, either both
the copper atoms are in sites of different symmetries and valence electrons are trapped, or they have nearly identical symmetry and the electron is delocalized between the two metal centers. The class I Cu$^{II}$-Cu$^{I}$ compounds are characterized by the lack of intervalence transfer (IT) transition and by four line EPR spectra, whereas in the class II compounds one or more IT bands and seven-line hyperfine splitting in EPR spectra are expected. 

Cu$^{II}$Cu$^{I}$(H,H)L$^+$ in a noncoordinating solvent like dichloromethane exhibited a seven-line EPR spectrum at room temperature that reverted to a four-line one at 200K. The electronic spectrum of this solution showed three strong absorptions at 600, 1175 and 1725 nm. However, the dichloromethane solution of Cu$^{II}$Cu$^{I}$(CO)(H,H)L$^+$, obtained by passing carbon monoxide through the solution Cu$^{II}$Cu$^{I}$(H,H)L$^+$, gave a four-line EPR spectrum at the ambient and low temperatures, and the electronic spectrum showed the presence of a single band at 600 nm. The greater conproportionation constant of 

Cu$^{II}$Cu$^{I}$(CO)(H,H)L$^+$ (1.9 x 10$^8$) relative to that of Cu$^{II}$Cu$^{I}$(H,H)L$^+$, both determined with the DMF solutions, indicates that the species Cu$^{II}$Cu$^{I}$(CO)(H,H)L$^+$ belong to the class I. The greater stability of this species is a consequence of more compatible steric environment for copper(I), that is, square pyramidal. It appears that in dichloromethane Cu$^{II}$Cu$^{I}$(H,H)L$^+$ is stereochemically nonrigid and probably there is an equilibrium of the type
\[\text{Cu(planar)-Cu(planar)L}^+ \rightleftharpoons \text{Cu(planar)-Cu(apically distorted planar)L}^+\]

Class II \hspace{2cm} Class I

The equilibrium shifts more to the right with the decrease of temperature. The thermal electron transfer, \(E_{\text{th}}\), has been estimated to be \(1.7 \times 10^{10} \text{s}^{-1}\) at 298K for the dichloromethane solution. This value indicates a relatively slow rate and may be due to a large conformal change. X-ray structure analysis of \([\text{Cu}^{II}\text{Cu}^{I}(\text{H,H})\text{L}]\text{ClO}_4\cdot0.5\text{CH}_3\text{OH}\) showed that the coordination about the copper(II), Cu1, is square planar; the second metal atom, i.e. copper(I), is disordered with 35% in the Cu2a site and 65% in the Cu2b site. In the Cu2b site, copper(I) is approximately planar, but the Cu2a is displaced 0.65 Å from the \(\text{N}_2\text{O}_2\) donor plane towards the aromatic ring of the adjacent molecule with an overall square pyramidal geometry. It should be mentioned that the molecular structure provides no evidence of thermal electron transfer in the solid state. The class II behavior at \(T < 200K\) in solution may be due to one of the conformational forms, viz. Cu1-Cu 2b.

We now turn our attention to the situation that prevails in the acetonitrile solutions of \([\text{Cu}^{II}\text{Cu}^{I}(\text{R,R'})\text{L}]^+\). We have observed a single absorption band for \([\text{Cu}^{II}\text{Cu}^{I}(\text{Me,Me})\text{L}]^+\) and \([\text{Cu}^{II}\text{Cu}^{I}(\text{Pr,Pr})\text{L}]^+\) at about 600 nm, so also was reported by
Gagne et al.\textsuperscript{5} for \([\text{Cu}^{II}\text{Cu}^{I}(H,H)L]^{+}\). Addison\textsuperscript{7} reported a four-line EPR spectrum for an acetonitrile solution of \([\text{Cu}^{II}\text{Cu}^{I}(\text{Me,Me})L]^{+}\) at room temperature. The values of $K_{\text{on}}$ for all these compounds in acetonitrile, except for the diformyl derivative for which the data is lacking, are significantly greater relative to that of \([\text{Cu}^{II}\text{Cu}^{I}(H,H)L]^{+}\) in DMF (see Table 3.4). Inasmuch as acetonitrile is a strong donor for copper(I) it is reasonable to assume that the copper(I) ion in the mixed-valent complexes gets solvated and acquires a square-pyramidal geometry. The net effect is the formation of class I compounds. We believe that the acetonitrile solutions of all mixed-valent copper complexes reported here, including the diformyl derivative, should exhibit four-line EPR spectra from low temperatures to the ambient temperature. Due to the lack of experimental facilities we at present are unable to verify this.

CONCLUSION

The present study was aimed at studying the relation between the redox potentials and the exchange magnetic interactions in the d1copper(II) complexes. Another objective was to stabilize the mixed-valent, Cu(II)-Cu(I) complexes by variation of the substituents. From the observations made we conclude
that the first electron-transfer occurs at the triplet state and the redox potentials are independent of singlet-triplet separation energies. Varying degree of stabilization of the mixed-valent species are brought about by electron releasing/withdrawing substituents; the most stable species can be obtained by using a electron-releasing substituent, conversely, a strong electron-withdrawing substituent will lead to destabilization of the mixed-valent species. Another conclusion that has been drawn is the lack of electron delocalization between the metal centers of mixed-valent species in a coordinating solvent like acetonitrile.
REFERENCES


