CHAPTER V

Trinuclear Copper(II) Complexes
Study of polynuclear Copper(II) complexes with more than two Copper(II) centres has also invited attention of the chemists, because such complexes provide synthetic models close to multinuclear biochemical systems. Polynuclear complexes are also known to be better industrial catalysts.

Detailed investigations of synthesis and characterization of series of trinuclear complexes of the type

\[
[M(TSB)\cdot M\cdot M(TSB)](ClO_4)_2, \text{ where } M = \text{Cu(II), Ni(II), Co(II), Fe(II) and Mn(II)},
\]

have been carried out by Sinn and coworkers.\textsuperscript{109–113} In these complexes, all the three metal ions are linked by oxygen bridges. It has been observed that for each grouping of metals, the observed magnetic moments are subnormal and decreases remarkably with decrease in temperature. These magnetic properties have been explained in terms of antiferromagnetic interactions between the central metal ion and the adjacent Copper(II) ions.

Antiferromagnetic interactions in discrete trinuclear complexes were first studied by Kambe,\textsuperscript{154} and he proposed that the magnetic properties of a group of trinuclear acetate compound of Fe(III) and Cr(III)\textsuperscript{155} could be explained in terms of spin spin interactions, the strength of the interaction being the same between each pair of atoms in the group of three. In all these cases, antiferromagnetic interaction takes place through one bridging atom.
Very recently Hatfield and coworkers\textsuperscript{156,157} reported a long range exchange interaction between two Copper(II) centres bridged by pyrazine ligands. Such long range spin spin interaction are also known to occur in the binuclear complexes of Copper(II), where two Copper centres are linked through a long bridge of imidazole.\textsuperscript{158} The magnetic properties of binuclear Copper(II) and Vanadyl(II) complexes have also been studied, where magnetic interaction is propagated through an extensive organic system, 1,2,4,5-tetraminobenzene.\textsuperscript{159}

Hence, in the present investigation, it was thought worthwhile to see if two Copper(II) complexes with a free coordinating site, can be made to combine with a third Copper(II) centre and to see the possibility of long range spin spin interaction through the aromatic rings.

Formation constant of the ternary complex, $[\text{CuA}_1^1L]$, where $A^1 = 2,2'$-bipyridyl and $L = 3,4$-dihydroxybenzaldehyde has been studied\textsuperscript{160} in solution. It has been observed that only hydroxy part of $L$ takes part in coordination and $-\text{CHO}$ group remains uncoordinated. It was thought possible that the two $-\text{CHO}$ groups may coordinate with another Copper(II) centre in non-aqueous solvent. Therefore, the complex $[\text{CuA}_1^1L]$ was isolated and was further treated with $\text{CuCl}_2\cdot2\text{H}_2\text{O}$ or $[\text{Cu(A-A)}]^{2+}$ to prepare trinuclear complexes
\[(\text{CuA}^1\text{L})_2 \cdot \text{CuCl}_2\] and \[(\text{CuA}^1\text{L})_2 \cdot \text{Cu(A-A)} \] (\text{ClO}_4)^2, \text{ where A-A is 2,2'-bipyridyl (A}^1\text{), 1,10-phenanthroline (A}^2\text{) or 2-(2'-pyridyl)benzimidazole (A}^3\text{).}

**EXPERIMENTAL**

**Material**

Analytical Reagent grade chemicals (> 99.9 % purity) were used for all the preparations. Cu(ClO\(_4\))\(_2\) \cdot 6\text{H}_2\text{O} was prepared by the method discussed in Chapter II. 2-(2'-pyridyl)benzimidazole was prepared by the method suggested in literature.\(^{125}\)

**Preparation of Mixed Ligand Complex \([\text{CuA}^1\text{L}]\)**

To an aqueous solution of CuCl\(_2\) \cdot 2\text{H}_2\text{O} (1 mol in 50 ml), an equimolar mixture of A\(^1\) (1 mol, 20 ml) and L (1 mol, 20 ml) in ethanol was added with constant stirring. The pH of the solution was then raised to 5.0 - 5.6 by the addition of aqueous ammonia solution and digested on a water bath for about two hours. Resulting solid was filtered, washed thoroughly with water - alcohol (1 : 1) mixture and dried in vacuum.

**Preparation of Trinuclear Complex \([\text{CuA}^1\text{L}]_2 \cdot \text{CuCl}_2\]**

To a solution of \([\text{CuA}^1\text{L}]\) (2 mol in 50 ml absolute
ethanol) was added a solution of \( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \) (1 mol in 20 ml absolute ethanol). pH of the reaction mixture was raised to 7 by adding liq. ammonia and refluxed for about three hours with constant stirring. Resulting solid was filtered, washed thoroughly with absolute ethanol and dried in vacuum.

**Preparation Of Trinuclear Complexes**

\[
\left[ (\text{Cu}^{1\text{L}})_2 \cdot \text{Cu}(\text{A-A}) \right] (\text{ClO}_4)_2
\]

A suspension of \( \left[ \text{Cu}(\text{A-A})(\text{ClO}_4)_2 \right] \) was prepared by adding \( \text{(A-A)} \) (0.1 mol in 10 ml absolute ethanol) to a solution of \( \text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \) (0.1 mol in 10 ml absolute ethanol). The resulting suspension was then added to \( \left[ \text{Cu}^{1\text{L}} \right] \) (0.2 mol) dissolved in 50 ml absolute ethanol. The pH of the reaction mixture was raised by the addition of liq. ammonia to a value of 7. The reaction mixture was then refluxed for four hours. Resulting solid was filtered, washed thoroughly with absolute ethanol and dried in vacuum.

The different complexes prepared were characterized by elemental analyses for Nitrogen and Copper, T.L.C., magnetic susceptibility measurements and IR, Reflectance and UV Visible spectral studies. The details of the techniques employed are the same as described in Chapter II.
### Table V1: Analytical and Magnetic Data of Mono- and Tri- Nuclear Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Analyses % *</th>
<th>(\mu_{\text{eff}}/\text{Cu(II) ion} ) in B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu}^1\text{L}])</td>
<td>Brown</td>
<td>17.56 (17.87)</td>
<td>7.41 (7.88)</td>
</tr>
<tr>
<td>([\text{Cu}^1\text{L}]_2 \cdot \text{CuCl}_2)</td>
<td>Brown</td>
<td>22.81 (22.65)</td>
<td>7.19 (6.65)</td>
</tr>
<tr>
<td>([\text{Cu}^1\text{L}]_2 \cdot \text{Cu}(\text{A}^1)) (\text{ClO}_4)_2</td>
<td>Olive green</td>
<td>16.53 (16.87)</td>
<td>7.52 (7.44)</td>
</tr>
<tr>
<td>([\text{Cu}^1\text{L}]_2 \cdot \text{Cu}(\text{A}^2)) (\text{ClO}_4)_2</td>
<td>Olive green</td>
<td>16.86 (16.52)</td>
<td>7.53 (7.28)</td>
</tr>
<tr>
<td>([\text{Cu}^1\text{L}]_2 \cdot \text{Cu}(\text{A}^3)) (\text{ClO}_4)_2</td>
<td>Olive green</td>
<td>16.67 (16.31)</td>
<td>7.92 (7.92)</td>
</tr>
</tbody>
</table>

* Calculated values are given in parentheses
**Table V 2: Infrared Spectra (cm\(^{-1}\)) of L, \([\text{Cu}^1\text{L}]\) and Trinuclear Complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4-dihydroxybenzaldehyde (L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 320 (s), 3 220 (s), 3 050 (w), 2 880 (w),</td>
</tr>
<tr>
<td></td>
<td>1 645 (s), 1 590 (s), 1 530 (s), 1 470 (m),</td>
</tr>
<tr>
<td></td>
<td>1 440 (s), 1 420 (m), 1 380 (s), 1 290 (s),</td>
</tr>
<tr>
<td></td>
<td>1 270 (m), 1 240 (w), 1 190 (s), 1 165 (s),</td>
</tr>
<tr>
<td></td>
<td>1 120 (s), 970 (s), 940 (w), 875 (s), 750 (s),</td>
</tr>
<tr>
<td></td>
<td>630 (s), 600 (m),</td>
</tr>
<tr>
<td>([\text{Cu}^1\text{L}])</td>
<td>3 120 (w), 3 040 (s), 2 830 (w), 1 650 (s),</td>
</tr>
<tr>
<td></td>
<td>1 610 (s), 1 600 (w), 1 565 (s), 1 545 (s),</td>
</tr>
<tr>
<td></td>
<td>1 480 (s), 1 450 (s), 1 430 (s), 1 330 (w),</td>
</tr>
<tr>
<td></td>
<td>1 290 (s), 1 260 (s), 1 210 (s), 1 180 (m),</td>
</tr>
<tr>
<td></td>
<td>1 170 (s), 1 115 (s), 1 055 (m), 1 035 (m),</td>
</tr>
<tr>
<td></td>
<td>970 (w), 955 (w), 870 (m), 810 (s), 770 (s),</td>
</tr>
<tr>
<td></td>
<td>760 (s), 730 (s), 660 (s), 645 (s), 615 (s)</td>
</tr>
</tbody>
</table>
|                                               | cont...
\[
\begin{align*}
\text{[CuA}^1\text{L}_2 \cdot \text{CuCl}_2] & \quad 3\ 120\ (w),\ 3\ 030\ (m),\ 2\ 900\ (w),\ 1\ 655\ (s), \\
& \quad 1\ 600\ (w),\ 1\ 570\ (s),\ 1\ 510\ (s),\ 1\ 480\ (s), \\
& \quad 1\ 455\ (m),\ 1\ 350\ (m),\ 1\ 310\ (w),\ 1\ 280\ (m), \\
& \quad 1\ 250\ (m),\ 1\ 210\ (m),\ 1\ 190\ (s),\ 1\ 150\ (m), \\
& \quad 1\ 080\ (m),\ 1\ 045\ (m),\ 980\ (w),\ 950\ (w), \\
& \quad 880\ (m),\ 820\ (m),\ 770\ (s),\ 750\ (s), \\
& \quad 650\ (s),\ 620\ (s)
\end{align*}
\]

\[
\begin{align*}
\text{[CuA}^1\text{L}_2 \cdot \text{Cu(A}^1\text{)\ (ClO}_4\text{)}_2] & \quad 3\ 400\ (b),\ 3\ 040\ (w),\ 1\ 635\ (m),\ 1\ 600\ (w), \\
& \quad 1\ 570\ (m),\ 1\ 490\ (s),\ 1\ 470\ (w),\ 1\ 445\ (s), \\
& \quad 1\ 380\ (w),\ 1\ 330\ (m),\ 1\ 300\ (s),\ 1\ 265\ (m), \\
& \quad 1\ 240\ (w),\ 1\ 220\ (m),\ 1\ 150\ (m),\ 1\ 120\ (s), \\
& \quad 1\ 100\ (s),\ 1\ 090\ (s),\ 1\ 035\ (w),\ 1\ 000\ (w), \\
& \quad 980\ (w),\ 940\ (w),\ 890\ (w),\ 850\ (w), \\
& \quad 770\ (s),\ 730\ (m),\ 640\ (m),\ 625\ (s)
\end{align*}
\]
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reflectance Spectra (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CuA(^1)L]</td>
<td>26 320, 20 000, 12 900</td>
</tr>
<tr>
<td>[(CuA(^1)L)(_2)•CuCl(_2)]</td>
<td>27 030, 22 730, 13 900 - 11 900 (broad band)</td>
</tr>
<tr>
<td>[(CuA(^1)L)(_2)•Cu(A(^1))] (ClO(_4))(_2)</td>
<td>27 030 (sh), 22 730, 13 900 - 12 200 (broad band)</td>
</tr>
<tr>
<td>[(CuA(^1)L)(_2)•Cu(A(^2))] (ClO(_4))(_2)</td>
<td>27 780 (sh), 25 000, 14 810 - 12 500 (broad band)</td>
</tr>
<tr>
<td>[(CuA(^1)L)(_2)•Cu(A(^3))] (ClO(_4))(_2)</td>
<td>27 780 (sh), 24 390, 14 810 - 12 120 (broad band)</td>
</tr>
</tbody>
</table>
Table V 4 : Electronic Spectra (cm$^{-1}$) of Ligands, Mixed Ligand Complex and its Trinuclear Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic Spectra (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'3,4-dihydroxybenzaldehyde : L)</td>
<td>42 750, 35 500, 31 600, 24 500</td>
</tr>
<tr>
<td>2,2'-Bipyridyl (A$^1$)</td>
<td>44 330, 41 170, 36 170, 24 800</td>
</tr>
<tr>
<td>[CuA$^1$L]</td>
<td>45 000 (sh), 39 000, 33 000, 32 000, 28 000</td>
</tr>
<tr>
<td>[(CuA$^1$L)$_2$.CuCl$_2$]</td>
<td>39 750, 33 200, 32 000, 28 250</td>
</tr>
<tr>
<td>[(CuA$^1$L)$_2$.Cu(A$^1$)] (ClO$_4$)$_2$</td>
<td>40 000, 33 250, 32 000, 28 250</td>
</tr>
</tbody>
</table>
Figure V 1
RESULTS AND DISCUSSION

Elemental analysis of the mixed ligand complex corresponds with the expected formula (Table V 1). The structure of the mixed ligand complex can be represented as shown in Figure V 1.

T.L.C. of above complex showed a single dot indicating purity of the complex.

IR spectrum of the complex, [CuL1A^2], (Table V 2) shows a band at 1650 cm\(^{-1}\) corresponding to \(\text{C} = \text{O}\) stretching, indicating that the carbonyl oxygen does not take part in coordination. The \(\text{O}=\text{H}\) band of 3,4-dihydroxy benzaldehyde (L) around 3400 cm\(^{-1}\) disappears, in mixed ligand complex, indicating dissociation of proton on coordination. The bands in the range 900 cm\(^{-1}\) and below may be due to out of plane bending vibration of C-H bond. The bands corresponding to M-O and M-N stretching occur at lower frequencies and hence could not be observed.

The visible absorption spectrum of [CuL1A^2] shows a broad band at \(\sim 625\) nm. This shows that the complex is square planar in nature.

The magnetic moment of the complex, [CuL1A^2], is 1.82 B.M., corresponding to spin only value of one unpaired electron.
A - A = A₁, A₂ or A₃

Figure V 3

Figure V 2

(CIO₄)²⁻
Though the complex was prepared by raising the pH with liq. ammonia, condensation of ammonia does not take place with aldehydic group. This was further confirmed from the IR spectrum of the complex. Absence of bands due to $\sim \text{C}=\text{N}$ and $\sim \text{N}-\text{H}$ group stretching frequencies indicate that schiff base formation does not take place.

This mixed ligand complex, $[\text{CuA}^1 \text{L}]$, has a potential coordinating $-\text{CHO}$ site. The free $-\text{CHO}$ groups of the two molecules of the mixed ligand complex, $[\text{CuA}^1 \text{L}]$, get coordinated with $\text{CuCl}_2$ or $[\text{Cu}(\text{A-A})]^{2+}$, resulting in the formation of the trinuclear complex (Figures V 2 and V 3).

Elemental analyses corresponds to the expected formulae (Table V 1). T.L.C. of these complexes in chloroform + methanol (1 : 1) showed a single dot, confirming their purity. Molar conductance could not be determined for these complexes due to their insufficient solubility. The presence of perchlorate in the outer sphere was confirmed from their IR spectra (Table V 2). No significant difference in IR spectral bands of the $[\text{CuA}^1 \text{L}]$ part occurs on coordination with $\text{CuCl}_2$ or $[\text{Cu}(\text{A-A})]^{2+}$ in the trinuclear complex.

Ligand field spectrum of $[\text{CuA}^1 \text{L}]$ complex (Table V 3) shows a d-d band at 12 900 cm$^{-1}$ and two charge transfer bands
at 26 320 cm\(^{-1}\) and 23 000 cm\(^{-1}\). Trinuclear complex 
\([(\text{CuA}^1\text{L})_2\text{CuCl}_2]\) shows a broad d-d band in the region 
13 200 - 11 900 cm\(^{-1}\) and charge transfer bands at 
27 030 cm\(^{-1}\) and 22 370 cm\(^{-1}\). Broadening of d-d band takes 
place due to the additional central Copper(II) ion, 
coordinated to two \(-\text{CHO}\) groups and two chlorides absorbing 
at a lower field than the two \([\text{CuA}^1\text{L}]\) centres. Similarly, 
the trinuclear complexes \([(\text{CuA}^1\text{L})_2\text{Cu(A-A)}]\) \((\text{ClO}_4)_2\) show 
charge transfer bands at 27 030 cm\(^{-1}\) and 22 370 cm\(^{-1}\) and a 
broad d-d band in the region 13 900 - 12 200 cm\(^{-1}\) due to the 
additional Copper(II) ion, coordinated to two \(-\text{CHO}\) groups 
and a tertiary diamine molecule.

Room temperature magnetic susceptibility measurements 
(Table V 1) show that \(\mu_{\text{eff}}\) per Copper(II) is less than 
that expected for one unpaired electron over each Copper(II) 
ion. This is obviously due to the antiferromagnetic 
interaction between Copper(II) centres. However, the mixed 
ligand complex \([\text{CuA}^1\text{L}]\) have \(\mu_{\text{eff}}\) value 1.82 B.M. that is 
typical of Copper(II) complexes and they exhibit no 
intermolecular exchange interaction. It can, therefore, be 
expected that there may not be any intermolecular exchange 
interaction in the trinuclear complexes also. It is 
reasonable to assign this antiferromagnetic coupling in the 
trinuclear complexes to a long range intramolecular 
interaction propagated through the coordinated aldehyde 
substituted catecholate dianion moiety.
In the trinuclear complexes studied, no significant difference in the magnetic moments occurs in 
$[\text{A}^1\text{CuL} \cdot \text{CuCl}_2 \cdot \text{LCuA}^1]$ or $[\text{A}^1\text{CuL} \cdot \text{Cu(A-A)} \cdot \text{LCuA}^1]^{2+}$, indicating that ligands over the middle Copper(II) centre does not affect the extent of exchange interaction.

The UV spectral data of the trinuclear complexes $[(\text{CuA}^1\text{L})_2 \cdot \text{CuCl}_2]$ and $[(\text{CuA}^1\text{L})_2 \cdot \text{Cu(A-A)}] \cdot (\text{ClO}_4)_2$ are given in Table V 3. Bands of $[\text{Cu(A-A)}]^{2+}$ part do not change significantly on coordination with the two $[\text{CuA}^1\text{L}]$ complexes, showing that the $[\text{Cu(A-A)}]^{2+}$ part does not have any significant orbital interaction with other parts.