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 $\left[M(TSB)\cdot M\cdot M(TSB)\right](ClO_4)_2$, where M = Cu(II), Ni(II), Co(II), Fe(II) and Mn(II), have been carried out by Sinn and coworkers.[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,[154] and he proposed that the magnetic properties of a group of trinuclear acetate compound of Fe(III) and Cr(III) [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[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.[158] The magnetic properties of binuclear Copper(II) and Vanadyl(II) complexes have also been studied, where magnetic interaction is propogated through an extensive organic system, 1,2,4,5-tetraminobenzene.[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, $[CuA^1L]$, where A^1 = 2,2'-bipyridyl and L = 3,4-dihydroxybenzaldehyde has been studied[160] in solution. It has been observed that only hydroxy part of L takes part in coordination and -CHO group remains uncoordinated. It was thought possible that the two -CHO groups may coordinate with another Copper(II) centre in non-aqueous solvent. Therefore, the complex $[CuA^1L]$ was isolated and was further treated with $CuCl_2.2H_2O$ or $[Cu(A\text{-}A)]^{2+}$ to prepare trinuclear complexes

$[(CuA^1L)_2 \cdot CuCl_2]$ and $[(CuA^1L)_2 \cdot Cu(A\text{-}A)]$ $(ClO_4)_2$, where A-A is 2,2'-bipyridyl (A^1), 1,10-phenanthroline (A^2) or 2-(2'-pyridyl)benzimidazole (A^3).

EXPERIMENTAL

Material

Analytical Reagent grade chemicals (> 99.9 % purity) were used for all the preparations. $Cu(ClO_4)_2.6H_2O$ 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 $[CuA^1L]$

To an aqueous solution of $CuCl_2.2H_2O$ (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 $[(CuA^1L)_2.CuCl_2]$

To a solution of $[CuA^1L]$ (2 mol in 50 ml absolute ethanol) was added a solution of $CuCl_2.2H_2O$ (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

$\left[(CuA^1L)_2\cdot Cu(A-A)\right](ClO_4)_2$

A suspension of $\left[Cu(A-A)(ClO_4)_2\right]$ was prepared by adding (A-A) (0.1 mol in 10 ml absolute ethanol) to a solution of $Cu(ClO_4)_2.6H_2O$ (0.1 mol in 10 ml absolute ethanol). The resulting suspension was then added to $\left[CuA^1L\right]$ (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 V 1 : Analytical and Magnetic Data of Mono- and Tri- Nuclear Complexes

Compound	Colour	Analyses % *				μ_{eff}/ Cu(II) ion in B.M.
		Cu	N	C	H	
$[CuA^1L]$	Brown	17.56 (17.87)	7.41 (7.88)	56.63 (57.38)	3.42 (3.38)	1.82
$[(CuA^1L)_2 \cdot CuCl_2]$	Brown	22.81 (22.65)	7.19 (6.65)	- -	- -	0.95
$[(CuA^1L)_2 \cdot Cu(A^1)]\ (ClO_4)_2$	Olive green	16.53 (16.87)	7.52 (7.44)	- -	- -	0.92
$[(CuA^1L)_2 \cdot Cu(A^2)]\ (ClO_4)_2$	Olive green	16.86 (16.52)	7.53 (7.28)	- -	- -	0.92
$[(CuA^1L)_2 \cdot Cu(A^3)]\ (ClO_4)_2$	Olive green	16.67 (16.31)	7.92 (7.92)	46.12 (47.24)	3.94 (2.82)	0.80

* Calculated values are given in parentheses

Table V 2 : Infrared Spectra (cm^{-1}) of L, $[CuA^1L]$ and Trinuclear Complexes

Compound				
3,4-dihydroxybenzaldehyde (L)	3 320 (s),	3 220 (s),	3 050 (w),	2 880 (w),
	1 645 (s),	1 590 (s),	1 530 (s),	1 470 (m),
	1 440 (s),	1 420 (m),	1 380 (s),	1 290 (s),
	1 270 (m),	1 240 (w),	1 190 (s),	1 165 (s),
	1 120 (s),	970 (s),	940 (w),	875 (s),
	750 (s),	630 (s),	600 (m),	
$[CuA^1L]$	3 120 (w),	3 040 (s),	2 830 (w),	1 650 (s),
	1 610 (s),	1 600 (w),	1 565 (s),	1 545 (s),
	1 480 (s),	1 450 (s),	1 430 (s),	1 330 (w),
	1 290 (s),	1 260 (s),	1 210 (s),	1 180 (m),
	1 170 (s),	1 115 (s),	1 055 (m),	1 035 (m),
	970 (w),	955 (w),	870 (m),	810 (s),
	770 (s),	760 (s),	730 (s),	660 (s),
	645 (s),	615 (s)		

cont...

$\left[(CuA^1L)_2 \cdot CuCl_2\right]$	3 120 (w), 3 030 (m), 2 900 (w), 1 655 (s), 1 600 (w), 1 570 (s), 1 510 (s), 1 480 (s), 1 455 (m), 1 350 (m), 1 310 (w), 1 280 (m), 1 250 (m), 1 210 (m), 1 190 (s), 1 150 (m), 1 080 (m), 1 045 (m), 980 (w), 950 (w), 880 (m), 820 (m), 770 (s), 750 (s), 650 (s), 620 (s)
$\left[(CuA^1L)_2 \cdot Cu(A^1)\right] (ClO_4)_2$	3 400 (b), 3 040 (w), 1 635 (m), 1 600 (w), 1 570 (m), 1 490 (s), 1 470 (w), 1 445 (s), 1 380 (w), 1 330 (m), 1 300 (s), 1 265 (m), 1 240 (w), 1 220 (m), 1 150 (m), 1 120 (s), 1 100 (s), 1 090 (s), 1 035 (w), 1 000 (w), 980 (w), 940 (w), 890 (w), 850 (w), 770 (s), 730 (m), 640 (m), 625 (s)

Table V 3 : Reflectance Spectra (cm^{-1})

Compound	
$[CuA^1L]$	26 320, 20 000, 12 900
$[(CuA^1L)_2 \cdot CuCl_2]$	27 030, 22 730, 13 160 - 11 900 (broad band)
$[(CuA^1L)_2 \cdot Cu(A^1)]\ (ClO_4)_2$	27 030 (sh), 22 730, 13 900 - 12 200 (broad band)
$[(CuA^1L)_2 \cdot Cu(A^2)]\ (ClO_4)_2$	27 780 (sh), 25 000, 14 810 - 12 500 (broad band)
$[(CuA^1L)_2 \cdot Cu(A^3)]\ (ClO_4)_2$	27 780 (sh), 24 390, 14 810 - 12 120 (broad band)

Table V 4 : Electronic Spectra (cm^{-1}) of Ligands, Mixed Ligand Complex and its Trinuclear Complexes

Compound	
3,4-dihydroxybenzaldehyde (L)	42 750, 35 500, 31 600, 24 500
2,2'-Bipyridyl (A^1)	44 330, 41 170, 36 170, 24 800
$[CuA^1L]$	45 000 (sh), 39 000, 33 000, 32 000, 28 000
$[(CuA^1L)_2 \cdot CuCl_2]$	39 750, 33 200, 32 000, 28 250
$[(CuA^1L)_2 \cdot Cu(A^1)] (ClO_4)_2$	40 000, 33 250, 32 000, 28 250

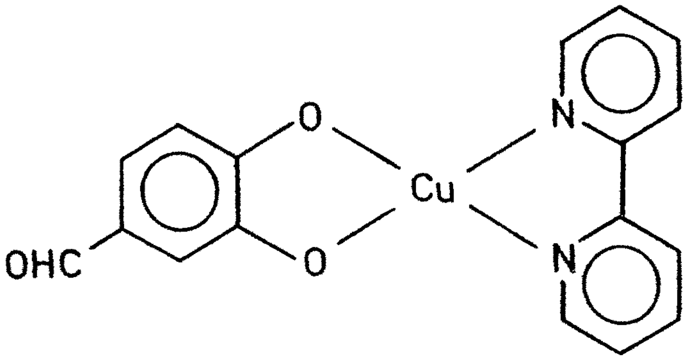


Figure V 1

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, $[CuA^1L]$, (Table V 2) shows a band at 1 650 cm^{-1} corresponding to $>C=O$ stretching, indicating that the carbonyl oxygen does not take part in coordination. The ν_{O-H} band of 3,4-dihydroxybenzaldehyde (L) around 3 400 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 $[CuA^1L]$ shows a broad band at $\sim$ 625 nm. This shows that the complex is square planar in nature.

The magnetic moment of the complex, $[CuA^1L]$, is 1.82 B.M., corresponding to spin only value of one unpaired electron.

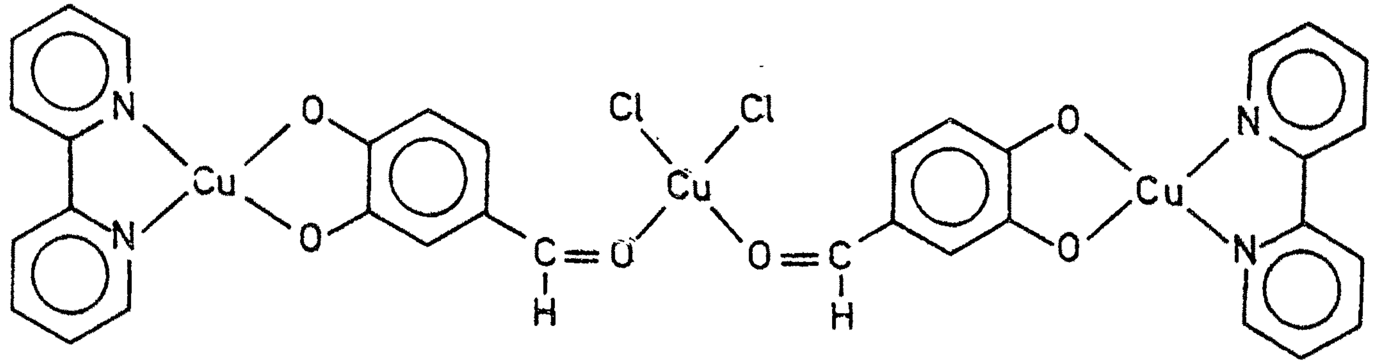
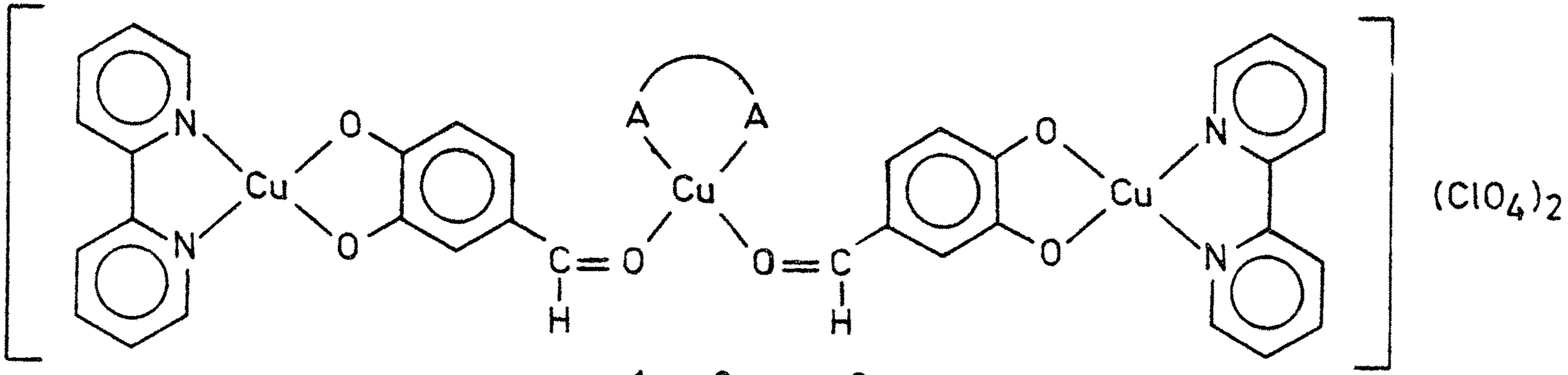


Figure V 2



A - A = A^1, A^2 or A^3

Figure V 3

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 $>C=N$ and $>N-H$ group stretching frequencies indicate that schiff base formation does not take place.

This mixed ligand complex, $[CuA^1L]$, has a potential coordinating -CHO site. The free -CHO groups of the two molecules of the mixed ligand complex, $[CuA^1L]$, get coordinated with $CuCl_2$ or $[Cu(A-A)]^{2+}$, 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[128] from their IR spectra (Table V 2). No significant difference in IR spectral bands of the $[CuA^1L]$ part occurs on coordination with $CuCl_2$ or $[Cu(A-A)]^{2+}$ in the trinuclear complex.

Ligand field spectrum of $[CuA^1L]$ 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 20 000 cm^{-1}. Trinuclear complex $[(CuA^1L)_2 \cdot CuCl_2]$ 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 -CHO groups and two chlorides absorbing at a lower field than the two $[CuA^1L]$ centres. Similarly, the trinuclear complexes $[(CuA^1L)_2 \cdot Cu(A\text{-}A)]\ (ClO_4)_2$ 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 -CHO groups and a tertiary diamine molecule.

Room temperature magnetic susceptibility measurements (Table V 1) show that μ_{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 $[CuA^1L]$ have μ_{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 propogated through the coordinated aldehyde substituted catecholate dianion moiety.

In the trinuclear complexes studied, no significant difference in the magnetic moments occurs in $\left[A^1CuL \cdot CuCl_2 \cdot LCuA^1\right]$ or $\left[A^1CuL \cdot Cu(A-A) \cdot LCuA^1\right]^{2+}$, 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 $\left[(CuA^1L)_2 \cdot CuCl_2\right]$ and $\left[(CuA^1L)_2 \cdot Cu(A-A)\right]$ $(ClO_4)_2$ are given in Table V 3. Bands of $\left[Cu(A-A)\right]^{2+}$ part do not change significantly on coordination with the two $\left[CuA^1L\right]$ complexes, showing that the $\left[Cu(A-A)\right]^{2+}$ part does not have any significant orbital interaction with other parts.