

## Studies on Co-Ordination Compounds of 3d-Block Metal Ions with Macrocyclic Ligands"



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The present thesis entitled 'studies on coordination compounds of 3d-block metal ions with macrocyclic ligands deals with preparation and characterization of an exciting series of a dozen of copper(II) coordination compounds with the tetraaza macrocyclic ligands mac and mac where mac 5, 6: 11,12- di (methoxybenzo) -1, 4, 7, 10- tetraaza-2, 3, 8, 9, -tetramethyl – cyclododeca – 1, 3, 5, 7, 9, 11 –hexaena and mac = 5, 6; 11, 12 – di (methoxybenzo) – 1, 4, 7, 10 –tetraaza – 2, 3, 8, 9, - tetraphenyl – cyclododeca – 1, 3, 5, 7, 9, 11 – haxaene.

Infrared spectra electronic spectra magnetic moment data , conductivity measurement and e. s. r. spectra has formed the basis of structural elucidation.

A series of complexes of the type  $(\text{CuL}_2\text{X})$  where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\frac{1}{2} \text{SO}_4^{--}$ ,  $\text{L} = \text{mac}$ ,  $\text{mac}$ , have been isolated from ethanolic medium during the course of present investigation.

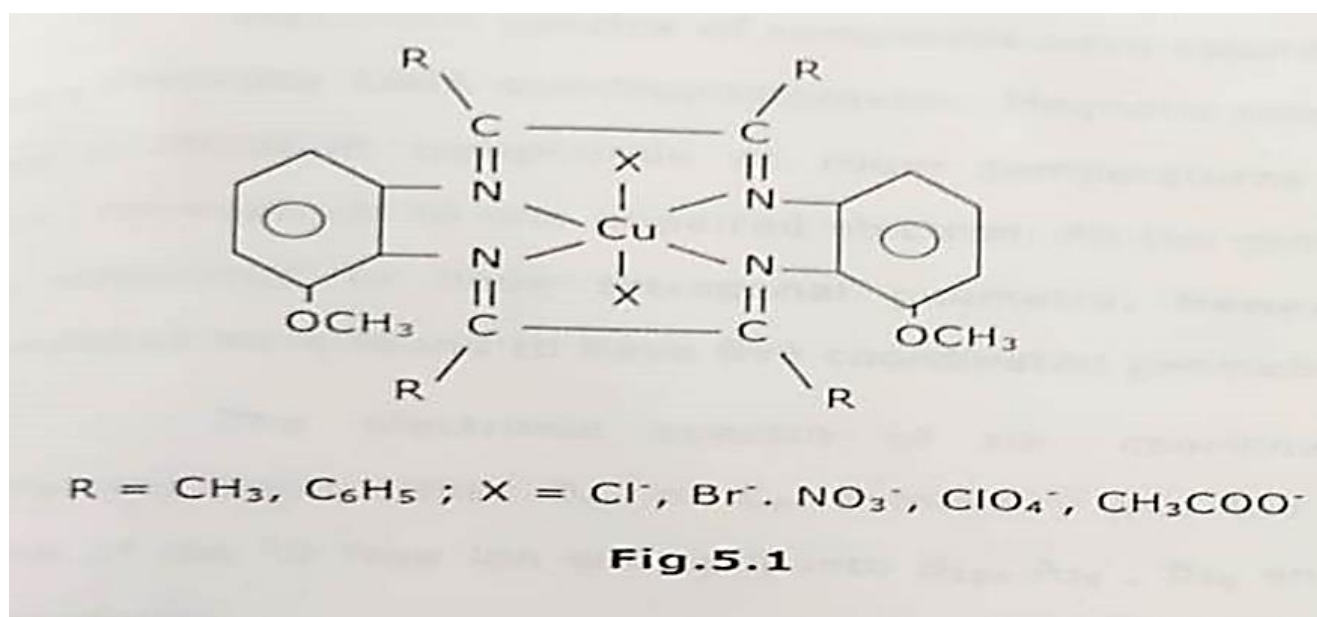
Although the i.r. spectra of all compounds are quite complex structurally important vibrational band such as  $\text{V}_{\text{C}=\text{N}}$ ,  $\text{V}_{\text{C}=\text{O}}$ ,  $\text{V}_{\text{NH}_2}$ ,  $\text{V}_{\text{C}-\text{N}}$  are quite discernible and provide unequivocal evidence concerning the nature of bonding of the ligands with the copper(II) ion.

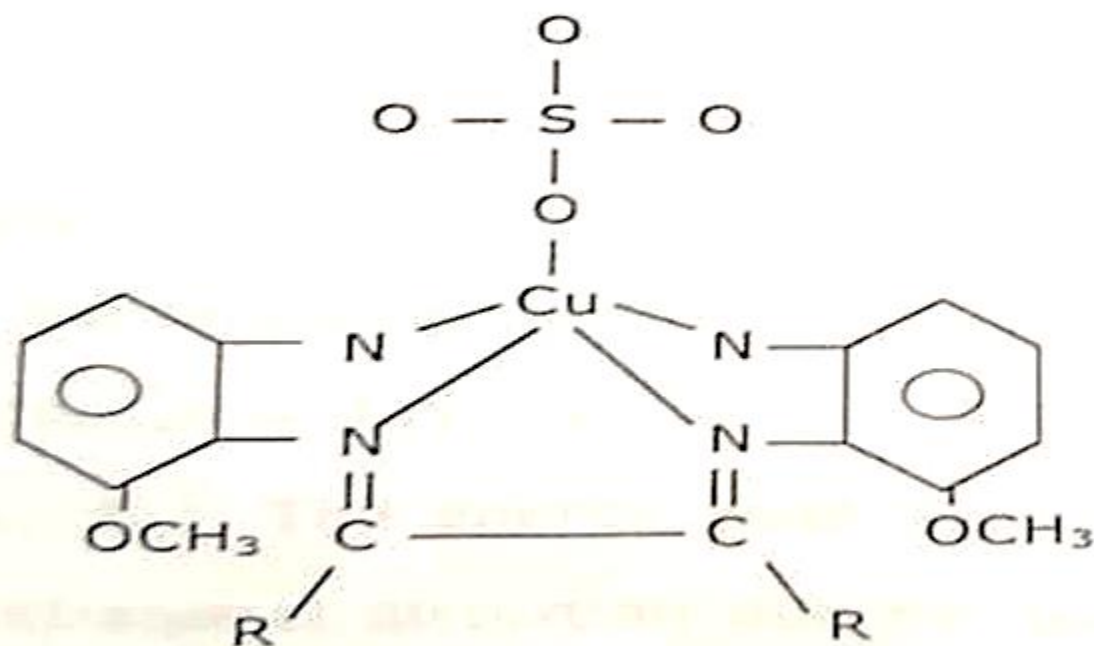
I.R. spectra of all the complexes do not show bands that can be assigned to  $\text{C}=\text{O}$  or  $\text{NH}_2$  groups. The strong bands appearing in the spectra of all the complexes at  $1370\text{--}1450\text{ cm}^{-1}$  ( $\text{C}=\text{N}$ ) indicate the presence of coordinated azomethine group. In the I.R. spectra if the nitrate complexes, bands at  $1470\text{--}1390$  and  $1340\text{--}1320\text{ cm}^{-1}$  show that nitrate act as unidentate. The acetate complexes show bands at  $1610\text{--}1625$  ( $\text{C}=\text{O}$ ) and  $(1305\text{--}1320)$  ( $\text{C}-\text{O}$ ) which indicate that acetate acts as unidentate in complexes<sup>3</sup>. I.R. spectra of the sulfato complexes show bands corresponding to monodentate sulfate. The bands are observed at  $\sim 940, 1040\text{--}1060$  and  $640\text{ cm}^{-1}$ . Perchlorato complexes also indicate monodentate coordination by the presence of a large number of bands in far ir and finger print

regions. The bands are observed in the regions 950-870 ( $\nu_2$ ), 1040-1025 ( $\nu_1$ ), 1160-1020 ( $\nu_4$ ), 480-460 ( $\nu_6$ ), 620-600 ( $\nu_5$ ) and 660-630 ( $\nu_3$ ) respectively.

I.R. spectra of the complexes show bands corresponding to monodentate sulfate. The bands are observed at -940, 1040-1060, 1180-1290 and 640  $\text{cm}^{-1}$ . Thus, a five coordinate structures can be adopted by complexes for coordination number five –trigonal bipyramidal and square-pyramidal. Practically, there appears to be little difference in energy between the two structures. The structures square-pyramidal and trigonal bipyramidal have the ground state configuration  $^2B_1$  (unpaired electron in the  $d_{x^2-y^2}$  orbital), and  $^2A_1$  (unpaired electron in the  $d_{z^2}$  orbital) respectively.

Some new bands appear in the region 700-900  $\text{cm}^{-1}$  which may be assigned to  $\nu_{\text{Cu-X}}$  (X=O, N, Cl, Br or anions) but the assignment is not possible with certainty due to complexity of the spectrum due to overlap of the absorption with imine or  $\text{CH}_2$  Groups. On the basis of above discussions structures as shown in fig.5.1 and 5.2 can be proposed for the coordination compounds.





**Fig.5.2**

#### Electronic Spectra and Magnetic Moment Data:

Electronic spectra of complexes were recorded in DMSO on a Shimadzu 160A spectrophotometer. Magnetic moments of all the coordination compounds at room temperatures (1.90-2.00 B.M.) corresponds to one unpaired electron. All the complexes may be considered to have tetragonal geometry. However, sulfato complexes were found to have five coordinated geometry.

The electronic spectra of six-coordinated CU(II) complexes have either  $D_{4h}$  or  $C_{4v}$  symmetry and the  $E_g$  and  $T_{2g}$  levels of the  $^2D$  free ion will split into  $B_{1g}$ ,  $A_{1g}$ ,  $B_{2g}$  and  $E_g$  levels respectively.

Thus three spin allowed transitions are expected in the visible and near-IR region, but only a few complexes are known in which such bands are resolved either by Gaussain analysis or by single crystal polarization studies. These bands have been assigned to the following transitions in order of increasing energy.

Both these factors tend to increase the value of  $g_{II}$ . The  $g$  values for the complexes studied follow the order:  $NO_3^- > Cl^- > MeCOO^- > ClO_4^- > Br^- > SO_4^{2-}$  which the positions of the anions in the spectrochemical series. Further, in an axial symmetry, the  $g$ -values are related by the expression,  $G = (G_{II} - 2) / (G_I - 2)$ , Which measures the exchange interaction between the copper centres in a polycrystalline solid. According to Hathaway and Billing, if the value of  $G$  is  $>4$ , the exchange interaction is negligible, which  $G < 4$  indicates a considerable exchange interaction in the solid complexes, suggesting that there is interaction between the copper centres.

Distinction between these two ground states can be made with the help of ESR spectra of the Cu(II) complexes. For system with  $g_3 > g_2 > g_1$ , the ratio  $(g_2 - g_1) / (g_3 - g_1)$ , called the parameter  $R$ , is a very useful parameter for this purpose. If the ground state is predominantly  $^2A_1$  the value of  $R$  is  $>1$ . On the other hand, for the ground state predominantly  $^2B_1$  the values of  $R$  is  $<1$ . The complexes under study show the values of  $R$  0.10 to be less than 1, thus indicating  $^2B_1$  as the ground state. Thus for  $[Cu(MAC/MAAC)SO_4]$  five coordinate square- pyramidal structure may be suggested.

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