

Copper Co-Ordination Compounds with Tetraaza Macrocyclic Ligands



Dr. Piyush Pyasa
M.Sc., Ph.D. (Chemistry)
B.R.A. Bihar University, Muzaffarpur (Bihar)

In the present chapter, structure have been assigned to the series of **copper (II) coordination** compound with the tetraaza macrocyclic ligands MAC and MAC'. Where MAC = 5, 6:11 12- di(methoxybenzo)-1, 3, 5, 7, 10-tetraaza- 2, 3, 8, 9,- tetramethyl- cyclododeca- 1, 3, 5, 7, 9, 11- hexaene 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- hexaene. Structural elucidation has been done on the basis of infrared spectra, electronic spectra, magnetic moment data, conductivity measurements and giving emphasis to e.s.r. spectra.

During the course of present investigation, a series of complexes of the type $[CuLX_2]$ (where $X = Cl^-$, Br^- , NO_3^- , ClO_4^- , CH_3COO^- , $\frac{1}{2} SO_4^{2-}$, $L = MAC, MAC'$, **have been isolated from** ethanolic medium.

The results of the present investigation are described in following sections:

SECTION- A

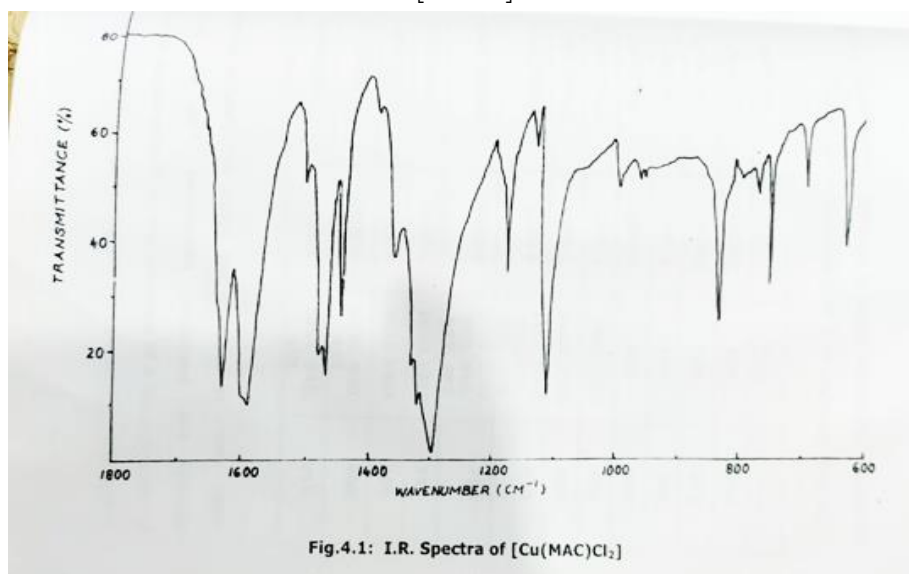
1. R. Spectra:

Infrared spectra (KBr) of the complexes have been recorded in the frequency region $4000 - 200 \text{ CM}^{-1}$ on a perkin Elmer 137 spectrometer. Vibration bands of structural significance are recorded in Table 4.1. and representative spectrum is shown in Fig . 4.1. The spectra have been analyzed for elucidation of their structure and bonding.

Although the I.R. spectra of all the compounds are quite complex, structurally important **vibration** band such as $>C=N$ stretch, $C=O$, NH_2 , ν_{Cu-X} ν_{Cu-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 $C=O$ or NH_2 groups¹. The strong bands appearing in the spectra of all the complexes at $1370-1450 \text{ cm}^{-1}$ ($C=N$) indicate the presence of coordinated azomethine group². In the I.R. spectra of the nitrate complexes, bands at $1470-1390$ and $1340-1320 \text{ cm}^{-1}$ show that nitrate acts as unidentate. The acetate complexes show bands at acetate acts as unidentate in complexes³. I.R. spectra of the silfato complexes show bands corresponding to

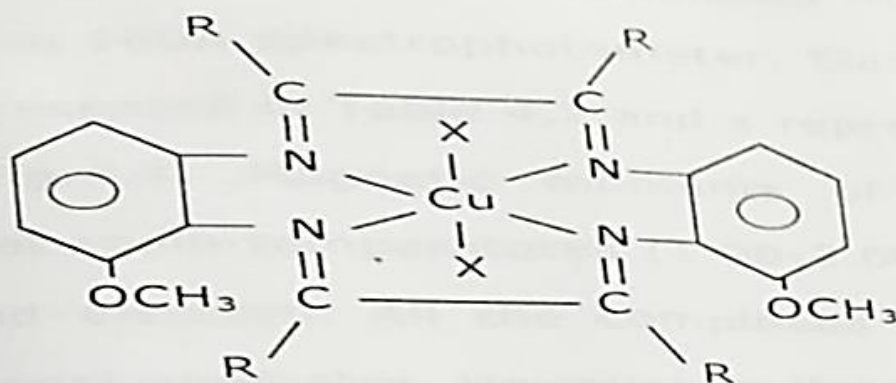
Table 4.1: Characteristic infrared spectral bands for **copper** (II) coordination compounds (cm^{-1}) of the type $[\text{CuLX}_2]$



Monodentate sulfate⁴. The bands are observed at ~ 940 , 1040 - 1060 and 640 cm^{-1} . Perchlorato complexes also indicate monodentate coordination^{5,6} 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 (ν_2) 1040 - 1020 (ν_1), 1160 - 1020 (ν_4) 480 - 460 (ν_6), 620 - 600 (ν_5) and 660 - 630 (ν_3) brespectively.

I.R. spectra of the complexes show bands corresponding to monodentate sulfate⁷. The bands are observed at - 940 , 1040 - 1060 , 1180 - 1290 and 640 cm^{-1} . Thus, a five coordinate structure is suggested for these complexes. Two basic structures⁸ can be adopted by complexes for coordination number five-trigonal bipyramidal and squire- pyramindal. Practically, there appears to be little sifference in energy⁹ between the two structures. The structures, square-pyramindal and trigonal bipyramindal have the ground state configuration $^2\text{B}_1$ (unpaired electron in the $d_{x^2-y^2}$ orbital), and $^2\text{A}_1$ (unpaired electron in the d_{z^2} orbital) respectively¹⁰.

Some new bands appear in the region 100 - 900 cm^{-1} which may be assigned to $\nu_{\text{Cu-X}}$ ($\text{X}=\text{O}$, N , Cl , Br or anions) but the assignment is notpossible with certainty due to complexity of the spectrum due to overlap of the absorption with imine or CH_2 groups. On the basis of above sidcussions strucres as show in Fig.4.2 and 4.3 can br proposed for the coordination compounds.



$R = \text{CH}_3, \text{C}_6\text{H}_5$; $X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{ClO}_4^-, \text{CH}_3\text{COO}^-$

Fig.4.2

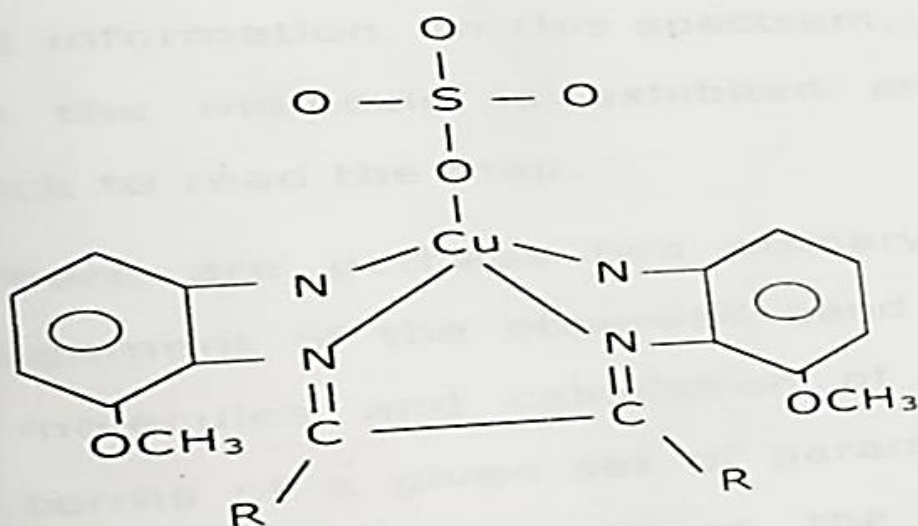


Fig.4.3

SECTION – B

Electronic spectra and magnetic moment data:

Electronic spectra of complexes were recorded in DMSO on a Shimadzu 160A spectrophotometer. Electronic spectral bands have been presented in Table 4.2 and a representative spectrum is shown in Fig.4.4 **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.

Whilst many physical techniques play their part in the elucidation of the geometries and electronic structure of a metal **complex**, a study of the electronic spectra can often provide the most detailed information. In this spectrum, a map of the energy levels within the molecule is exhibited provided the observer knows the trick to read the map.

There are perhaps two primary stages in this map reading, assignment of the observed band to specific transitions within the molecules and calculation of the transition of the terms of a given set of parameters. The assignment depends upon amongst other things, the stereochemistry of the molecules thus band assignments necessarily lead to some knowledge about the stereochemistry of the complex.

Table 4.2: Magnetic moment and electronic spectral bands (cm^{-1}) of $[\text{CuLX}_2]$ complexes.
 Intensities within the brackets are on the arbitrary Backman scale of 0-2.

The energy parameters depend upon the chemical bonding within the molecule and therefore can **provide** information about the **bonding**. In cubic molecules the parameters generally employed are Dq , the crystal field splitting parameter. The variation of these with respect to the metal and ligand give rise to the well known spectrochemical and nephelauxetic series. These parameters can provide information about the degree of and/or **bonding in the metal ligand band, about the effective on the metal** are the mean d orbital radius.

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. Energy level diagram for copper (II) ion in crystal fields of O_h and D_{4h}

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 Gaussian analysis or by single crystal polarization studies. These bands have been assigned to the following transitions in order of increasing energy: $^2B_{1g} \rightarrow ^2A_{1g}(d_{x^2-y^2} \rightarrow d_{z^2})$, $^2B_{1g} \rightarrow ^2B_{2g}(d_{x^2-y^2} \rightarrow d_{xy})$ and $^2B_{1g} \rightarrow ^2E_g(d_{x^2-y^2} \rightarrow d_{xz}, d_{yz})$. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn-Teller effect¹¹. The electronic spectra of the present complexes (Table 4.2) show one characteristic band at $10515\text{--}14814\text{ cm}^{-1}$ except the acetate complex which shows two characteristic bands at 11409 and 17452 cm^{-1} , assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ transition, respectively. The $^2B_{1g}$ and $^2B_{2g}$ transition is usually not observed as a separate band in tetragonal field. The splitting of the 2E_g state is a measure of the planar field is constant in all the present complexes, the change in position of the bands may be due to the axial field only. In the Cu(II) complexes, the $^2B_{1g} \rightarrow ^2A_{1g}$ transition is shifted to higher energy, the order being $\text{Cl}^- < \text{NO}_3^- < \text{MeCOO}^- < \text{ClO}_4^- < \text{Br}^- < \text{SO}_4^{2-} < \text{BF}_4^-$.

SECTION –C

ESR studies

It is **generally accepted that only an** MO model adequately account for the electronic properties of transition metal compounds. The orbitals regard to optical and magnetic properties, are best regarded as MO's are usually written as liner combination (1) Of atomic orbitals. The determination of the expansion coefficient in equation (1) is obviously of great importance in discussing the electron distribution in a molecule. The value of MO calculations on metal complexes is still rather uncertain¹² in spite of much effort in the past. Experimental measurements which can be directly related to MO coefficients have obvious appeal and many attempts have been made to use e.s.r. data in this way. Special attempts has been paid to tetragonal copper (II) compounds since these usually give rise to an theoretical treatment by invoking the 'one hole' formalism for the d⁹ configuration.

Maki and McGarvey and Kivelson and Neimann derived expressions for MO coefficients and deduced numerical values for these coefficients in the filled anti-bonding MO's (i.e. the 'd-orbitals') for a number of tetragonal Cu(II) systems by analysis of their ESR spectra. These workers pointed out that there were many approximations and assumptions in their calculations; many integrals were neglected or approximated, and relatively crude hydrogen like atomic wave functions were used in the evaluation of overlap integrals. Moreover, the d-d transition energies required were estimated on the basis of dubious assignments of the electronic spectra.

Since the pioneering work of Smith, better atomic wave functions for the evaluation of molecular integrals have become available, and the d-d spectra of copper(II) complexes are better understood. Yet little attempt has been made to reassess the earlier work. Even in quite recent work, the approximate equations have been accepted without question. The numerical values of metal-ligand overlap integrals question. The numerical values of metal-ligand overlap integrals estimated in the early work using crude wave functions have been quoted in recent literature. Without regard for the fact that such integrals are steep functions of the interatomic distance and should be evaluated separately for each particular compound under consideration, by use of the best crystallographic data available.

References:

1. N.B. Colthup, L.H. Dally and S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York (1964).
2. C. N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York (1963).
3. B.J. Hathaway and A.E. Underhill, J. Chem. Soc. (1961) 3091.
4. Ibid.
5. S. Chandra and S.D. Sharma, J. Indian Chem. Soc., 79 (2002) 496.
6. L. Scaconi, Transition Met. Chem., 4(1968)221.
7. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Amsterdam (1968).