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SHORT NOTE ON THE DETERMINATION OF Cu (II) COMPLEXES STRUCTURES.

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Abstract :- In this various research paper we have tried to determination of the structures of the complexes by employing various. Physico chemical methods like elemental analysis, electrical conductance and magnetic moment measurement, I.R and electronic behavior of the complexes.

Key words :- Magnetic property, octahedral, magnetic moment, electronic spectral, tetrahedral field.

INTRODUCTION

In this paper determination of Cu (II) structures are dependent on (1) magnetic properties (2) Date of magnetic moment (3) Electronic Spectral behavior and (4) Date of electronic spectra of the [Cu (L) B_2] complexes.

Magnetic properties of Copper (II) complexes :-

The valence shell electronic configuration of copper is $3d^{10}4s^1$. Thus Cu(II) is a $3d^9$ system having one unpaired electron in 3d-orbital.

There is one and only one free ion term ^2D for d^9. In weak octahedral field ground term for d^9 is ^2E_g and in weak tetrahedral field the ground term for d_9 is ^2T_g.

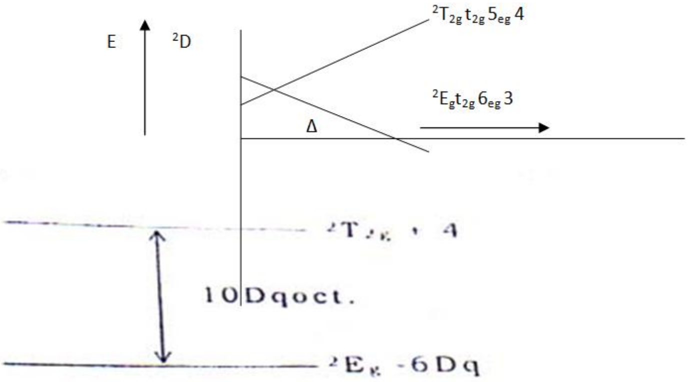

Fig. – 53 (Splitting in octahedral field)

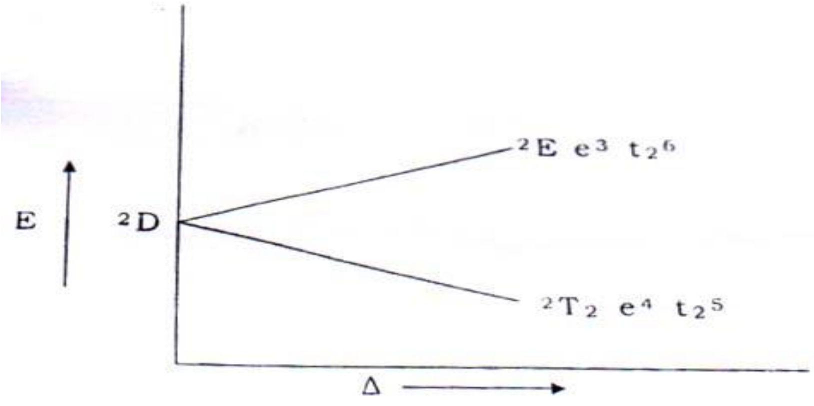

Fig.-55
(Splitting in tetrahedral field)

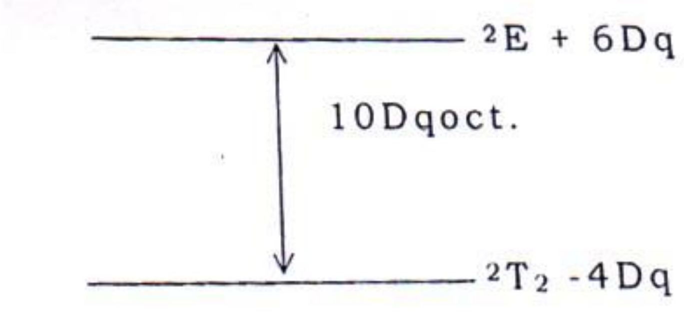

Fig.-56

In the case of distortion either by tetragonal (Non equivalence of ligands) or by Jahn Teller distortion, T_{2g} splits as B_{2g} and E_{2g} and E_{2g} which further spits as A_{1g} and B_{1g}.

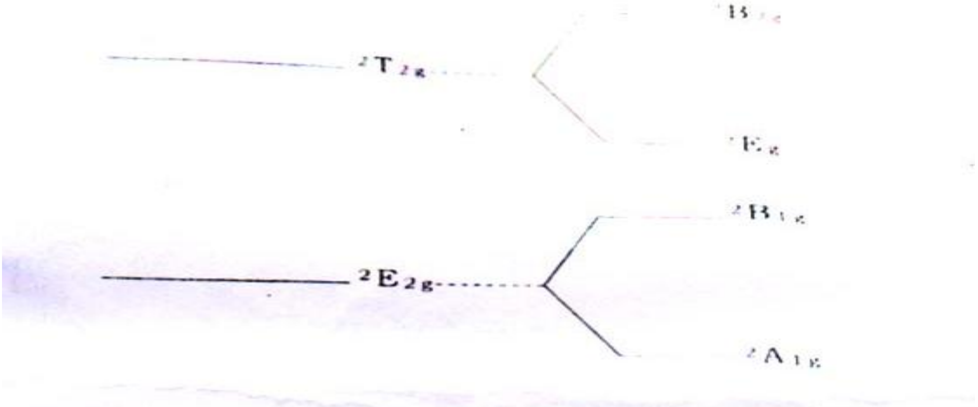

Fig.57

(Octahedral Distortion)

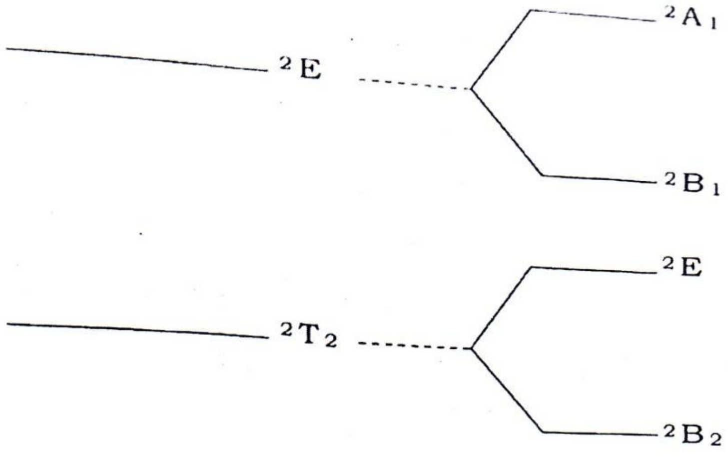

Fig.58

(Tetrahedral Distortion)

Cu(II) – $3d^9$ has one unpaired electron, so Cu(II) may form outer orbital octahedral complex by sp^3d^2 hybridisation and tetrahedral complexes by sp^3 hybridisation. On promotion of an 3d-electron to 5s orbital, one of five 3d-orbitals may be made empty to take part in dsp^3 hybridisation for the formation of square planar complexes.

It is evident that all three classes of Cu(II) complexes contain on unpaired electron and so all are expected to exhibit paramagnetic character corresponding to 1.73 B.M.

$\mu_s = \sqrt{n\ (n+1} = \sqrt{3} = 1.73$ B.M.

In weak octahedral field ground term is ^2E_g and as there is no orbital contribution, there is contribution from first order Zeeman Effect :

$\mu_{eff} = \mu s\ (1 - \frac{2\lambda}{10Dq})$

If for Cu (II) = -8.30 cm^{-1} and 10Dq is 13000 cm^{-1}

$\mu_{eff} = 1.73\ [1 - \frac{2(-830)}{10Dq}]$

$\mu_{eff} = 41.73\ (1 + \frac{2\ x\ 830}{13000}) = 1.90$ B.M.

μ_{eff} for Cu (II) octahedral to be greater than $\mu_{s.}$

Ground term for Cu(II) complexes in tetrahedral field is $^2T_2$. So there is orbital contribution due to T-ground term. Hence μ_{eff} for tetrahedral Cu(II) complexes is expected to be greater term $\mu_{s.}$ μ_{eff} for tetrahedral Cu(II) complexes have been reported in the range of 2.15 – 2.0 B.M. [23]. Large orbital contribution to magnetic moment has been used as a evidence for tetrahedral Cu(II) complexes[24], [25]. In distorted octahedral ground term is $^2A_{1g}$ and so neither orbital contribution from first order Zeeman Effect is expected and so μ_{eff} for distorted octahedral is expected to be near μ_s value only.

However a large number of Cu(II) complexes with subnormal values of magnetic moment as room temperature have been reported [26-29]. Such complexes have the values or magnetic moment in the range of 0 to 1.73 B.M. The complexes which display magnetic moment value below 1.73 B.M are referred as magnetically subnormal complexes[30].

In case of subnormal complexes, the magnetic moment value of complexes, the lowering of magnetic moment value is attributed to exchange interaction or metal-metal bonding leading to partial overlap or unpaired electron of bivalent copper in its complexes.

Copper forms many complexes in which Cu-Cu distances are short enough to indicate significant M-M interaction but in no case actual Cu-Cu bonds are present[31]. Attempts to specify the detailed nature of this interaction have been plagued by controversy and there are still considerable difference of opinion about its precise nature[32]. Melkin[33] has interpreted antiferromagnetic exchange between coupled pairs of Cu-atoms. 4

Data of Magnetic moment of the $[Cu(L)B_2]$ Complexes :-

Complexes	Colour	μ eff (B.M)	Magnetic Properties
1. $[Cu(C_{15}H_{16}N_2O_2)(H_2O)_2]$	Green	1.98	Paramagnetic
2. $[Cu(C_{15}H_{16}N_2O_2)(NH_3)_2]$	Deep green	1.90	Paramagnetic
3. $[Cu(C_{15}H_{16}N_2O_2)(C_9H_7N)_2]$ (Quinoline)	Parrot green	1.96	Paramagnetic
4. $[Cu(C_{15}H_{16}N_2O_2)\ (C_6H_5NC)_2]$ (Phenyl isocyanide)	Green	2.00	Paramagnetic
5. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_5N)_2]$ (Pyridine)	Green	1.92	Paramagnetic
6. $[Cu(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ (α- picoline)	Parrot green	1.96	Paramagnetic
7. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_4NCH_3)_2]$ (β-picoline)	Parrot green	1.94	Paramagnetic
8. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_4NCH_3)_2]$ (γ – picoline)	Green	1.92	Paramagnetic

In spite of several favourable observations in support of the above measurable difference between the magnetic moment value and geometry of the complex, The magnetic moment data can not be used as the only criteria for the elucidation of geometry of Cu(II) complexes, because a number of other factors also effects the above data as it is quite evident from Cu (accetylacetonato)$_2$ complex. In fact this complex is square planar but suggests tetrahedral structure on the basis of magnetic data.

In the present investigation, the values of magnetic moment obtained for the Cu (L) B_2 complexes are in the range of 1.90 – 2.00 B.M suggesting the distorted octahedral nature of the complexes[34].

Electronic Spectral Behaviour of Cu (II) Complexes.

The electronic spectra of Cu (II) complexes have been explained on the basis of crystal field model [35-37].

Cu (II) complexes in weak octahedral or weak tetrahedral field are expected to give on d-d band i.e. $^2E_g \rightarrow 2T_{2g}$ and $2T \rightarrow {}^2E_2$ respectively.

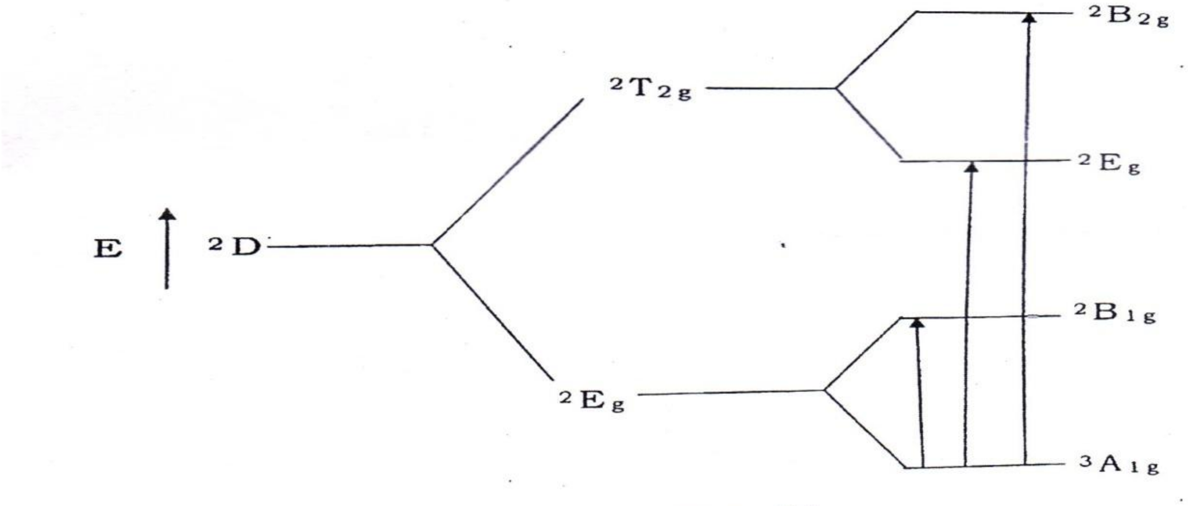

Fig.59

The values of for $^{\varepsilon}$ for octahedral is expected in the range of ten and tetrahedral in the range of hundred. But taking into consideration Jahn-Teller distrortion the d-d band in both case is expected to broad and unsymmetrical. In the distorted octahedral or tetrahedral three d-d bands are expected.

Holm et al38, Goodgame and Cotton[39] reported three bands for octahedral Cu(II) complexes in the range of 10,000 cm^{-1} to 14,500 cm^{-1}.

The energy level diagram in case of square planar complexes of Cu (II) as suggested by Ballhausen[40], gives rise to three transition in square planar or distorted octahedral.

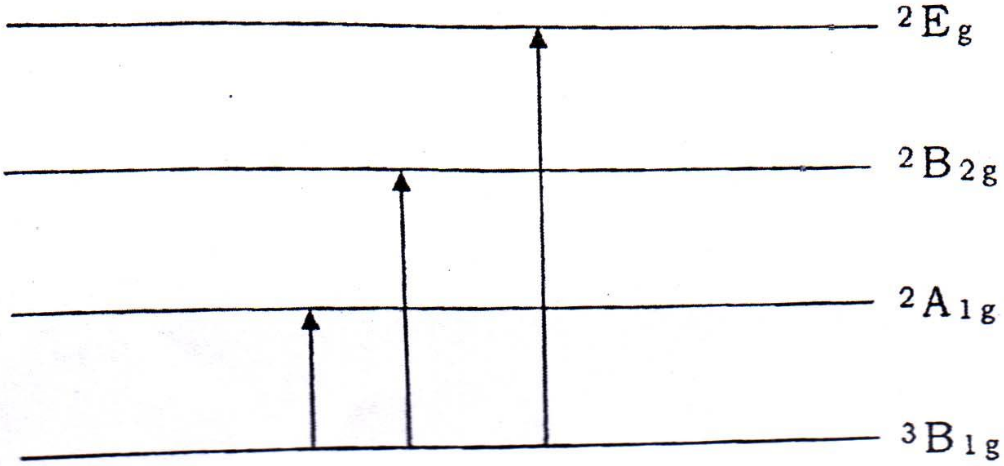

Fig.60

In the visible spectra of square planar and tetrahedral Cu (II) complexes three bands have been reported. Hathaway et al41 have reported three bands (18000 cm-1, 16000 cm-1 and 1200 cm-1) of [Cu(en)2] SO4 complex alongwith several other Cu(en)2+ complexes with slight difference in band positions are tentatively assigned as the $^2E_g \rightarrow {}^2B_{1g}$, $^2A_{1g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions respectively. According to figgis42, the Cu (II) complexes with acetylacetone display two bands in the range of 15000 cm-1 and 18000 cm-1 and bands at higher energies due to charge transfer. He assigned the two bands due to transition $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$.

Some workers have reported a band around 15500 cm^{-1} for square planar Cu (II) complex which may assigned as $^2B_{1g} \rightarrow {}^2E_g$ for tetrahedral [43-44] complexes transitions occur around 7500 $^{cm-1}$ to 11000 $^{cm-1}$ corresponding to $^2T_2 \rightarrow {}^2E$. However Sacconi et al[45] studying the electronic spectra of salicylideneamino Cu (II) complexes, reported that flattening of the tetrahedral geometry results in the splitting of both ground and excited levels giving rise to four transitions. They however obtained only three peaks at 8500, 13600 and 21000 $^{cm-1}$ and assigned a pseudo tetrahedral geometry.

A. Ramchandraiah et al50 have reported bands at 10500 and 14000 cm-1 for pseudo-tetrahedral Cu (II) complexes. An extra low intensity band assigned to $dx^2 . y^2 \rightarrow d_z^2$ transition was reported for certain Cu (I) Schiff base complexes, with pseudo – tetrahedral geometry[46].

Thus the presence of three bands instead of one for Cu (II) complexes can be obtained due to perturbation of ground as well as excited term of tetragonal or distorted tetrahedral [47-51] complexes.

The electronic spectra of the Cu (II) complexes under taken for study are given the table.

Data of electronic spectra of the [Cu(L)B_2] complexes.

Complexes	cm^{-1}	ε
1. $[Cu(C_{15}H_{16}N_2O_2)(H_2O)_2]$	15600	12.40
2. $[Cu(C_{15}H_{16}N_2O_2)(NH_3)_2]$	15900	12.90
3. $[Cu(C_{15}H_{16}N_2O_2)(C_9H_7N)_2]$ (Quinoline)	15500	12.50
4. $[Cu(C_{15}H_{16}N_2O_2)\ (C_6H_5NC)_2]$ (Phenyl isocyanide)	15400	12.40
5. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_5N)_2]$ (Pyridine)	15700	12.70
6. $[Cu(C_{15}H_{16}N_2O_2)(C_5H_4NCH_3)_2]$ (α- picoline)	15400	12.40
7. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_4NCH_3)_2]$ (β-picoline)	15650	12.60
8. $[Cu(C_{15}H_{16}N_2O_2)\ (C_5H_4NCH_3)_2]$ (γ – picoline)	15550	12.50

B = broad

In our present investigation the electronic spectra for Cu (II) complexes obtained are in the range of 15200 – 16100 cm^{-1} due to $^2E_g \rightarrow {}^2T_{2g}$ indicates the distorted octahedral structure of the complexes.

1. R. Spectra of the [Cu(L) B2] complexes :

By the proper examination of the I.R. spectra of the Cu(II) complexes and their comparison with that of the ligand, it is concluded that in almost all complexes phenolic U(OH), imine U(NH), azomethine, U(C=N) and U(C-N) bands of the ligand molecule are remarkably changed after complex formation. A strong and sharp band due to the vibrations of (O-H) and (N-H) bonds of the ligand obtained at 3230cm^{-1} disappears in all the complexes with a formation of new broad band in the complexes at about 3430 cm^{-1} indicating the presence of the free –NH group even in the complexes. The disappearance of the strong band located at 3230 cm^{-1} further suggests the deprotonation of the phenolic (OH) proton present in ligand moiety. The azomethine band at 1650 cm^{-1} in the ligand molecule is also shifted to lower frequency in almost all the complexes by 60 to 50 cm^{-1}. This shift of U(C = N) band towards lower frequency in the complexes suggests the coordination of the azomethine nitrogen of the ligand in the formation of the complexes. The strong and sharp band due to imine group (N – H) of the ligand located at 3430 cm^{-1} is also shifted to lower frequency by 3550 cm^{-1} indicating the coordination of imine nitrogen in the complex formation.

A strong and sharp band obtained at 1450 1470 cm^{-1} due to U(C-N) vibration has been reduced by 20-25 cm^{-1} in the complexes supporting the coordination of imine nitrogen in the bond formation with metal cations.

The medium and sharp band located at 1300 cm^{-1} in the ligand obtained due to the deformation vibration of phenolic –OH disappears in all the complexes supporting the deprotonation of the phenolic –OH and coordination of phenolic oxygen to the metal atom. The U(C-O) vibration of phenolic –(C-O) group shifts to higher frequency in the complexes suggesting increase in the bond order of (C – O) group in the complexes. The appearance two bands at around 420 – 460 cm^{-1} and 510 – 570 cm^{-1} due to U(M – N) and U(M – O) vibrations respectively in the complexes further suggests the coordination of nitrogen and oxygen atoms of the ligand in the complex formation.

The case of aquo-complexes, the appearance of one mole band in the range of 750 – 830 cm^{-1} due to the rocking the wagging mode of vibrations, suggests that H2O is present in the coordination sphere. A separate band for water molecule is not obtained due to the overlapping of U (OH) vibration.

The complexes containing quiloline pyridine and different picolines, however, display some extra bands in the finger print and for infrared region.

The pyridine ring breathing mode of vibration located at 960 – 1000 cm^{-1}

In the complexes indicates has been taken to be characteristic vibrations of coordinated pyridine and different picolines. From the I.R spectral studies, it has been obtained that the frequency of free phenyl isocyanide (2180 cm^{-1}) has been shifted to 2240 cm^{-1} in the complexes indicating the coordination of nitrogen atom of phenyl isocyanide in the complex formation.

A broad a medium band around 830, 780 and 720 cm^{-1} obtained in the case of some complexe support the coordination of α, β, and γ–picolines.

Thus on the basis of elemental analysis, measurement of electrical conductance and magnetic moment, I.R and electronic spectral behavior, it may be suggested that Ni(I I) ions forms octahedral complexes with the ligand 1, 3-bis(0-hydroxy aniline) propane (LH2) in presence of water, ammonia, quinoline, phenyl-isocyanide, pyridine and different picolines.

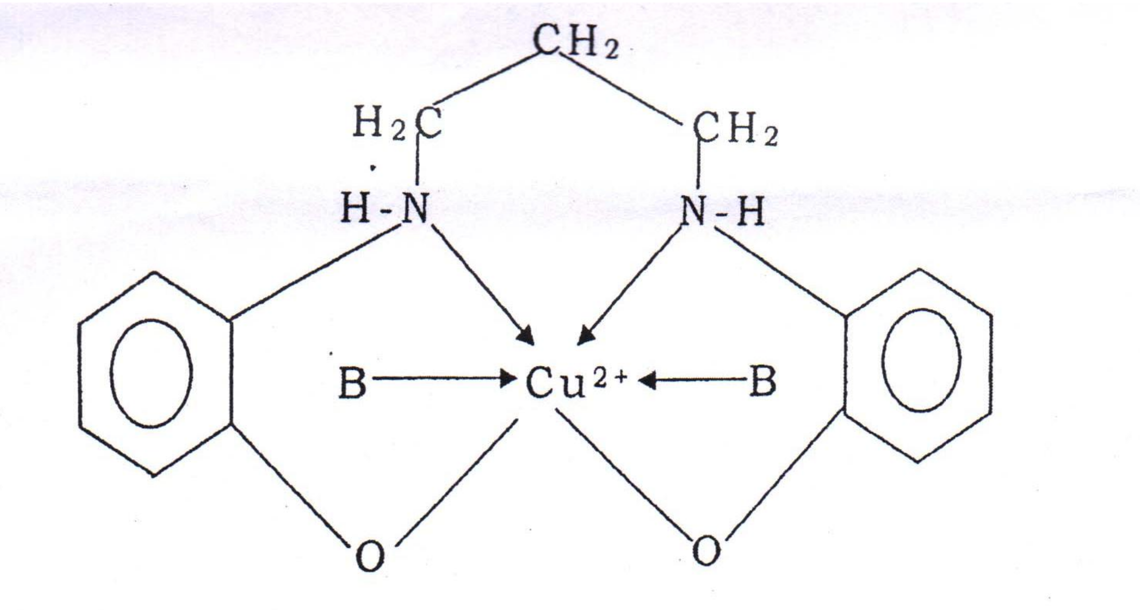

Fig.-61

Where

B = water, ammonia, quinoline, pheny-lisocyanide
α, β, and γ–picolines.

Conclusion :-

In this research paper we get that Cu (II) complexes, there is only one board and unsymmetrical band located at 15200 – 16100 cm-1 ($^2E_g \rightarrow {}^2T_{2g}$) which indicates the octahedral nature of the complexes.

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