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Thermal Investigation and Stereochemical Studies of Copper (II) Complexes of Some Heterocyclic ligands

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ABSTRACT

Cu(II) complexes of some heterocyclic ligands such as 2,2'-bipyridyl and 1,10 –phenanthroline, were synthesized. The complexes were characterized by elemental analyses, thermal analyses, IR spectra, electronic spectra, magnetic moment measurement and conductivity measurements. They were found to have the following compositions: $\left[CuL^1Cl_2\right],\left[CuL^2Cl_2\right],\left[CuL^1{}_2Br_2\right].2H_20$ *and* $\left[CuL^2{}_2Br_2\right].3H_20,$ *where* $L^1=2,2'$*-bipyridyl(bipy) and* $L^2=1,10$ *- phenanthroline(phen). The complexes which are four coordinated, appear to possess square planar geometry while the six coordinated complexes have distorted octahedral geometry.Thermodynamic parameters such as activation energy (Ea*), enthalpy change* $\left(\Delta H\right)$ *and entropy change* $\left(\Delta S\right)$ *for dehydration and decomposition reactions of the complexes, were evaluated using some standard methods. The order of stability of the complexes (with respect to thermal decomposition temperature and Ea* from TGA curve) follows the trend: phen > bipy.*

Keywords: Cu(II), 2,2'-bipyridyl, 1,10–phenanthroline, thermal analyses and thermodynamic parameters.

INTRODUCTION

The ligands 2,2'bipyridyl(bipy) and 1,10– phenothroline (Phen) act as bidentate and chelating agents. Although works on similar Cu(II) complexes of the above mentioned ligands had been reported earlier [1-7], in the present cases the compositions differ from that of earlier.

Till now, to the best of my knowledge, no one has done the thermal investigation (analyses) and stereochemical changes of these complexes in the solid state in detail. The main aim of the present work is to synthesize and characterize the copper (II) complexes of 2,2'-bipyridyl and 1,10-phenanthroline and to carry out thermal investigations of the complexes in solid state for studying stereochemical changes, and also to evaluate the thermodynamic parameters like activation energy (Ea*), enthalpy change $\left(\Delta H\right)$ and entropy change $\left(\Delta S\right)$ with the help of some standard methods [8-10].

Stability order of complexes with respect to thermal decomposition temperature and Ea* (from TGA Curve) have been drawn.

EXPERIMENTAL SECTION

Copper(II)Chloride (ARGrade) and Copper (II) bromide pure were used as received. Both 2,2'-bipyridyl and 1,10 –phenanthroline were of AR grade and were used as received. Ethanol and diethylether were dried using the standard procedure [11].

Preparation of Metal Complexes:

$\left[Cu\left(bipy\right)Cl_2\right](1)$ and $\left[Cu\left(phen\right)Cl_2\right](2)$:- Complex (1) was prepared by adding 15 ml ethanolic solution of 2,2'-bipyridyl (3mmol) to 20ml of Copper(II)chloride solution (3mmol) in ethanol with constant stirring. Fine bluish-green complex separated out immediately. It was filtered, washed with and dry ether and dried over fused calcium chloride in a dessiccator. Yield is *ca* 80%.

Complex (2) was prepared in the same way. Here colour of the complex is green and yield is *ca* 85%.

$\left[Cu\left(bipy\right)_2 Br_2\right].2H_20(3)$ and $\left[Cu\left(Phen\right)_2 Br_2\right].3H_20(4)$:- Complex (3) was obtained when 30 ml ethanolic solution of $CuBr_2\left(3mmol\right)$ was mixed with 25ml ethanolic solution of $2,2'$- bipyridyl (6mmol). After a prolonged vigorous stirring of the resulting mixture, deep green coloured complex separated out. It was, then, filtered, washed with dry ether and dried over fused calcium chloride in a dessiccator. Yield is *ca* 80%.

Complex (4) was prepared in the same manner as mentioned above. Here the colour of the complex is green and yield is *ca* 80%.

Copper was estimated gravimetrically using the standard procedure [12]. C,H and N analyses were done by Perkin-Elmer 240C and Carlo Erba 1106 elemental analysers. Thermal investigations (both TGA and DTA) were carried out on a Shimadzu Thermal Analyzer DT-30 under a dynamic nitrogen atmosphere with a heating rate of 10^0C min^{-1} and α - abumina as the standard reference substance.

Activation energy (Ea*) was evaluated from the TGA Curve using the equation of Horowitz and Metzger [8] and from the DTA Curve using that of Borchardt and Daniels [9]. ΔH was evaluated from the DTA curve using the relation [9], $\Delta H = KA,$ Where K is the heat transfer Co-efficient (Cell Constant or Calibration Constant, here the cell is platinum Crucible and its constant, K was evaluated using indium metal as Calibrant), and A is the total area under the particular DTA Curve measured with a compensating planimeter with optical tracer of Fuji Corona 027. ΔS was calculated form the relation [10], $\Delta S = \frac{\Delta H}{Tm}$, Tm being the DTA peak temperature in Kelvin.

Infrated and far i.r-spectra were recorded with Beckmann IR20A and Perkin Elmer 783 spectrometers in KBr and polythene powder discs. Electronic spectra were recorded with the help of Beckmann DU-6 spectrophotometer using ethanol and dimethylformamide (DMF) as the reference solvents. The effective magnetic moments were evaluated from magnetic susceptibility measurements with EG and G PAR 155 vibrating sample magnometer at room temperature. Conductivity measurements of the complexes in DMF at the concentration of 10^{-3}M, were carried out at room temperature with conductivity bridge 305 Systronics (India) using a dip-type cell. Solid residues, obtained after pyrolysis, were identified with the help of qualitative analysis.

RESULTS AND DISCUSSION

From elemental analyses, magnetic moment values and electronic spectral data (Table -1), IR spectral data (Table-2), thermal analyses (Table-3), conductance measurent values and qualitative analysis, it has been confirmed that both copper (II) chloride and Copper (II) bromide from complexes with $2,2'$- bipyridyl(bipy) and 1,10 – phenanthroline(phen) having the formulae: $\left[Cu\left(bipy\right)Cl_2\right](1)$, $\left[Cu\left(phen\right)Cl_2\right](2)$, $\left[Cu\left(bipy\right)_2 Br_2\right].2H_2O(3)$ and $\left[Cu\left(phen\right)_2 Br_2\right].3H_2O(4)$ respectively (as shown in Table 1). Complexes (1) and (2) possess square planar geometry while complexes (3) and (4) possess distorted octahedral geometry. Complexes with phenanthroline are found to be more stable than that of bipyridyl.

Elemental analyses, Magnetic moment and Electronic spectra:

Elemental analyses of the complexes (1) to (4) (Table 1) prove that the ligands $2,2'$-bipyridyl (bipy) and 1,10 – phenanthroline (phen) are coordinated with copper in their corresponding complexes. Their magnetic moment values (Table-1) ranges from 1.85-1.88 B.M. which shows the mononuclear nature of all the complexes [13] and also further supports square planar geometry [14] in case of complexes (1) and (2) but distorted octachedral geometry in case of complexes (3) and (4). The electronic spectral data (Table-1) also, further, supports the geometries of the complexes [15].

TABLE -1: Elemental analyses, magnetic movement and electronic spectral data of $2,2'$ bipyridyl (bipy) and 1,10 – phenanthroline (phen) complexes of $Cu(II)$

Compounds	Colour	Elemental Analyses: Found (Calcd.)%				μ_{eff} (B.M)	$\lambda_{max}\,(nm)$
		Cu	C	H	N		
(1) $\left[CuL^1Cl_2\right]$	Bluish Green	21.93(21.85)	41.13(41.32)	2.71(2.77)	9.24(9.63)	1.86	-
(2) $\left[CuL^2Cl_2\right]$	Green	20.20 (20.18)	45.69(45.80)	2.45(2.56)	8.50(8.90)	1.85	712
(3) $\left[CuL^1{}_2Br_2\right].2H_2O$	Deep Green	11.16(11.11)	41.73(41.98)	3.10(3.49)	9.96(9.79)	1.88	750
(4) $\left[CuL^2{}_2Br_2\right].3H_2O$	Green	10.00(9.96)	45.25(45.16)	3.11(3.44)	8.84(8.78)	1.87	740

Here, $L^1 = 2,2'-bipyridyl(bipy)$ and $L^2 = 1,10-phenanthroline(phen)$

Infrared Spectral studies:

The key IR spectral data of complexes (1) to (4), are shown in Table 2. In case of complex (1), 2(*Cu*-*Cl*) bands appear at 281 and 300 cm^{-1} respectively showing the cis position of two *Cl*-atoms in this complex [16]. And the $\nu(Cu-N)$ bands appear at 427 and 485 cm^{-1} respectively [7,17-19]. Similarly in case of complex (2), the two $\nu(Cu-N)$ band appear at 404 and 435 cm^{-1} respectively and that of $\nu(Cu-Cl)$ bands appear at 293 and 318 cm^{-1} respectively showing the occupation of two cis-positions by two *Cl*-atoms. Such cis – position of two *Cl*-toms in complexes (1) and (2) supports their square planar geometry.

In case of complexes (3) and (4), the $\nu(Cu-N)$ bands appear in the range 423-493 cm^{-1}[7,17-19] and that of $\nu(Cu-Br)$ bands appear in the range 245-307 cm^{-1} [16]. Appearance of $\nu(Cu-Br)$ bands at 254 and 292 cm^{-1} for complex (3) indicate the at 245 and 307cm^{-1} for complex (4) indicate linkages of two *Br*-atoms in cis-position in each case[16].

Further, appearance of $\nu(OH)$ bands and $\delta(HOH)$ bands for both complexes (3) and (4) in the ranges 3400 – 3525 cm^{-1} and 1603 - 1650 cm^{-1} respectively indicate the presence of lattice H_2O molecules in case of the complexes (3) and (4) [16,18].

TABLE -2: Key IR spectral bands (cm^{-1}) of Metal Complexes

Metal Complexes	$\nu(OH)$	$\delta(HOH)$	$\nu(Cu-N)$	$\nu(Cu-Cl)/\nu(Cu-Br)$
(1) $\left[CuL^1Cl_2\right]$	-	-	$485(w)$ $427(w)$	$300(w)$ $281(vw)$
(2) $\left[CuL^2Cl_2\right]$	-	-	$435(s)$ $404(w)$	$318(vs)$ $293(s)$
(3) $\left[CuL^1{}_2Br_2\right].2H_2O$	$3525(br)$ $3400(w)$	$1650(vs)$ $1610(vs)$	$440(s)$ $423(ms)$	$292(s)$ $254(w)$
(4) $\left[CuL^2{}_2Br_2\right].3H_2O$	$3520(br)$ $3495(w)$	$1625(ms)$ $1603(w)$	$493(w)$ $437(w)$	$307(s)$ $245(w)$

Here, v=very, s=strong, m=medium, w=weak and br= broad.

Molar Conductance measurements:

The molar conductance values of the complexes in DMF, were found to be of very low values as they were in the range 15-20 $ohm^{-1}cm^2mol^{-1}$. This shows their non – electrolytic nature [14, 20]. Further this establishes the fact that the halide ions $\left(Cl^-\ and\ Br^-\right)$ are directly coordinated with the copper metal in all the complexes.

Thermal Analyses Studies:

When thermal investigation of complex (1) has been carried out under non-isothermal condition, it shows one exothermic peak in DTA at 285^0C but the corresponding TGA curve shows no mass loss (Fig. 1). The peak is probably due to some phase transition. The enthalpy and entropy changes for the phase transition have been evaluated and found to be 47 KJ mol^{-1} and 84 $JK^{-1}mol^{-1}$ respectively. On further heating, the complex $\left[Cu\left(bipy\right)Cl_2\right]$ loses one bipyridyl molecule in the temperature range 293-393^0C. The corresponding DTA curve shows one exotherm at 367^0C. The values of Ea*, ΔH and ΔS for this step are 122 (64 from DTA), 71 $KJmol^{-1}$ and 111$JK^{-1}mol^{-1}$ respectively (Table-3). The probable mechanistic path of decomposition is shown in the Scheme 1.

On heating, the complex (2) undergoes decomposition and is converted into $CuCl_2$ via the formation of the intermediate $\left[Cu\left(phen\right)_{0.5}Cl_2\right]$ in the temperature ranges 300-518 and 518-634^0C. The corresponding DTA curve shows endothermic peaks which appear at 318 and 420, 472^0C (Fig. 1). The activation energy, enthalpy and entropy changes for the first and second step of decompositions are given in Table 3. The probable mechanistic path of decomposition is also shown in the Scheme 1.

TABLE -3: Thermal parameters of $2,2'-bipyridyl(L^1)$ and $1,10-Phenanthroline(L^2)$ complexes of $Cu(II)$
(Values to the nearest whole number)

Decomposition Reactions	Temperature range (^{0}C)	DTA peak temperature (^{0}C)		Ea* $\left(KJmol^{-1}\right)^a$		Enthalpy change, ΔH $\left(KJmol^{-1}\right)$	Entropy Change, $\Delta S\left(JK^{-1}mol^{-1}\right)$
		Endo	Exo	TGA	DTA		
1(a) $\left[CuL^1Cl_2\right] \xrightarrow[Transition]{phase} \left[CuL^1Cl_2\right]$	-	-	285	-	-	47	84
(b) $\left[CuL^1Cl_2\right] \rightarrow CuCl_2$	293-393	-	367	122	64	71	111
2(a) $\left[CuL^2Cl_2\right] \rightarrow \left[CuL^2{}_{0.5}Cl_2\right]$	300-518	318	-	130	-	25	42
(b) $\left[CuL^2{}_{0.5}Cl_2\right] \rightarrow CuCl_2$	518-634	420[b],472	-	202	102	190	274
3(a) $\left[CuL^1{}_2Br_2\right].2H_2O \rightarrow \left[CuL^1{}_2Br_2\right]$	25-90	86	-	-	-	23	64
(b) $\left[CuL^1{}_2Br_2\right] \rightarrow \left[CuL^1Br_2\right]$	90-225	225	-	95	65	146	293
(c) $\left[CuL^1Br_2\right] \rightarrow CuBr_2$	235-372	288[b],343	-	94	65	143	255
4(a) $\left[CuL^2{}_2Br_2\right].3H_2O \rightarrow \left[CuL^2{}_2Br_2\right]$	27-115	105	-	-	-	20	53
(b) $\left[CuL^2{}_2Br_2\right] \rightarrow CuBr_2$	115-588	-	-	66	-	-	-

[a] *In some cases thermodynamic parameters are not possible to evaluate due to some irregular nature of the TGA and DTA curves.*
[b] *DTA peak temperature used for the evaluation of entropy change.*

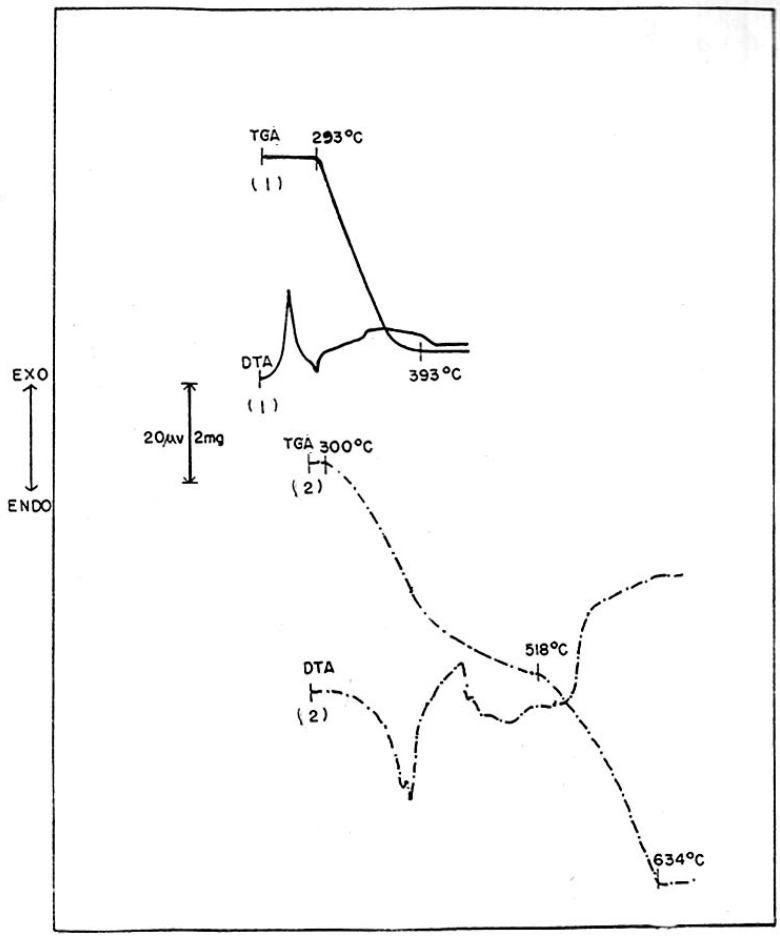


Fig. 1 Thermal curves of [Cu(bipy)Cl2] (1) (——) sample mass 7.1 mg and [Cu(phen)Cl2] (2) (– – –) sample mass 14.3 mg.

On heating, the complex (2) undergoes decomposition and is converted into $CuCl_2$ via the formation of the intermediate $\left[Cu\left(phen\right)_{0.5}Cl_2\right]$ in the temperature ranges 300-518 and 518-634^{0}C. The corresponding DTA curve shows endothermic peaks which appear at 318 and 420, 472^{0}C (Fig. 1). The activation energy, enthalpy and entropy changes for the first and second step of decompositions are given in Table 3. The probable mechanistic path of decomposition is also shown in the Scheme 1.

The complex (3) on heating loses two molecules of lattice water in the temperature range 25-90^{0}C. The corresponding DTA curve shows an endothermic peak at 86^{0}C (Fig.2). The values of enthalpy and entropy changes for the dehydration process were 23KJmol^{-1} and 64JK^{-1}mol^{-1} respectively. On further heating, the complex $\left[Cu\left(bipy\right)_2Br_2\right]$ is converted into $CuBr_2$ via the intermediate $\left[Cu\left(bipy\right)Br_2\right]$ in the temperature ranges 90-235^{0}C and 235-372^{0}C. $\left[Cu\left(bipy\right)Br_2\right]$ has been isolated by keeping the rate of heating at about 1^{0}C min^{-1} in the step 3(b) and is characterized by the usual procedure. For the steps 3(b) and 3(c) the DTA peaks are endothermic and appear at 225 and 288, 343^{0}C. The activation energy for both the steps has been calculated from TGA and DTA and the values are 95 and 65 KJmol^{-1} for step 3(b), and 94 and 65 KJmol^{-1} for step 3(c) (Table 3). The enthalpy changes are calculated and the values are 146 and 143 KJmol^{-1} or the steps 3(b) and 3(c) respectively. The probable mechanistic paths of decompositions are also shown in the scheme1.

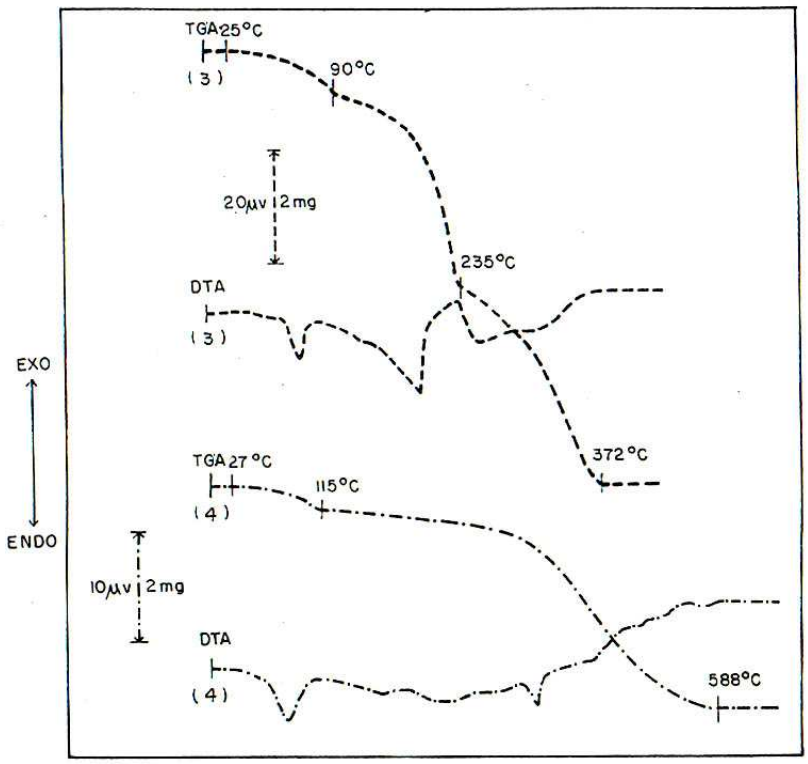
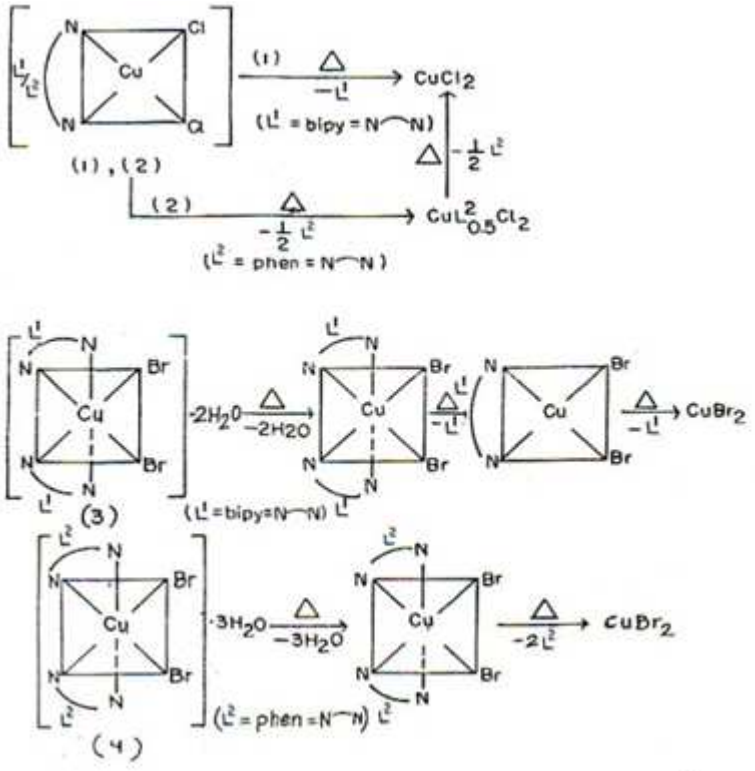


Fig 2 Thermal curves of $[Cu(bipy)_2Br_2].2H_2O$ (3) (----) sample mass 10.7 mg and $[Cu(phen)_2Br_2].3H_2O$ (4) (-·-·-·) sample mass 12.4 mg.



Scheme 1

The complex (4), on heating under non-isothermal condition, first loses three molecules of lattice water in the temperature range 27-115^{0}C and the corresponding DTA curve shows one endotherm and the peak appears at 105^{0}C (Fig.2). The enthalpy and entropy changes for the step 4(a) are 20 KJmol^{-1} and 53JK^{-1}mol^{-1} respectively. The anhydrous complex $\left[Cu\left(phen\right)_2 Br_2\right]$ on further heating, is converted into $CuBr_2$ in the temperature range 115-588^{0}C by losing two molecules of phenanthroline. The activation energy from the TGA curve has been evaluated and its value is 66KJmol^{-1}. The probable mechanistic path of decomposition process is shown in the Scheme 1.

CONCLUSION

$CuCl_2$ and $CuBr_2$ form square planar and distorted octaludral complexes respectively with $2,2'$- bipyridyl as well as 1,10 – phenanthroline, in which the halide ligands are in cis- positions.

Further, the stability order of the complexes on the basis of their therm al decomposition temperature and Ea* (from TGA) follows the trend:

1,10-phenanthroline complex> $2,2'$-bipyridyl complex, which is also the trend in Spectrochemical series.

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