



Thermal Investigation and Stereochemical Studies of Methylamine, Diethylamine and Triethylamine Complexes of Copper(II)

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Methylamine, diethylamine and triethylamine complexes of copper(II) were synthesized. The complexes were characterized by elemental and thermal analysis, infrared and electronic spectra and magnetic moment measurement. They were found to have the following compositions: $[\text{CuL}^1_2\text{Cl}_2] \cdot 5\text{H}_2\text{O}$, $[\text{CuL}^2(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$, $[\text{CuL}^3(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$, $[\text{CuL}^1_2\text{Br}_2] \cdot 2\text{H}_2\text{O}$ and $[\text{CuL}^2_2\text{Br}_2] \cdot 4\text{H}_2\text{O}$, where L^1 = methylamine (MeA), L^2 = diethylamine (DEtA) and L^3 = triethylamine (TEtA). The complexes were found to be four coordinated and appear to possess square planar geometry. Thermal investigation was carried out and stereochemical changes which occurred during thermal investigations, were studied. Thermodynamic parameters such as activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS) for dehydration and decomposition reactions of the complexes were evaluated by using some standard methods. The order of stability of the complexes (with respect to E_a^* from TGA curve) follows the trend: TEtA > DEtA > MeA. The probable mechanistic path of dehydration and decomposition reactions is also shown.

Key Words: Methylamine, Diethylamine, Triethylamine, Cu(II), Thermal analysis, IR and Electronic spectra, Magnetic moment, Activation energy, Enthalpy, Entropy change.

INTRODUCTION

The ligands methylamine (MeA), diethylamine (DEtA) and triethylamine (TEtA) act as unidentate ligands. Although works on the Cu(II) complexes of some of the above mentioned ligands had been reported earlier¹⁻⁴, the composition, in the present cases, differ from that of the earlier. In our best of knowledge, no report is published on the thermal investigation and stereochemical changes of these complexes in the solid state in details. The main aim of the present work is to synthesize and characterize the Cu(II) complexes of methylamine (MeA), diethylamine (DEtA) and triethylamine (TEtA) to carry out their thermal investigation in the solid state for studying stereochemical changes and to evaluate the thermodynamic parameters like activation energy (E_a^*), enthalpy change (ΔH) and entropy change (ΔS). On the basis of basicities of ligands, stability of the complexes with respect to E_a^* have been discussed.

EXPERIMENTAL

Copper(II) chloride (AR Grade), copper(II) bromide pure, methylamine (Aldrich Chemical Co., USA), diethylamine (Merck, Germany) and triethylamine (Merck, Germany) were used as received. Ethanol and diethylether were dried using the standard procedures⁵.

Preparation of complexes

[Cu(MeA)₂Cl₂]·5H₂O (1): A dry ethanolic solution (30 mL) of copper chloride (3 mmol) was intimately mixed with 20 mL of methylamine (6 mmol) and the resulting solution was stirred gently when finegranular complex (blue in colour) separated out. It was filtered, washed with ether and then dried in a desiccators over fused calcium chloride. Yield: ca. 75 %.

[Cu(DEtA)(H₂O)Cl₂]·3H₂O (2) and [Cu(TEtA)(H₂O)Cl₂]·3H₂O (3): To 25 mL of dry ethanolic solution of copper chloride (2 mmol) 15 mL of diethylamine (2 mmol) was added. After mixing the resulting mixture, it was stirred gently. Immediately fine granular purple coloured complex (2) separated out. It was washed with dry ether and dried over fused calcium chloride in a desiccator. Yield: ca. 70 %. Similarly, [Cu(TEtA)(H₂O)Cl₂]·3H₂O (3) which is light green in colour, was prepared in the same way as mentioned above (yield: ca. 75 %).

[Cu(MeA)₂Br₂]·2H₂O (4): This complex was prepared in the same way as mentioned in complex (1) (yield is ca. 70 %).

[Cu(DEtA)₂Br₂]·4H₂O (5): To 25 mL ethanolic solution of CuBr₂ (3 mmol) is added 20 mL of diethylamine (6 mmol) with constant stirring. Immediately purple coloured complex separated out. It was then filtered, washed with ether and dried over fused calcium chloride in a desiccator. Yield: ca. 78 %.

Copper has been gravimetrically estimated by using the standard procedure⁶. C, H and N analyses were done by Perkin-Elmer 240C and Carlo Erba 1106 elemental analysers and results of elemental analyses have been given in Table-1. Qualitative analyses do not respond to the tests for Cl⁻ or Br⁻ showing that they are within the complex zones of the corresponding complexes. Thermal investigations (TGA and DTA) have been carried out on a Shimadzu Thermal Analyzer DT-30 under a dynamic nitrogen atmosphere, with a heating rate of 10 °C min⁻¹ and α -alumina as the standard reference substance. Activation energy (E_a^*) was evaluated from the TGA curve using the equation of Horowitz and Metzger⁷ and from DTA curve using the equation of Borchardt and Daniels⁸. ΔH has been evaluated from the DTA curve using the relation⁸, $\Delta H = KA$, 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 a calibrant) and A is the total area under the particular DTA curve measured with a compensating planimeter with optical tracer of Fuji Corona O27. ΔS was calculated from the relation⁹, $\Delta S = \Delta H/T_m$, T_m being the DTA peak temperature in Kelvin. Infrared and far IR spectra were recorded with Beckman IR 20A and Perkin Elmer 783 spectrometers in KBr and polythene powder discs. Electronic spectra were recorded with the help of the Beckman DU-6 spectrophotometer using ethanol, dimethyl formamide and dimethyl sulphoxide as the reference solvents. The effective magnetic moments were evaluated from magnetic susceptibility measurements with EG and G PAR 155 vibrating sample magnetometer at room temperature. Solid residues obtained after pyrolysis, have been identified with the help of qualitative analyses.

RESULTS AND DISCUSSION

From elemental analyses IR data (Table-1) and electronic spectral data (Table-2) and thermal analyses (Table-3) of the

complexes, it has been confirmed that copper(II) chloride and copper(II) bromide form complexes with methylamine (MeA), diethylamine (DEtA) and triethylamine (TEtA) having the formulae: $[\text{Cu}(\text{MeA})_2\text{Cl}_2] \cdot 5\text{H}_2\text{O}$ (1), $[\text{Cu}(\text{DEtA})(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ (2), $[\text{Cu}(\text{TEtA})(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ (3), $[\text{Cu}(\text{MeA})_2\text{Br}_2] \cdot 2\text{H}_2\text{O}$ (4) and $[\text{Cu}(\text{DEtA})_2\text{Br}_2] \cdot 4\text{H}_2\text{O}$ (5).

Complexes (1), (2), (3), (4) and (5) are blue, purple, light green, blue and purple, respectively and their magnetic moment values are 1.90, 1.75, 1.78, 1.93 and 1.91 BM, respectively (Table-1) showing their mononuclear nature and square planar geometries¹⁰. The λ_{max} (nm) which ranges from 325-704 nm in case of complexes (3) and (5), further support their square planar geometry¹¹.

IR Spectral studies: For complexes (1) to (3), $\nu(\text{Cu-Cl})$ bands appear in the range 353-230 cm⁻¹ and further the *cis*-position of two chlorine atoms in each complex, is indicated by the possession of two $\nu(\text{Cu-Cl})$ bands in each case¹² (Table-2). Similarly the $\nu(\text{Cu-Br})$ bands for complexes (4) and (5) appear in the ranges 300-215 cm⁻¹ as shown in Table-2 and the presence of two $\nu(\text{Cu-Br})$ bands indicate the *cis*-position¹² of the two bromine atoms of both the complexes (4) and (5).

Further, appearance of $\nu(\text{Cu-N})$ bands of complexes (1) to (5) in the range 477-420 cm⁻¹ prove that the amines are co-ordinated to the metal through N-atom¹⁹⁻²¹. Similarly appearance of $\nu(\text{Cu-O})$ bands of complexes (2) and (3) at 615 and 610 cm⁻¹, respectively, established the fact that for these two complexes one H₂O molecule is co-ordinated to the metal atom through O-atom in each complex¹³.

Again presence of lattice water molecules in the five complexes, are indicated by appearance of $\nu(\text{OH})$ and $\delta(\text{HOH})$ in the ranges 3470-3100 and 1630-1575 cm⁻¹, respectively¹² (Table-2) with overlapping of corresponding stretching and bending frequencies of water and amine. From the above IR spectral studies, it has, further, been confirmed that the

TABLE-1
ELEMENTAL ANALYSES, MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF METHYLAMINE (MeA),
DIETHYLAMINE (DEtA) AND TRIETHYLAMINE (TEtA) COMPLEXES OF Cu(II)

Compound	Colour	Yield (%)	Elemental analysis (%): found (calcd.)				μ_{eff} (B.M.)	λ_{max} (nm)
			Cu	C	H	N		
(1) $[\text{CuL}_2^1\text{Cl}_2] \cdot 5\text{H}_2\text{O}$	Blue	75	22.20 (22.16)	8.40 (8.37)	6.71 (6.97)	9.59 (9.77)	1.90	–
(2) $[\text{CuL}^2(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	Purple	70	22.75 (22.71)	17.10 (17.17)	6.65 (6.80)	5.05 (5.00)	1.75	–
(3) $[\text{CuL}^3(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	Light green	75	20.81 (20.64)	23.45 (23.40)	7.50 (7.47)	4.36 (4.55)	1.78	435, 325
(4) $[\text{CuL}_2^1\text{Br}_2] \cdot 2\text{H}_2\text{O}$	Blue	70	19.81 (19.75)	7.96 (7.46)	4.20 (4.35)	8.56 (8.71)	1.93	–
(5) $[\text{CuL}_2^2\text{Br}_2] \cdot 4\text{H}_2\text{O}$	Purple	78	14.51 (14.38)	21.04 (21.73)	6.40 (6.79)	6.66 (6.34)	1.91	704, 355

Here L¹ = methylamine (MeA), L² = diethylamine (DEtA) and L³ = triethylamine (TEtA).

TABLE-2
KEY IR BANDS (cm⁻¹) OF METAL COMPLEXES

Compounds	$\nu(\text{NH}) + \nu(\text{OH})$	$\delta(\text{HNH}) + \delta(\text{HOH})$	$\nu(\text{Cu-O})$	$\nu(\text{Cu-N})$	$\nu(\text{Cu-Cl}) / \nu(\text{Cu-Br})$
(1) $[\text{CuL}_2^1\text{Cl}_2] \cdot 5\text{H}_2\text{O}$	3440 (s, br), 3340 (s, br), 3100 (br)	1610 (w), 1575 (w)	–	475 (s), 455 (w)	318 (m), 255 (w)
(2) $[\text{CuL}^2(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	3450 (ms), 3368 (ms), 3235 (vs)	1625 (br)	615 (w)	465 (br)	353 (w), 315 (s)
(3) $[\text{CuL}^3(\text{H}_2\text{O})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	3440 (s), 3355 (s)	1630 (br), 1605 (w)	610 (s)	477 (m)	315 (w), 230 (w)
(4) $[\text{CuL}_2^1\text{Br}_2] \cdot 2\text{H}_2\text{O}$	3470 (s, br), 3265 (s, br)	1600 (s), 1588 (vw)	–	455 (w), 420 (s, br)	300 (w), 298 (vw)
(5) $[\text{CuL}_2^2\text{Br}_2] \cdot 4\text{H}_2\text{O}$	3400 (br), 3220 (w)	1610 (vs)	–	460 (m), 425 (s, br)	220 (s), 215 (w)

Bands for vibrational frequencies of NH₂ and H₂O [$\nu(\text{NH})/\nu(\text{OH})$ and $\delta(\text{NH}_2)/\delta(\text{H}_2\text{O})$] are overlapped.

TABLE-3
THERMAL PARAMETERS OF METHYLAMINE (L¹), DIETHYLAMINE (L²), TRIETHYLAMINE (L³)
COMPLEXES OF Cu(II) (Values To The NEAREST WHOLE NUMBER)

Decomposition reactions	Temp. range (°C)	DTA peak temperature (°C)		E _a * (KJ mol ⁻¹)*		Enthalpy change*, ΔH (KJ mol ⁻¹)	Entropy change* ΔS (JK ⁻¹ mol ⁻¹)
		Endo	Exo	TGA	DTA		
1(a) [CuL ₂ ¹ Cl ₂].5H ₂ O → CuCl ₂	29-143	95	–	44	40	186	505
2(a) [CuL ² (H ₂ O)Cl ₂].3H ₂ O → [CuL ² (H ₂ O)Cl ₂]	64-157	130	–	141	–	17	42
(b) [CuL ² (H ₂ O)Cl ₂] → CuCl ₂	157 – 320	278	–	67	95	44	80
3(a) [CuL ³ (H ₂ O)Cl ₂].3H ₂ O → [CuL ³ (H ₂ O)Cl ₂]	28-60	48	–	–	102	27	84
(b) [CuL ³ (H ₂ O)Cl ₂] → CuCl ₂	60-150	104	–	79	79	39	103
4(a) [CuL ₂ ¹ Br ₂].2H ₂ O → [CuL ₂ ¹ Br ₂].H ₂ O	27-53	46	–	–	–	9	28
(b) [CuL ₂ ¹ Br ₂].H ₂ O → CuBr ₂	53-170	101	–	–	47	63	168
5(a) [CuL ₂ ² Br ₂].4H ₂ O → [CuL ₂ ² Br ₂]	67-122	110, 114, 120	–	–	–	–	–
(b) [CuL ₂ ² Br ₂] → CuBr ₂	122-374	300, 320, 335, 374	–	59	–	–	–

*In some cases thermodynamic parameters are not possible to evaluate due to some irregular nature of the TGA and DTA curves.

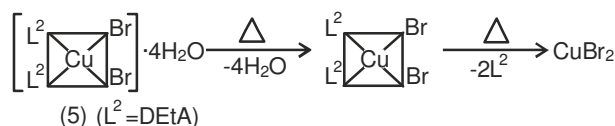
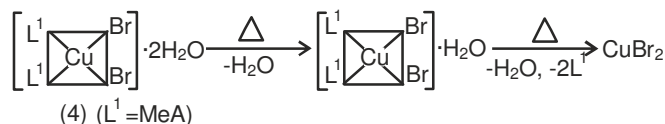
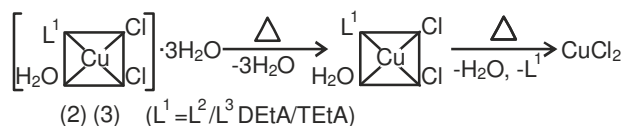
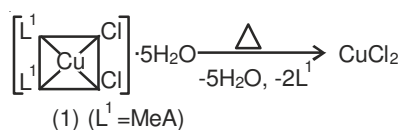
presence of halogen atoms in the *cis*-positions in all the five complexes, support their square planer geometry.

Thermal analysis studies: On heating under non-isothermal condition the complex (1) undergoes dehydration and deamination in a single step in the temperature range 29-143 °C (Fig. 1). The DTA curve shows an endothermic peak at 95 °C. The activation energy evaluated from TGA and DTA curves are 44 and 40 KJ mol⁻¹, respectively (Table-3). Enthalpy change (ΔH) and entropy change (ΔS) are evaluated and tabulated in Table-3. The mechanistic path of decomposition is shown in the **Scheme-I**.

On heating, the complex (2) first losses three molecules of lattice water in the temperature range 64-157 °C. The DTA peak appears at 130 °C and is endothermic (Fig. 1). On further heating, the complex [Cu(DETA)(H₂O)Cl₂] is converted into CuCl₂ in the range 157-320 °C and the corresponding DTA peak appears at 278 °C. Activation energy for the first step (dehydration) is 141 KJ mol⁻¹ and for the second step 67 and 95 KJ mol⁻¹ (from TGA and DTA curves, Table-3). The enthalpy changes for the first and second steps are 17 and 44 KJ mol⁻¹, respectively and the entropy changes are 42 and 80 JK mol⁻¹, respectively. The probable path of decomposition is shown in the **Scheme-I**.

The complex (3), upon heating under non-isothermal condition, is converted into CuCl₂ in two steps (Fig. 1). First step corresponds to loss of three molecules of lattice water in between 28-60 °C and the second step involves the loss of one molecule of triethylamine along with one molecule of coordinated water in the range 60-150 °C. Both the steps in DTA curve are endothermic and the corresponding peaks appear at 48 and 104 °C. The values of activation energy evaluated from the DTA curve for the first step and second step are 102 and 79 KJ mol⁻¹, respectively (both from TGA and DTA curves Table-3). The enthalpy changes for the first and second steps are 27 and 39 KJ mol⁻¹ and the corresponding entropy changes are 84 and 103 J K⁻¹ mol⁻¹, respectively (Table-3). The probable mechanistic path of decomposition reaction is shown in the **Scheme-I**.

When the complex (4) is heated under non-isothermal condition, it losses first one molecule of lattice water in the temperature range 27-53 °C. The corresponding DTA peak is endothermic and appears at 46 °C (Fig. 3). The enthalpy and



Scheme-I: Dehydration and decomposition steps of [CuL¹₂Cl₂].5H₂O (1), [CuL²(H₂O)Cl₂].3H₂O (2), [CuL³(H₂O)Cl₂].3H₂O (3), [CuL¹₂Br₂].2H₂O (4), [CuL²₂Br₂].4H₂O (5)

entropy changes are evaluated and found to be 9 KJ mol⁻¹ and 28 J K⁻¹ mol⁻¹, respectively. Further, on heating the complex [Cu(MeA)₂Br₂].H₂O is converted into CuBr₂ by elimination of one molecule of lattice water and two molecules of methylamine in between 53-170 °C. This is also reflected in the DTA curve and an endothermic peak appears at 101 °C (Fig. 2). The activation energy evaluated from DTA peak is 47 KJ mol⁻¹. The enthalpy and entropy changes are also calculated and the values are 63 KJ mol⁻¹ and 168 J K⁻¹ mol⁻¹, respectively. The probable mechanistic path of decomposition is also shown in the **Scheme-I**.

The complex [Cu(DEtA)₂Br₂].4H₂O (5) on heating, loses four molecules of lattice water in one step in the temperature range 67-122 °C as observed in the TGA curve. The corres-

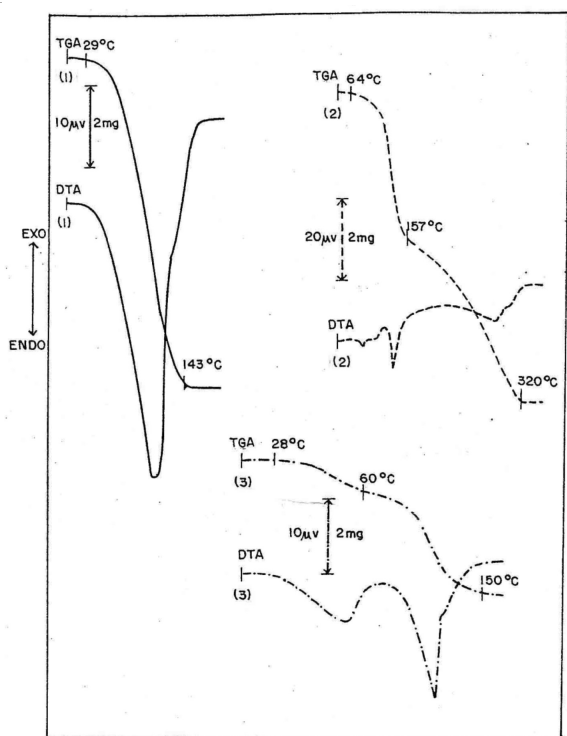


Fig. 1. Thermal curves of $[\text{Cu}(\text{MeA})_2\text{Cl}_2]\cdot 5\text{H}_2\text{O}$ (1) (—) sample mass 15.1 mg; $[\text{Cu}(\text{DEtA})(\text{H}_2\text{O})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (2) (---) sample mass 11.8 mg and $[\text{Cu}(\text{TEtA})(\text{H}_2\text{O})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (— · —) sample mass 7.9 mg

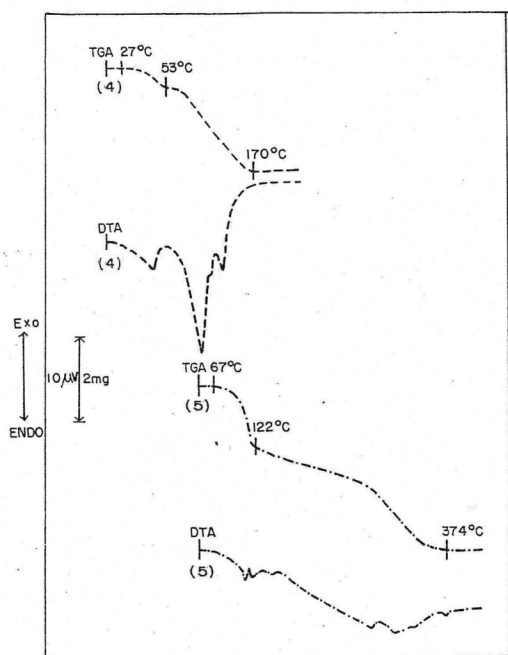


Fig. 2. Thermal curves of $[\text{Cu}(\text{MeA})_2\text{Br}_2]\cdot 2\text{H}_2\text{O}$ (4) (---) sample mass 10.8 mg; $[\text{Cu}(\text{DEtA})_2\text{Br}_2]\cdot 4\text{H}_2\text{O}$ (— · —) sample mass 7.2 mg

ponding DTA curve contains three endothermic peaks which appear at 110, 115 and at 120 °C, respectively (Table-3). On further heating, the complex $[\text{Cu}(\text{DEtA})_2\text{Br}_2]$ is converted into

CuBr_2 by losing two molecules of diethylamine in the temperature range 122–374 °C. The corresponding DTA curve shows four endothermic peaks (Fig. 2 and Table-3). Activation energy for this step has been evaluated from the TGA curve and the value is 59 KJ mol^{-1} . The probable mechanistic path of decomposition is shown in the **Scheme-I**.

The probable mechanistic paths of dehydration and decomposition reactions which are based on mass loss from TGA curves of the complexes (1) to (5), are shown in **Scheme-I**.

Conclusion

All the complexes $[\text{Cu}(\text{MeA})_2\text{Cl}_2]\cdot 5\text{H}_2\text{O}$ (1), $[\text{Cu}(\text{DEtA})(\text{H}_2\text{O})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (2), $[\text{Cu}(\text{TEtA})_2(\text{H}_2\text{O})\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (3), $[\text{Cu}(\text{MeA})_2\text{Br}_2]\cdot 2\text{H}_2\text{O}$ (4), $[\text{Cu}(\text{DEtA})_2\text{Br}_2]\cdot 4\text{H}_2\text{O}$ (5) possess square planar geometry. No systematic conclusion is possible to draw with respect to thermal stability and activation energy but following results are noteworthy *e.g.*, in case of amine complexes of CuCl_2 , the order of stability follows the trend: $\text{TEtA} > \text{DEtA} > \text{MeA}$. Similarly in case of amine complexes of CuBr_2 , the order of stability follows the trend: $\text{DEtA} > \text{MeA}$. Such stability trend may be due to the decreasing basicity of the ligands in the order: $\text{TEtA} > \text{DEtA} > \text{MeA}$. Higher the basicity of the ligand, the more is the stability of the complex¹⁴.

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