



## A THERMAL ANALYSIS STUDY OF 1, 2-DIPIPERIDINOETHANE COMPLEXES OF COBALT, NICKEL, MERCURY AND CADMIUM BY TG-DTG-DTA TECHNIQUES

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A number of complexes of the general formula  $ML_2$ , ( $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Hg(II)}$ ;  $L = 1,2\text{-dipiperidinoethane (DPE)}$ ) were prepared and studied by means of thermogravimetry (TG) and differential thermal analysis (DTA). Their compositions were investigated by elemental analysis to ensure their purity and structural elucidations were based on conductivity measurements, room temperature magnetic measurements, proton NMR, and IR spectra. Thermal decomposition of these distorted tetrahedral complexes and their ligand took place in two distinct steps upon heating up to  $760^\circ\text{C}$ , with the loss of inorganic and organic fragments. The thermal degradation of all the complexes in static air atmosphere started at temperatures lower than those observed for the free ligand degradation. The composition of intermediates formed during degradation was confirmed by microanalysis and IR spectroscopy. The residues after heating above  $600^\circ\text{C}$  corresponded to metal oxide except for  $\text{Hg(II)}$  complex, which behaved differently. It is found that thermal stability of the complexes increases in the following sequence:

$\text{Hg(II)} < \text{Ni(II)} < \text{Co(II)} < \text{Cd(II)}$

**Keywords :** DPE,  $M(\text{DPE})_2$  Complexes, Physicochemical study, Thermal degradation

### 1. Introduction

Much work is currently being carried out on the preparation and characterization of  $[M(L)X_2]$  and  $[M(L)(\text{NO}_3)_2]$ , where  $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$  and  $\text{Cd(II)}$ ,  $X = \text{Cl}, \text{Br}$  and  $L = 1,3\text{-dipiperidino-propane (DPP)}$  or  $1,2\text{-dipiperidinoethane (DPE)}$  [1-2]. Thermal properties of these complexes have been investigated by S. Rehman et al. and M. Arshad et al. [3-5] to understand the mechanisms of decomposition and the nature of decomposition products. The preparation, characterization and thermal properties of the complexes with the composition  $ML(\text{NO}_3)_2$ , where  $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$  and  $\text{Cd(II)}$ ;

$L = (\text{CH}_2\text{NC}_5\text{H}_{10})_2$  (1,2-dipiperidinoethane) have already been presented [5].

Thermogravimetry (TG) and differential thermal analysis (DTA) are valuable techniques for studying the thermal properties of various compounds. However, no systematic study has been made of the thermal behavior for the metal complexes of 1,2-dipiperidinoethane. This work is a continuation of the series of studies on the thermal decomposition of complexes formed between transition metals and DPP or DPE. The 1,2-dipiperidinoethane is a biologically active molecule which has been used as a neurotoxic agent due to in vivo conversion to a selective

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cholinesterase inhibitor. Administration produces seizures and central nervous system lesions [6-9]. In the present work, the preparation, characterization and thermal properties of metal complexes of the type  $M(\text{DPE})_2$ , where  $M = \text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Cd(II)}$ , and DPE have been described.

## 2. Experimental

Salts of transition metals and other chemicals were of analytical grade and used without further purification. Solvents were distilled before use. The partial dehydration of metal salts was carried out in vacuum oven for several hours around 80-100 °C.

### 2.1. Synthesis of 1,2-dipiperidinoethane

The ligand was synthesized as reported [10]. Briefly, piperidine (0.25 mole) in absolute ethanol (40 ml) was added drop-wise to 0.1 mole of 1,2-dibromoethane in ethanol (20 ml). The contents were refluxed for about 8 hours at 80 °C. The reaction mixture was left overnight to get dipiperidinoethane dihydrobromide crystals with a yield of 80%.

### 2.2. Preparation of ligand solution

The ligand 1,2-dipiperidinoethane dihydrobromide was dissolved in minimum amount of methanol to which a calculated amount of alcoholic potassium hydroxide was added. Potassium bromide, which precipitated immediately was removed by filtration. The filtrate was used as a ligand solution.

### 2.3. Synthesis of solid complexes

All the complexes were prepared using similar general procedure [1]. Approximately 10 m moles of partially dehydrated salt was dissolved in a minimum amount of anhydrous solvent. Ethanol was used as solvent for the synthesis of all the metal complexes. The ligand (sufficient to exceed a 1:2 ligand to metal ratio) was also dissolved in minimum amount of the same solvent and slowly added to the hot metal salt solution with constant stirring. The mixture was stirred and kept at 50 °C for half an hour, then cooled for about 20 minutes. The metal complexes precipitated either immediately or on cooling. Complexes were washed thrice with ether and dried under vacuum at 50 °C.

### 2.4. Physicochemical techniques

The metal contents and anion were determined by using standard analytical procedures [11-12]. Carbon, hydrogen and nitrogen were determined

using CHN analyzer, Carloerba Mod. 1106. The infrared spectra of the complexes and those of intermediates of their thermal decomposition were recorded on a PYE UNICAM infrared spectrophotometer in the range of 4000-400  $\text{cm}^{-1}$  using KBr discs. Ultraviolet and visible absorption spectra of complexes were obtained on Jasco DEC-1 Spectrophotometer with 1 cm matched quartz cells in the range of 200-900 nm using various solvents. Mass spectra of the ligand were measured on MAT 312 mass spectrometer, whereas proton NMR spectra were recorded with Bruker (AM-300) instrument using tetramethyl silane (TMS) as internal standard. Chemical shifts are reported as  $\delta$  (ppm) values. The molar conductance of the solution of complexes was measured on a conductivity meter type HI 8333. All the measurements were carried out at room temperature using freshly prepared solutions. The magnetic susceptibilities data on the complexes were determined by Guoy method at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a standard. The magnetic moments were calculated using Pascal's constants [13]. The thermoanalytical measurements were carried out with NETZSCH simultaneous thermal analyzer STA 429. Samples were contained in an aluminum crucible Al 203 (8 mm dia  $\times$  10 mm depth) with central base recess. The crucible was then adjusted on palladium/ruthenium crucible support platform, which gave a proportional signal to the recorder and computer interface to plot the weight loss of sample against temperature.

## 3. Results and Discussion

The results of the elemental analysis are presented in Table 1, which indicated the expected composition of the complexes. The proton NMR of 1,2-dipiperidinoethane in  $\text{D}_2\text{O}$  with TMS as internal standard showed a singlet at 1.55 ppm for terminal hydrogen, a singlet at 1.75 ppm for 8 hydrogens attached to the ring carbons, a singlet at 3.20 ppm for 8 hydrogens attached to the ring carbons adjacent to nitrogen atoms and a singlet for 4 ethyl hydrogens at 3.70 ppm. The IR spectrum of DPE showed vibrations in the range of 2990-2880  $\text{cm}^{-1}$  and 1228-1070  $\text{cm}^{-1}$ , which indicated the presence of C-H and C-N bonds in the molecule, respectively [14-15]. A mass peak of moderate intensity at  $m/Z$  196 corresponding to a molecular ion  $(\text{C}_{12}\text{H}_{24}\text{N}_2)^+$  was observed in the spectrum of DPE. The base peak at  $m/Z$  98 is probably due to the formation of N-methyl piperidine cation radical, while the signals at  $m/Z$  112 could be assigned to N-ethyl piperidine

Table 1. Analytical data for 1, 2-dipiperidinoethane and investigated complexes.

Composition	Appearance	% C Found	% H Found	% N Found	% Metal	% Anion
$(\text{CH}_2\text{NC}_5\text{H}_{10})_2(\text{HBr})_2$ (DPE)	White	40.33 *(40.24)	7.75 (7.26)	7.56 (7.82)	--	--
$\text{Co}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ (I)	Bluish Green	---	---	---	11.27 (11.59)	49.72 (49.89)
$\text{Ni}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ (II)	Green	---	---	---	11.59 (11.55)	49.73 (49.91)
$\text{Hg}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ (III)	White	---	---	---	30.00 (30.84)	39.13 (39.02)
$\text{Cd}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ (IV)	Dirty White	---	---	---	19.63 (19.99)	44.87 (45.14)

\*Figures in parentheses are the calculated values

fragment due to loss of piperidine moiety which appeared at  $m/z$  84. The ligand 1,2-dipiperidinoethane behaves as a bidentate ligand and bears resemblance to 1,2-dimorpholinoethane (DME) [16-18]. The data shown in Table 1 indicate that only one DPE molecule like DME is found to coordinate with metal ion and form complexes of the general formula  $\text{M}(\text{DPE})\text{I}_2$ , where  $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Hg}(\text{II}), \text{Cd}(\text{II})$  and DPE = 1,2-dipiperidinoethane. The complexes soluble in DMSO are  $\text{CoLI}_2$  and  $\text{NiLI}_2$  while  $\text{HgLI}_2$  and  $\text{CdLI}_2$  are soluble in acetone (Table 2). Infrared spectra

of metal complexes clearly indicate that C-N stretchings are shifted to lower and in some cases to higher frequencies with changes in sharpness and intensities. In these complexes the bands at 1170 and 1130  $\text{cm}^{-1}$  which are assigned to C-N stretching vibrations, appear to have been split into four distinct bands. The strong one moves to lower side and is observed at about 1108  $\text{cm}^{-1}$  whereas the other two weak bands shift toward higher side and appear at 1172 and 1160  $\text{cm}^{-1}$  (Table 3). The shifts are almost to the same extent with minor variations in position and intensities. This is caused by the withdrawal of electron density from C-N bond where nitrogen atom becomes coordinated to the metal ion. Thus, DPE behaves as a bidentate ligand like substituted ethylenediamine coordinating through nitrogen atoms. The molar conductance (Table 2) values, ranging from 8.76 to 10.83  $\text{mS cm}^{-1}$ , show that complexes are non-electrolytic in these media and clearly reveal that anions are coordinated with the metal atoms. The magnetic moment of  $\text{Co}(\text{II})$  complex is 4.75 BM, which is characteristic value for the presence of three unpaired electrons, while that for  $\text{Ni}(\text{II})$  complex it is 3.29 BM, indicating the presence of two unpaired electrons. The solution spectra of  $\text{Co}(\text{II})$  complex exhibited two bands, which could be assigned to transition  ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_1(\text{P})$ , for  $\nu_3$  in Td symmetry. The low energy transition,

Table 2. Molar conductance and magnetic moment for complexes,  $\text{M}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ 

Complex	Solvent	Molar Conductance ( $\text{mS mol}^{-1}$ )	$\mu_{\text{eff}}$ (BM)
I	DMSO	10.64	4.75
II	DMSO	10.83	3.29
III	Acetone	10.44	--
IV	Acetone	8.76	--

DMSO = Dimethyl sulphoxide

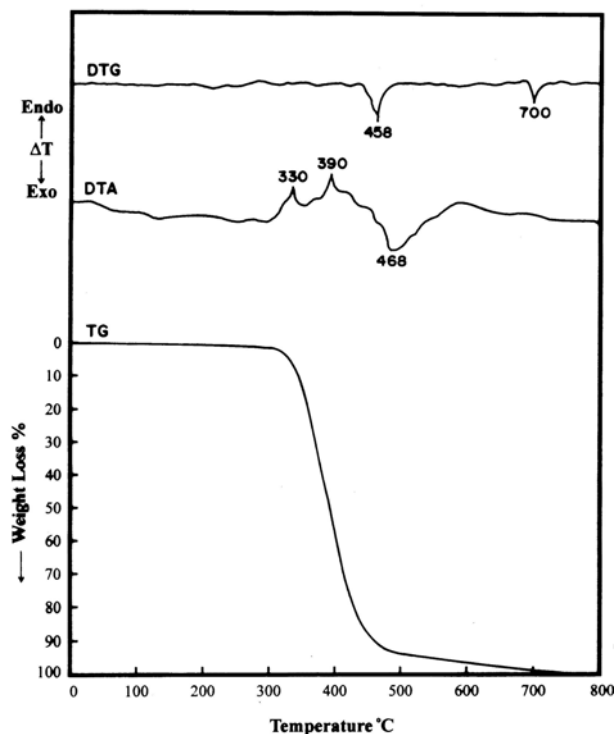
Table 3. IR spectra for DPE and its metal complexes.

Compound	IR Spectra $\text{cm}^{-1}$
	$\nu(\text{C-N})$
DPE	1150s, 1135w
I	1170m, 1160vw 1130sh, 1120vs
II	1175m, 1160vw 1132vw, 1115vs
III	1172m, 1155w 1135sh, 1125vs
IV	1172w, 1160w 1130w, 1106vs

m = medium, s = sharp, w = wide, vw = very wide,  
sh = shoulder vs = very sharp

${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_2(\text{P})$ ,  $\nu_2$  was not observed. The intensities and band widths are in accordance with the Td symmetry [18]. The non-electrolytic behaviour and high spin type magnetic moments of 3.29 BM for Ni(II) complexes are clearly indicative of Td coordination geometry with iodide ion as a unidentate ligand and the strong bands observed can be assigned to transition,  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$ ,  $\text{V}_3$  in tetrahedral symmetry [20]. The solution spectra of copper nitrate complex exhibited only two bands. The electronic transitions are consistent with  $\text{C}_{2v}$  symmetry and are in the range  $12000 - 22000 \text{ cm}^{-1}$ . Four transitions are to be expected but only two were observed. Similar spectra were observed for other copper (II) complexes having  $\text{CuN}_2\text{X}_2$  chromophore vibrations [19].

The thermal curves (TG, DTG and DTA) of 1,2-dipiperidinoethane and its complexes were recorded in static air atmosphere from ambient to  $800^\circ\text{C}$  presented in Figs. 1-5. The characteristic data and stages of pyrolysis regarding the thermal behaviour of ligand (DPE) and its complexes (I, II, III and IV) are given in Table 4. The TG and DTA curves reveal that the ligand 1,2-dipiperidinoethane (DPE) decomposes in two steps in the temperature range  $320^\circ\text{C} - 720^\circ\text{C}$  (Fig.1). In the first step, the ligand loses piperidine and N-methylenepiperidine by the breakage of C-N and C-C bonds around  $320 - 460^\circ\text{C}$  with an accompanying endothermic effect and the

Figure 1. Thermal curves of  $(\text{CH}_2\text{NCH})_2$  in air atmosphere.

intermediate is then decomposed exothermally in the temperature range  $460 - 720^\circ\text{C}$  (2nd step) liberating methylene group. The first endothermic peak at about  $330^\circ\text{C}$  may be attributed to the phase changes during the melting and second sharp endothermic peak at  $390^\circ\text{C}$  corresponds to the loss of two species. The second step is slower one and ascribed to the oxidation and vaporization of methylene indicating that pyrolysis is exothermic in nature. Heating of sample above  $700^\circ\text{C}$  leaves no final residue. The sequence of loss is comparable with mass spectrum [1,9].

The thermal decomposition of  $\text{Co}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$  (I) takes place in the temperature range of  $200 - 560^\circ\text{C}$  (Fig. 2). The first step involves decomposition ( $200 - 390^\circ\text{C}$ ) in which the complex loses N-methylene piperidine. In the second stage, the intermediate decomposes further with the evolution of  $-\text{CH}_2\text{NC}_5\text{H}_{10}$  moiety of the ligand followed by the decomposition and evolution of  $\text{I}_2$  leaving  $\text{CoO}$  as final residue.

The complex,  $\text{Ni}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$  (II), loses N-methylenepiperidine moiety in the temperature range  $190 - 340^\circ\text{C}$  and for this decomposition, the DTA curve shows one endothermic peak at  $328^\circ\text{C}$  (Fig. 3). The intermediate is not stable at this temperature and as the temperature is raised, the

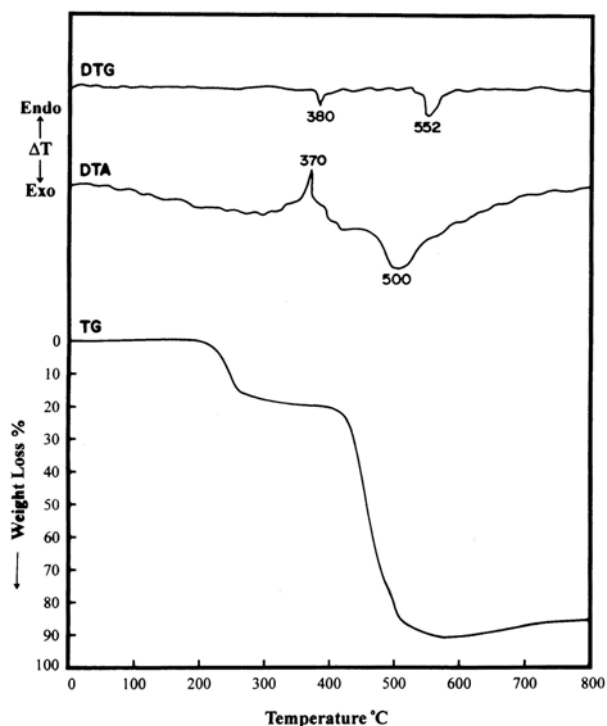


Figure 2. Thermal curves of  $\text{Co}(\text{CH}_2\text{NC}_5\text{H}_{10})_2 \cdot \text{I}_2$  in air atmosphere

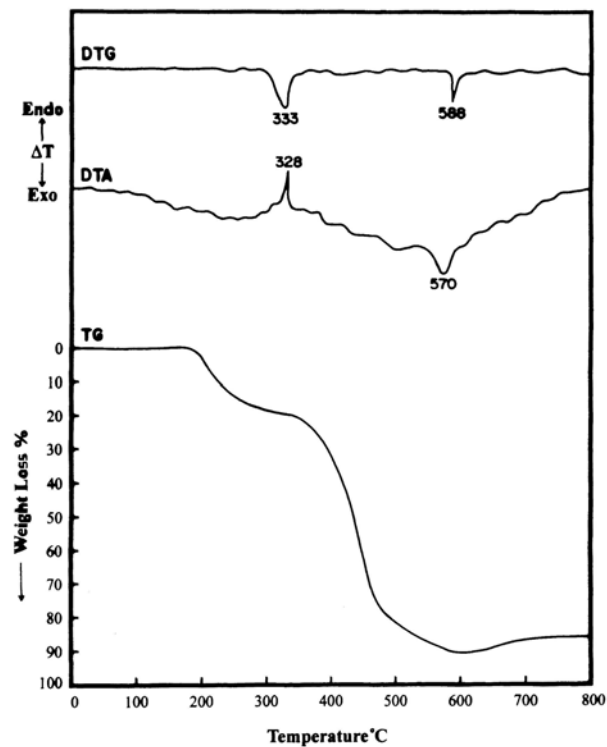


Figure 3. Thermal curves of  $\text{Ni}(\text{CH}_2\text{NC}_5\text{H}_{10})_2 \cdot \text{I}_2$  in air atmosphere

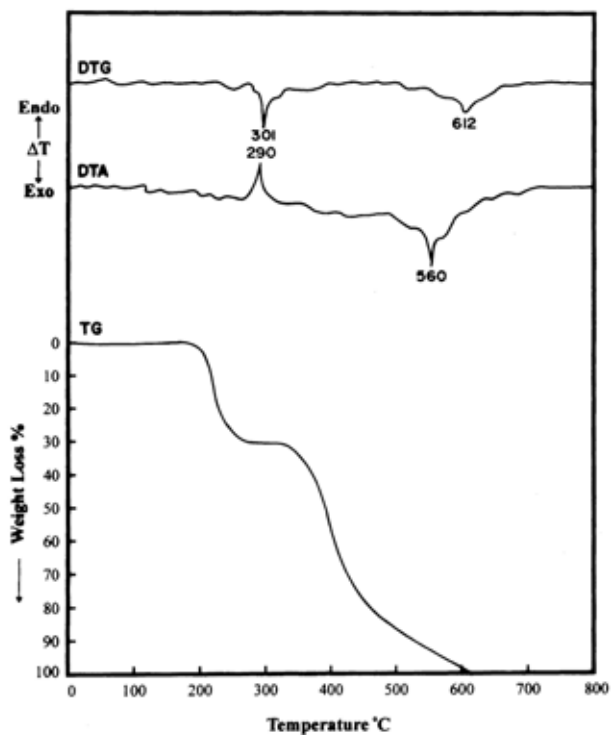


Figure 4. Thermal curves of  $\text{Hg}(\text{CH}_2\text{NC}_5\text{H}_{10})_2 \cdot \text{I}_2$  in air atmosphere

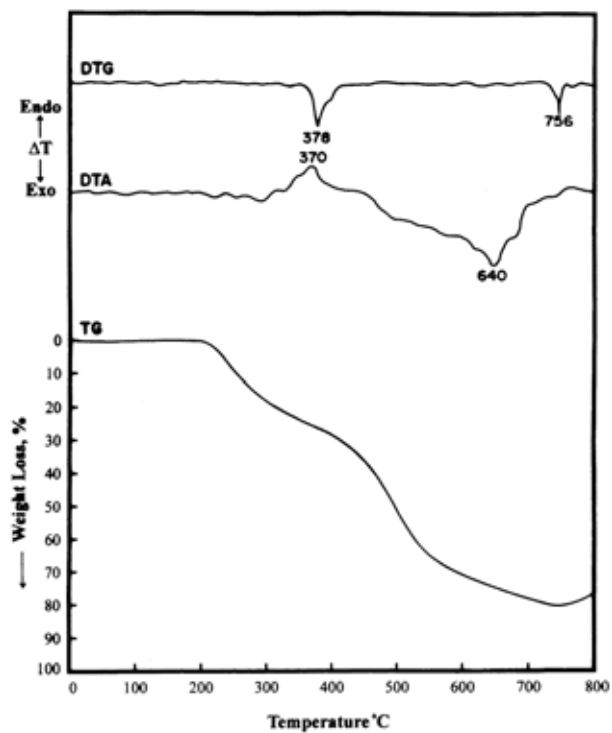


Figure 5. Thermal curves of  $\text{Cd}(\text{CH}_2\text{NC}_5\text{H}_{10})_2 \cdot \text{I}_2$  in air atmosphere.

Table 4. Thermoanalytical results for the complexes,  $M(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$ .

Compound	DTA Peak Temp. °C	TG	Weight Loss, %		Phenomena
		Temperature range, °C	Calc.	Found	
DPE	330(-), 390(-)	320-460	92.85	91.84	$\text{C}_5\text{H}_{11}\text{N}$ , $\text{C}_6\text{H}_{12}\text{N}$ - $\text{CH}_2$ -
	468(+)	460-720	7.14	8.00	
I	370(-)	200-390	19.26	20.34	$\text{C}_6\text{H}_{12}\text{N}$ $\text{C}_6\text{H}_{12}\text{N} + \text{I}_2$ CoO
	500(+)	390-560	69.15	69.72	
	--	>560	14.72	14.89	
II	328(-)	190-340	19.27	20.21	$\text{C}_6\text{H}_{12}\text{N}$ $\text{C}_6\text{H}_{12}\text{N} + \text{I}_2$ NiO
	570(+)	340-600	69.18	69.56	
	--	> 600	14.69	15.03	
III	290(-)	180-310	30.13	30.69	$2\text{C}_6\text{H}_{12}\text{N}$ Hg + $\text{I}_2$
	560(+)	310-620	69.86	69.31	
IV	370(-)	210-390	34.86	35.06	$2\text{C}_6\text{H}_{12}\text{N}$ $\text{I}_2$ CdO
	640(+)	390-760	45.14	45.77	
	--	>760	22.83	23.11	

Temp. = Temperature, Calc. = Calculated (-) = Endothermic (+) = Exothermic

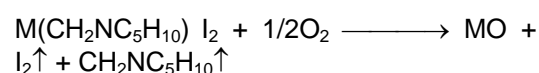
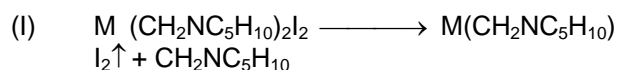
complex decomposes further and finally yields a residue of NiO.

The DPE moiety begins to come off in the temperature range of 180-310 °C (first step) for the complex,  $\text{Hg}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$  (III). Further decomposition of the complex occurs in second step in the range 310-620 °C (Fig. 4) which shows no end product. The DTA curve shows endothermic and exothermic peaks at 290 °C and 560 °C respectively, corresponding to the first and the second step of the TG curve.

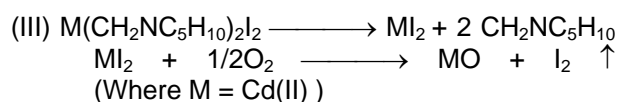
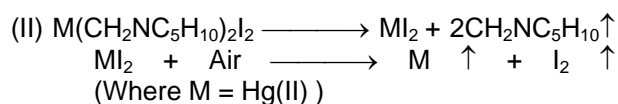
When heated in a static air atmosphere, the  $\text{Cd}(\text{CH}_2\text{NC}_5\text{H}_{10})_2\text{I}_2$  (IV) is stable upto 210 °C and begins to decompose in two steps in the temperature range 210-760 °C (Fig. 5). Endothermic and exothermic peaks accompany the decomposition processes at 370 °C and 640 °C respectively. Heating the sample above 760 °C leaves the respective metal oxide as residue [21-23].

On the basis of observed thermal decomposition studies, it can be inferred that all the complexes undergo thermal decomposition in

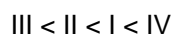
two steps according to the following general equations:



(Where M = Co(II) and Ni(II) )



While comparing the thermal stabilities of complexes on the basis of initial temperature of decomposition [24-25], the following sequence of increasing thermal stability was observed.



The highest thermal stability is displayed by the complex IV. The solid residues comprised 14-24 % of the initial mass (except for Hg (II) complex) and elemental analysis indicated that these were pure metal oxides.

#### 4. Conclusions

1. The available experimental data allow to suggest that the prepared complexes of different metals as well as ligand decompose in a two-step process.
2. All the complexes possessing distorted tetrahedral geometry show almost a similar decomposition pattern (except for ligand and Hg(II) complex, which behave differently) with the evolution of inorganic and organic fragments when heated above 700 °C leaving corresponding metal oxides as residue.
3. Ligand appears to be more stable than the complexes as it exhibits higher initial decomposition temperature.
4. The coordination of metal ion to ligand is responsible for weakening of the system, that's why complexes start losing weight at lower temperatures and at a faster rate, and consequently, decomposition of complexes is completed earlier than that of pure ligand.
5. The intermediate products are not stable over a long range of temperature and decompose soon after their formation.
6. Cadmium complex shows greater thermal stability, probably owing to the lower distortion of the tetrahedral structure and the smaller size of cadmium ions [26].

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