A thermal analysis study of 1,2-dipiperidinoethane complexes of cobalt, nickel, copper, zinc and cadmium by TG–DTG–DTA techniques

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Abstract

A number of complexes of the general formula $ML(NO_3)_2$, (M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); L = 1, 2-dipiperidinoethane (DPE)) were prepared and studied by means of TG–DTG–DTA techniques. Their compositions were investigated by elemental analysis in order to ensure their purity and structural elucidations were based on conductivity measurements. room temperature magnetic measurement, 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 720°C with the loss of inorganic and organic fragments and show almost the same mode of decomposition. The thermal degradation of all the complexes in static air atmosphere starts at temperature lower than observed for free ligand degradation. The composition of intermediates formed during degradation was confirmed by microanalysis and IR spectroscopy. The residues after heating above 600°C correspond to metal oxide. It follows from the results that thermal stability of the complexes increases in the following sequence: Ni(II) < Co(II) < Cu(II) < Zn(II) < Cd(II). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Much work is currently being carried out on the preparation and characterisation of $[M(L)X_2]$ and $[M(L)(NO_3)_2]$, where M = Co(II), Ni(II), Zn(II) and Cd(II), X = Cl, Br and L = 1, 3-dipiperidino-propane (DPP) or 1,2-dipiperidinoethane (DPE) [1,2]. We have also investigated their thermal properties [3–5] to understand the mechanisms of decomposition and the nature of decomposition products. In a previous paper, we have already described the preparation, characterisation and thermal properties of the complexes with the composition $ML(NO_3)_2$, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II);

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L $= CH_2(CH_2NC_5H_{10})_2$ (1,3-dipiperidinoproprane)
[5].
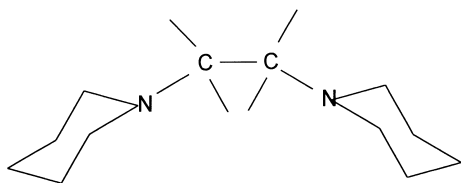
1,2-Dipiperidinoethane(DPE)

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 behaviour for the metal complexes of 1,2-dipiperidinoethane. The preparation and characterisation of these metal complexes by elemental analysis, IR spectroscopy, UV visible spectroscopy, conductance and magnetic susceptibility studies were reported earlier [1]. This work is a continuation of the studies [3,5] on the thermal decomposition of complexes formed between transition metals and DPP. In the present work, we describe the preparation, characterisation and thermal properties of metal complexes of the type $M(DPE)(NO_3)_2$, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and DPE $= 1, 2$-dipiperidinoethane.

2. Experimental

2.1. Reagents

Salts of transition metals and other chemicals obtained from standard source suppliers 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 at 80–100°C.

2.2. Synthesis of 1,2-dipiperidinoethane

The ligand was synthesised by the reported method [6]. Briefly, piperidine (0.25 mol) in absolute ethanol (40 ml) was added drop wise to 0.1 mol of 1,2-dibromoethane in ethanol (20 ml). The contents were refluxed for about 8 h at 80°C. The reaction mixture

was left overnight to get dipiperidinoethane dihydrobromide crystals with a yield of 80%.

2.3. 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 ligand solution.

2.4. Synthesis of solid complexes

All the complexes reported were prepared using similar general procedure. Approximately 10 mmol of partially dehydrated salt was dissolved in 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 min. The metal complexes precipitated either immediately or on cooling. They were washed thrice with ether and dried under vacuum at 50°C.

2.5. Analysis procedures and instrumentation

2.5.1. Elemental analysis

The metal contents were determined by reported procedures [7,28], whereas nitrate ion are determined by phenoldisulfonic acid method [8]. Carbon, hydrogen and nitrogen were determined with CHN analyser, Carloerba Mod. 1106.

2.5.2. Infrared spectra

The infrared spectra of the complexes and those of intermediates of their thermal decomposition were recorded with PYE UNICAM infrared spectrophotometer in the range 4000–400 cm^{-1} using the KBr discs.

2.5.3. UV and visible absorption spectra

Ultra violet and visible absorption spectra of complexes were obtained on Jasco DEC-1

Table 1
Analytical data for 1,2-dipiperidinoethane and its metal complexes

Compound	Composition	Appearance	Decomposition point (°C)	%C Found	%H Found	%N Found	Metal (%)	Anion (%)
–	DPE(HBr)$_2$	White	340	40.33 (40.24)[a]	7.75 (7.26)	7.56 (7.82)	–	–
I	Co(DPE)(NO$_3$)$_2$	Bluish green	207	38.22 (38.00)	6.21 (6.33)	15.09 (14.77)	15.37 (15.55)	32.49 (32.72)
II	Ni(DPE)(NO$_3$)$_2$	Green	179	38.27 (38.02)	6.55 (6.33)	15.13 (14.78)	15.27 (15.50)	32.41 (32.74)
III	Cu(DPE)(NO$_3$)$_2$	Green	210	37.09 (37.54)	6.49 (6.25)	14.85 (14.60)	16.26 (16.56)	32.06 (32.33)
IV	Zn(DPE)(NO$_3$)$_2$	White	241	37.15 (37.56)	6.97 (6.26)	14.31 (14.60)	16.37 (16.52)	32.39 (32.34)
V	Cd(DPE)(NO$_3$)$_2$	White	266	33.13 (33.30)	5.67 (5.55)	13.23 (12.95)	25.72 (25.99)	28.13 (28.67)

[a] Figures in parentheses are the calculated values.

spectrophotometer with 1 cm matched quartz cells in the range 200–900 nm using various solvents.

2.5.4. Mass and NMR spectra

Mass spectra of the ligand was measured on MAT 312 mass spectrometer, whereas proton NMR spectra were recorded with Bruker (AM-300) instrument using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported as δ (ppm) values.

2.5.5. Molar conductance

The molar conductance of the solution of complexes was measured on a conductivity meter type HI 8333. All the measurements were taken at room temperature on freshly prepared solutions.

2.5.6. Magnetic susceptibilities

The magnetic susceptibilities data on the complexes were determined by Guoy method at room temperature using $Hg[Co(SCN)_4]$ as standard. The magnetic moments were calculated using Pascal's constants [9].

2.5.7. Thermal measurement

The thermoanalytical measurements were carried out with Netzsch simultaneous thermal analyser STA 429. Samples were contained in an aluminium crucible Al 203 (8 mm dia × 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.

Table 2
Values of molar conductance, magnetic moment for complexes, $M(DPE)(NO_3)_2$

Complex	Solvent	Molar conductance (mS mol^{-1})	μ_{eff} (BM)
I	DMSO[a]	12.16	4.34
II	DMSO	12.32	3.15
III	Nitromethane	12.71	2.22
IV	Acetone	9.63	–
V	Acetone	9.88	–

[a] Dimethyl sulphoxide.

3. Results and discussion

The results of the elemental analysis (Table 1) proved the expected composition of the complexes. The proton NMR of 1,2-dipiperidinoethane in D_2O with TMS as internal standard showed a singlet at 1.55 ppm for terminal hydrogen, a singlet at 1.75 ppm for eight hydrogens attached to the ring carbons, a singlet at 3.20 ppm for eight hydrogens attached to the ring carbons adjacent to nitrogen atoms and a singlet for four ethyl hydrogens at 3.70 ppm. The IR spectrum of DPE showed vibrations in the range 2990–2880 cm^{-1} and 1228–1070 cm^{-1}, which indicate the presence of C–H and C–N bonds in the molecule, respectively [10,11]. A mass peak of moderate intensity at *m/z* 196 corresponding to molecular ion $(C_{12}H_{24}N_2)^+$ 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

Table 3
Maxima of absorption bands in electronic and IR spectra for DPE complex (m: medium, s: sharp, w: wide, vw: very wide, sh: shoulder)

Complex	Maxima of absorption bands			
	Electronic spectra		IR spectra (cm^{-1})	
	λ_{max} (nm)	v (cm^{-1})	ε_{max} (M^{-1} cm^{-1})	v (C–N)
I	655	15,270	367	1175m, 1165w, 1130vw, 1105s
	405	24,690	57	
II	645	15,500	158	1172m, 1165vw, 1135sh, 1112s
	510	19,610	243	
	665	15,040	177	
III	685	14,600	52	1175m, 1165vw, 1135sh, 1112vs
	445	22,470	165	
IV	–	–	–	1175w, 1165vw, 1135vw, 1110vs
V	–	–	–	1175m, 1165vw, 1138vw, 1110s

the signals at *m/z* 112 could be assigned to *N*-ethyl piperidine 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) [12–14]. 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 M(DPE)(NO$_3$)$_2$, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and DPE = 1,2-dipiperidinoethane. The complexes are soluble in DMSO, CoL(NO$_3$)$_2$, NiL(NO$_3$)$_2$ in acetone ZnL(NO$_3$)$_2$, CdL(NO$_3$)$_2$ and CuL(NO$_3$)$_2$ is soluble in nitromethane (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 1150

and 1135 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 1110 cm^{-1}, whereas the other two weak bands shift toward higher side and appear at 1175 and 1165 cm^{-1} (Table 3). The shifts are almost to the same extent with minor variation in position and intensities. This is caused by the withdrawal of electron density from C to N bond, where nitrogen atom becomes coordinated to the metal ion. Thus, DPE behaves as bidentate ligand like substituted ethylenediamine coordinating through nitrogen atoms. The molar conductance (Table 2) values, ranging from 9.63 to 12.32 mS mol^{-1}, show that complexes are non-electrolytic in these media and clearly indicate that anions are coordinated with the metal atoms. The magnetic moment of Co(II) complexes is 4.34 BM,

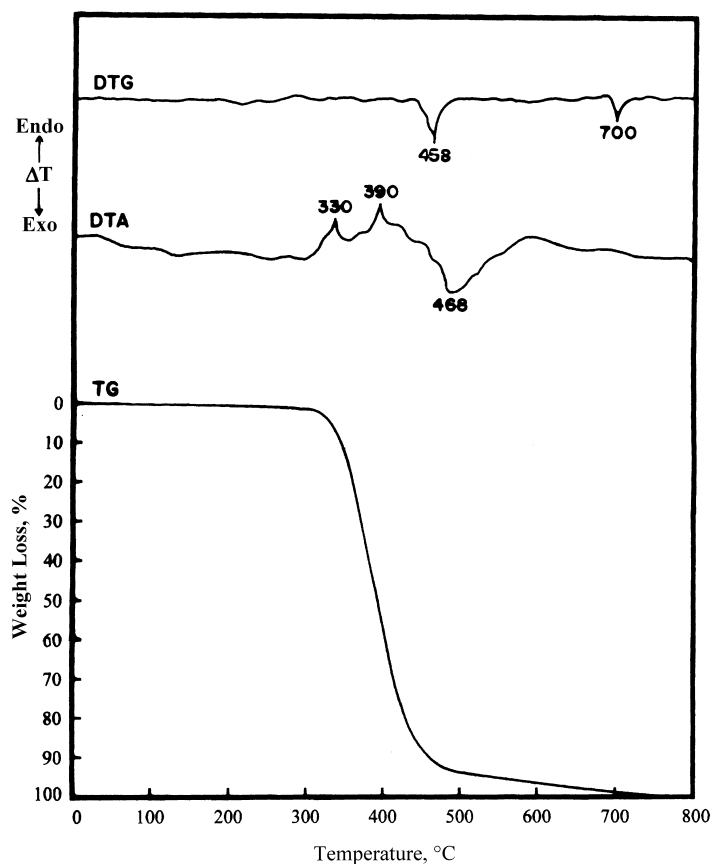Fig. 1. Thermal curves of (CH$_2$NC$_5$H$_{10}$)$_2$ in air atmosphere.

which is characteristic value for the presence of three unpaired electrons, while that for Ni(II) complex it is 3.15 BM, indicating the presence of two unpaired electrons. The value 2.22 is for Cu(II) complex, which is characteristic for the presence of a single unpaired electron. The solution spectra of Co(II) complex exhibited two bands, which could be assigned to transition $^4A_2(F) \rightarrow {}^4T_1(P)$, for v_3 in Td symmetry. The low energy transition, $^4A_2(F) \rightarrow {}^4T_2(P)$, v_2 was not observed. The intensities and band widths are in accordance with the Td symmetry [15]. The non-electrolytic behaviour and high spin type magnetic moments of 3.15 BM for Ni(II) complexes are clearly indicative of Td coordination geometry with nitrate ion as unidentate ligand and the strong bands observed can be assigned to transition. $^3A_1(F) \rightarrow {}^3T_1(P)$, v_3 in tetrahedral symmetry [16]. The solution spectra of copper nitrate complex exhibit only two bands. The

electronic transition are consistent with C_{2v} symmetry and are in the range 12,000–22,000 cm^{-1}. Four transition are to be expected but only two were observed. Similar spectra is observed for other copper(II) complexes having CuN_2X_2 chromophore vibrations [15].

The thermal curves (TG, DTG and DTA) of 1, 2-dipiperidinoethane and its complexes were recorded in static air atmosphere (Figs. 1–6) from ambient to 720°C. The characteristic data and stages of pyrolysis regarding the thermal behaviour of ligand and its complexes are given in Table 4. The TG and DTA curves reveal that the ligand 1,2-dipiperidinoethane decomposes in two steps in the temperature range 320–720°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°C with an accompanying endothermic effect and the intermediate is then decomposed exothermally in the tempera-
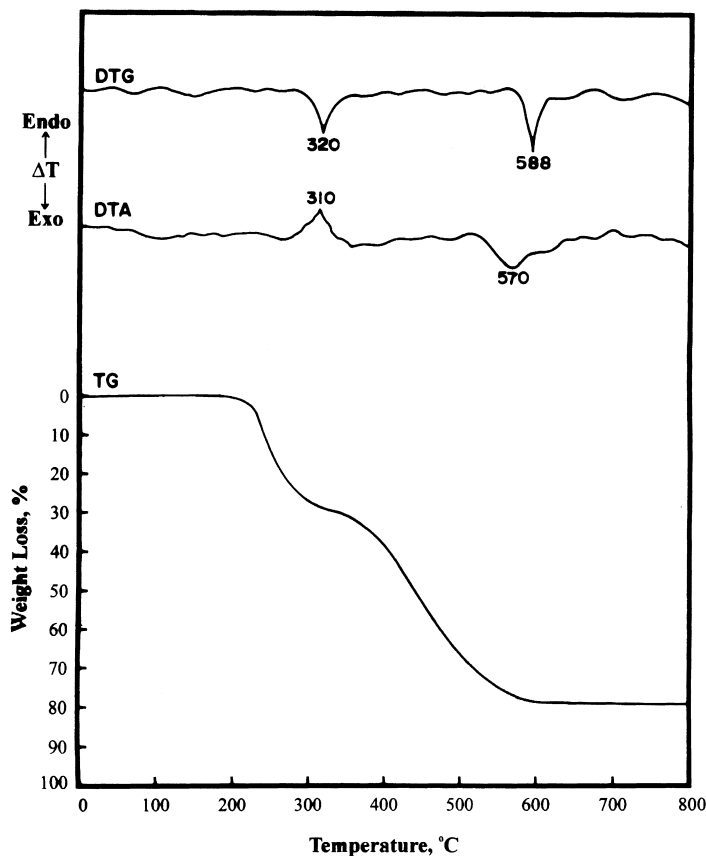

Fig. 2. Thermal curves of $Co(CH_2NC_5H_{10})_2(NO_3)_2$ in air atmosphere.
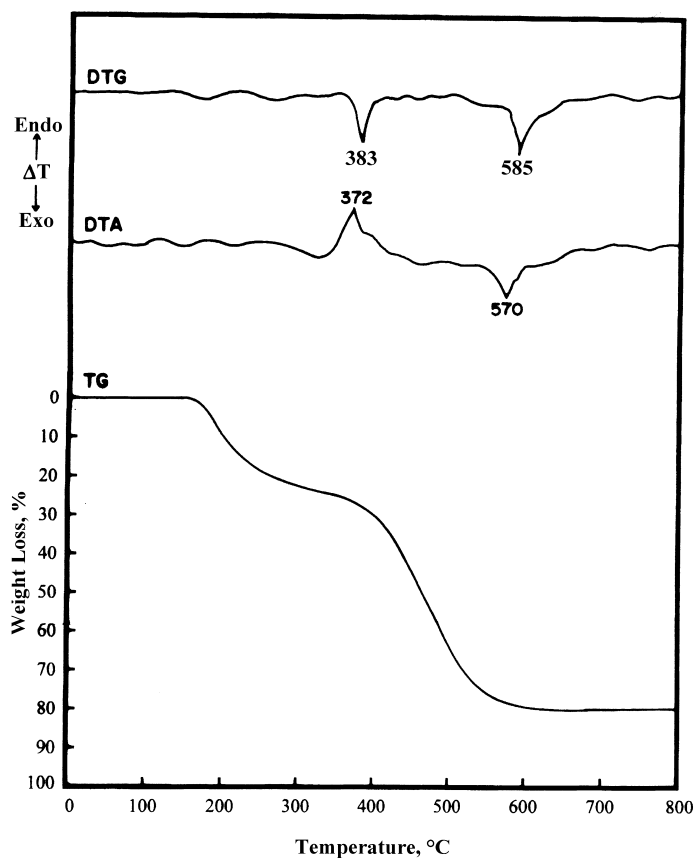
Fig. 3. Thermal curves of $Ni(CH_2NC_5H_{10})_2(NO_3)_2$ in air atmosphere.

Table 4
Thermoanalytical results for the complexes, $M(DPE)(NO_3)_2$ ((−), endothermic (+), exothermic)

Compound	DTA peak temperature (°C)	TG, temperature range (°C)	Weight loss (%)		Phenomena
			Calculated	Found	
DPE	330(−), 390(−)	320–460	92.85	91.84	$C_5H_{11}N$, $C_6H_{12}N$
	468(+)	460–720	7.14	8.00	$-CH_2-$
I	310(−)	200–330	28.50	28.77	N_2O_5
	570(+)	330–600	51.74	50.88	$2C_6H_{12}N$
	−	>600	19.77	20.33	CoO
II	372(−)	170–390	28.51	29.00	N_2O_5
	570(+)	390–590	51.76	51.00	$2C_6H_{12}N$
	−	>590	19.74	20.12	NiO
III	362(−)	200–380	28.16	29.67	N_2O_5
	567(+)	380–580	51.10	50.23	$2C_6H_{12}N$
	−	>580	20.74	21.31	CuO
IV	370(−)	230–380	28.02	27.00	N_2O_5
	639(+)	380–650	50.86	51.32	$2C_6H_{12}N$
	−	>650	21.12	22.56	ZnO
V	370(−)	260–390	24.97	25.00	N_2O_5
	577(+)	390–600	45.34	46.11	$2C_6H_{12}N$
	−	>600	29.71	30.23	CdO
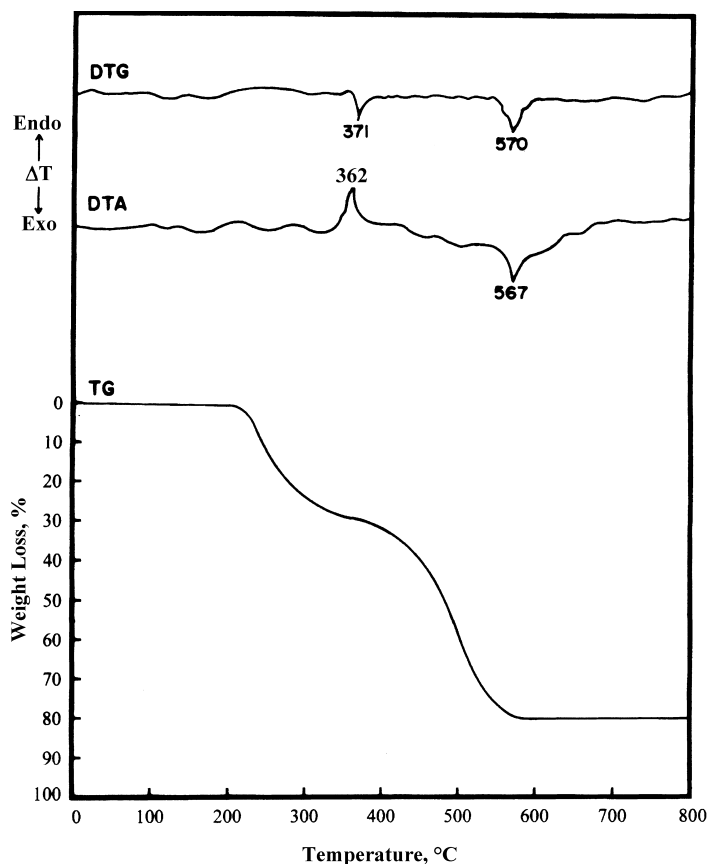
Fig. 4. Thermal curves of Cu(CH$_2$NC$_5$H$_{10}$)$_2$(NO$_3$)$_2$ in air atmosphere.

ture range 460–720°C (second step) liberating methylene group. The first endothermic peak at about 330°C may be attributed to the phase changes during the melting and second sharp endothermic peak at 390°C corresponds to the loss of two species. The second step is slower one and corresponds to the oxidation and vaporisation of methylene indicating that pyrolysis is exothermic in nature. Heating of sample above 700°C leaves no final residue. The sequence of loss is comparable with mass spectrum [1,17]. The TG and DTA curves reveal that the complexes decompose in two stages. The TG curves show that first stage involves the loss of two nitrate radicals in the form of N$_2$O$_5$ [5,18–21] for all the complexes. The second decomposition stage involves one step, which appear as exothermic peaks in the DTA curves. The residue left in the crucible consists of corresponding metal oxide [22–24].

3.1. Characteristic features of the thermal decomposition of the complexes

(1) Co(DPE)(NO$_3$)$_2$. The thermal decomposition of this complex takes places in the temperature range 200–600°C (Fig. 2). The first step involves decomposition (200–330°C) in which the complex loses two nitrate radicals in the form of N$_2$O$_5$. In the second stage, the intermediate decomposes further with the evolution of 1,2-dipiperidinoethane and leaves CoO as final residue.

(2) Ni(DPE)(NO$_3$)$_2$. The complex loses its nitrate radicals in the temperature range 170–390°C and for this decomposition the DTA curve shows one endothermic peak at 372°C (Fig. 3). The intermediate is not stable at this temperature, subsequently as the temperature is raised, the complex decomposes further and finally yields a residue of NiO.
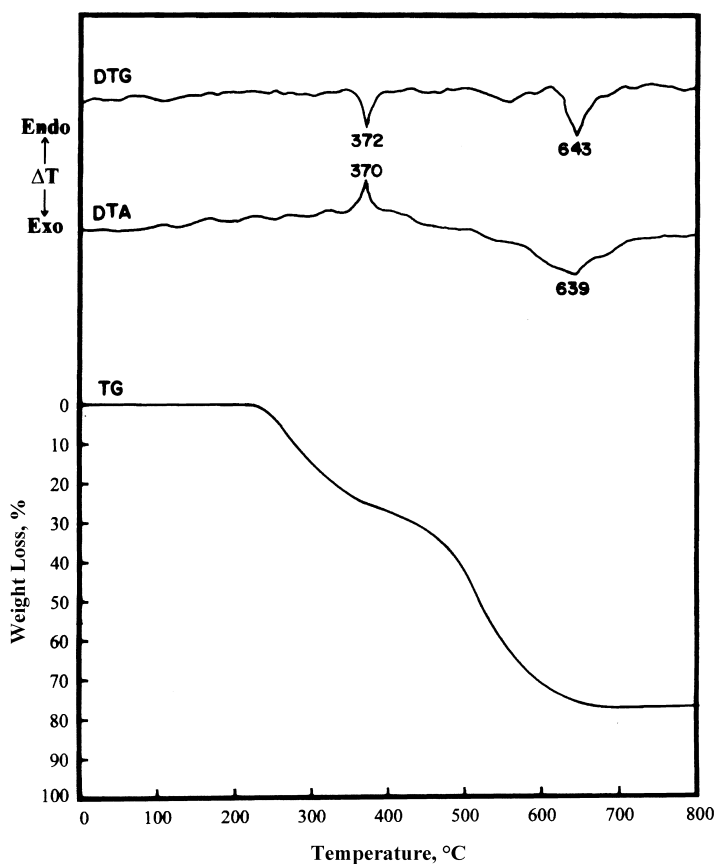
Fig. 5. Thermal curves of $Zn(CH_2NC_5H_{10})_2(NO_3)_2$ in air atmosphere.
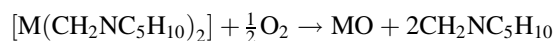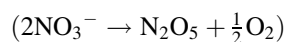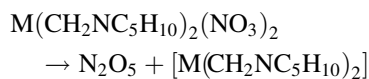
(3) $Cu(DPE)(NO_3)_2$. The nitrate radicals begin to come off in the temperature range 200–380°C (first step). Further decomposition of the complex occurs in second step in the range 380–580°C (Fig. 4). The residue of the foregoing decomposition is CuO. The DTA curve shows endothermic and exothermic peaks at 362 and 567°C, respectively, corresponding to the first and the second step of the TG curve.

(4) $Zn(DPE)(NO_3)_2$. This complex loses two nitrate radicals in the temperature range 230–380°C (Fig. 5) and for this step of decomposition the DTA curve shows a strong endothermic peak (370°C). In the second stage of decomposition (380–650°C), another peak at 639°C in the DTA curve indicates that this decomposition stage is exothermic in nature. The end product is ZnO.

(5) $Cd(DPE)(NO_3)_2$. When heated in a dynamic air atmosphere, this complex is stable up to 260°C and

begins to decompose in two steps in the temperature range 260–600°C (Fig. 6). Endothermic and exothermic peaks accompany the decomposition processes at 370 and 577°C, respectively. Heating the sample above 600°C leaves the respective metal oxide as residue.

On the basis of the observed thermal decomposition studies, it can be inferred that all the complexes undergo thermal decomposition in two steps according to the following general equations:

$$M(CH_2NC_5H_{10})_2(NO_3)_2$$
$$\rightarrow N_2O_5 + [M(CH_2NC_5H_{10})_2]$$
$$(2NO_3{}^- \rightarrow N_2O_5 + \tfrac{1}{2}O_2)$$
$$[M(CH_2NC_5H_{10})_2] + \tfrac{1}{2}O_2 \rightarrow MO + 2CH_2NC_5H_{10}$$
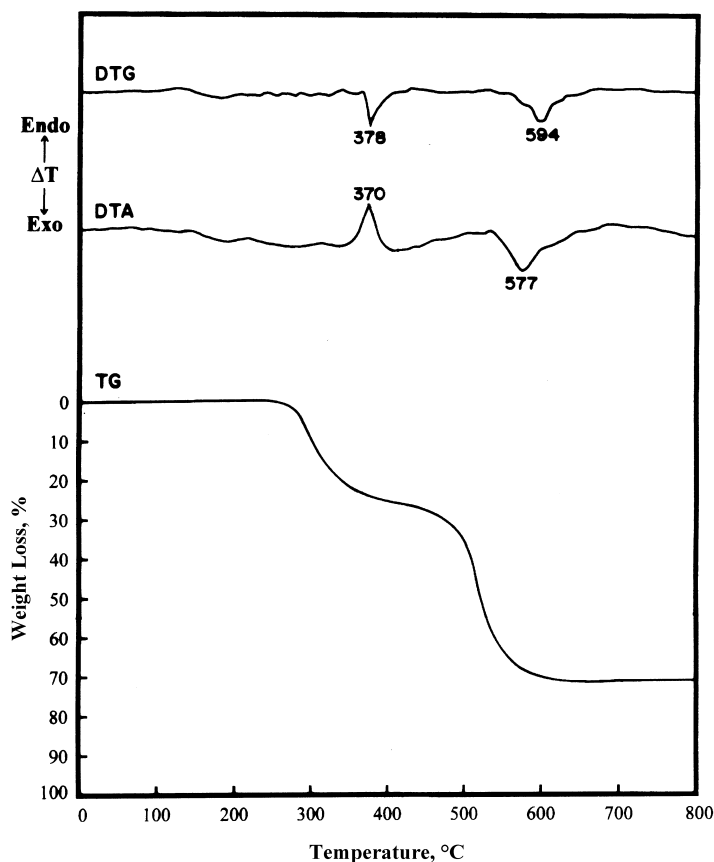
where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Fig. 6. Thermal curves of $Cd(CH_2NC_5H_{10})_2(NO_3)_2$ in air atmosphere.

While comparing the thermal stabilities of complexes on the basis of initial temperature of decomposition [25,26], the following sequence of increasing thermal stability was observed.

II < I < III < IV < V

The highest thermal stability is displayed by the complex V. The solid residue comprised of 19–30% of the initial mass and elemental analysis indicated that these were pure metal oxides.

4. Conclusion

The available experimental data allow us to suggest that the prepared complexes of different metals as well as ligand decompose in two step process. All the complexes possessing distorted tetrahedral geometry show almost a similar decomposition pattern with the evolution of inorganic and organic fragments when heated above 600°C leave corresponding metal oxides as residue except for ligand, which behaves differently. Ligand appears to be more stable than the complexes as it exhibits higher initial decomposition temperature. The coordination of metal ion to ligand is responsible for weakening of the system, that is why complexes start losing weight at lower temperature and at a faster rate and consequently, decomposition of complexes is completed earlier than that of pure ligand. The intermediate products are not stable over a long range of temperature and decompose soon after their formation. The source of oxygen in the formation of residue (metal oxide) appears to have arisen from the decomposition product and not from the atmosphere [18,19]. Zinc and cadmium complexes show greater thermal stability, probably owing to the lower

distortion of the tetrahedral structure and the smaller size of zinc and cadmium ions [27].

Acknowledgements

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