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Thermoanalytical (TG, DTA and DTG) behavior of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) halide complexes of 1,3-dipiperidinopropane

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Abstract

The halide complexes of transition metals with 1,3-dipiperidinipropane of the general formula $M(CH_2(CH_2NC_5H_{10})_2)Br_2$, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), have been synthesized and characterized by elemental analysis, electronic and IR spectra, room temperature magnetic moment studies and conductivity measurements. The thermal behavior of these complexes has been studied by TG and DTA.

All these complexes show two steps weight loss upon heating up to 700°C, with simultaneous loss of organic and inorganic fragments and show almost similar mode of decomposition. Their compositions were confirmed by microanalytical analysis and IR spectroscopy. The residues after heating correspond to metal oxide. Cadmium forms the most thermally stable complex.

Keywords: Thermoanalytical behavior; Halide complexes; 1,3-Dipiperidinopropane

1. Introduction

In our earlier studies relating to the preparation and characterization of $[M(L)C1_2]$, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and L = 1,3-dipiperidinopropane (DPP), we have investigated their composition [1]. In a previous communication, we described the preparation, characterization and thermal properties of the complexes with the composition $M(L)(NO_3)_2$, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and $L = CH_2(CH_2NC_5H_{10})_2$ [2]. The molecule, DPP behaves as a bidentate ligand and bears resemblance to 1,3-dimorpholinopropane (DMP) in terms of chromophoric environment [3–5]. In spite of the considerable importance of this biologically active molecule [6–7], very little work has been done on the synthesis of metal complexes of this ligand in solid form [8].

Methods of thermal analysis have made tremendous progress during the last few decades and have found

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Table 1
Analytical data on investigated complexes

Complex	Decomposition point (°C)	Appearance	Metal (%)		Anion (%)		C (%)		H (%)		N (%)	
			Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
DPP(HBr)$_2$	304	White	–	–	–	–	41.93	41.61	7.59	7.75	7.53	7.46
(I) Co(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$	209	Deep blue	13.74	13.64	37.27	37.49	36.38	36.65	6.06	6.30	6.53	6.67
(II) Ni(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$	228	Green	13.69	13.62	37.29	37.03	36.40	36.39	6.06	6.36	6.53	6.72
(III) Cu(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$	128	Blue	14.66	14.38	36.87	36.66	35.99	36.27	5.99	6.21	6.46	6.63
(IV)Zn(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$	209	White	14.62	14.70	36.89	36.30	36.01	36.13	6.00	6.18	6.46	6.61
(V) Cd(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$	230	White	23.30	23.05	33.14	32.93	32.35	32.61	5.39	5.62	5.80	5.92

Table 2
Values of molar conductance, magnetic moments, maxima of absorption bands in electronic spectra and IR spectra for complexes, M(DPP)Br_2

Complex	Molar conductance (mS mol^{-1})	μ_{eff} (BM)	Maxima of absorption bands					
			Electronic spectra			IR spectra (cm^{-1})		
			λ_{max} (nm)	ν (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	$\nu_{C–N}$	$\nu_{M–X}$	$\nu_{M–N}$
I			540	18 520	215	1160vs[a], 1130vs 1110s[b]		
	8.29	4.60	635	15 750	290		350	295
			670	14 930	310			
II	7.35	3.58	400	25 000	55	1165vs, 1135vs 1103m[c]	365	225
			690	14 490	212			
III			540	18 520	275	1170w[d], 1160sh[e] 1130sh, 1118s		
	8.29	1.78	675	14 810	177		355	290
			785	12 740	128			
IV	4.80	–	–	–	–	1178m, 1170sh 1130m, 1115vs	370	290
V	3.92	–	–	–	–	1165w, 1150w 1135sh, 1105vs	350	280

[a] vs, Very sharp.
[b] s, Sharp.
[c] m, Medium.
[d] w, Wide.
[e] sh, Shoulder.

Table 3
Thermoanalytical results of 1,3-DPP and its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in air atmosphere

Complex	TG results temperature range (°C)	Stage	DTA results temperature peak (°C)	Weight loss (%)		Evolved moiety
				Found	Calculated	
$CH_2(CH_2NC_5H_{10})_2$	280–450	1	(−)[a]300	39.44	40.00	Piperidine
	450–520	2	(−)400	47.10	46.66	*N*-methylenepiperidine
	520–680	3	(+)[b]480	14.11	13.33	Ethylene
I	211–330	1	(−)300	27.18	26.12	*N*-ethylenepiperidine
	330–640	2	(+)590	60.91	60.13	*N*-methylenepiperidine + Br_2
	>640	Residue	–	18.31	17.51	CoO
II	225–390	1	(−)360	27.41	26.14	*N*-ethylenepiperidine
	390–620	2	(+)550	61.21	60.16	*N*-methylenepiperidine + Br_2
	>620	Residue	–	18.22	17.43	NiO
III	190–340	1	(−)126,270	26.46	25.85	*N*-ethylenepiperidine
	340–620	2	(+)560	60.56	59.51	*N*-methylenepiperidine + Br_2
	>620	Residue	–	19.84	18.37	CuO
IV	213–340	1	(−)270	26.21	25.74	*N*-ethylenepiperidine
	340–620	2	(+)580	58.43	59.24	*N*-methylenepiperidine + Br_2
	>620	Residue	–	19.11	18.70	ZnO
V	227–440	1	(−)370	24.73	20.33	*N*-ethylenepiperidine
	440–700	2	(+)560	57.61	56.37	*N*-methylenepiperidine + Br_2
	>700	Residue	–	26.93	26.62	CdO

[a] (−), Endotherrmic.
[b] (+), Exothermic.

wide spread practical applications. Nowadays these techniques are important tool in research and routine analysis. TG and DTA are valuable techniques for the study of the thermal properties of various compounds [9–18].

The aim of the present work is to pursue a more detailed study of the transformation of these complexes, which they undergo upon heating and to understand the mechanism of their decomposition to examine the conditions and products of their thermal decomposition. Furthermore, we will also describe the preparation, characterization and thermal properties of these tetrahedral complexes with the composition $M(DPP)Br_2$, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical grade and solvents were distilled before use. Complexes were prepared by the methods as reported earlier [1].

2.2. Synthesis of ligand

The ligand 1,3-DPP was synthesized by the reported procedure [19]. Piperdine (0.25 mol) in absolute methanol (40 ml) was added drop-wise to (0.1 mol) dibromopropane in methanol (20 ml). The contents were refluxed for 8 h at 80°C. The reaction

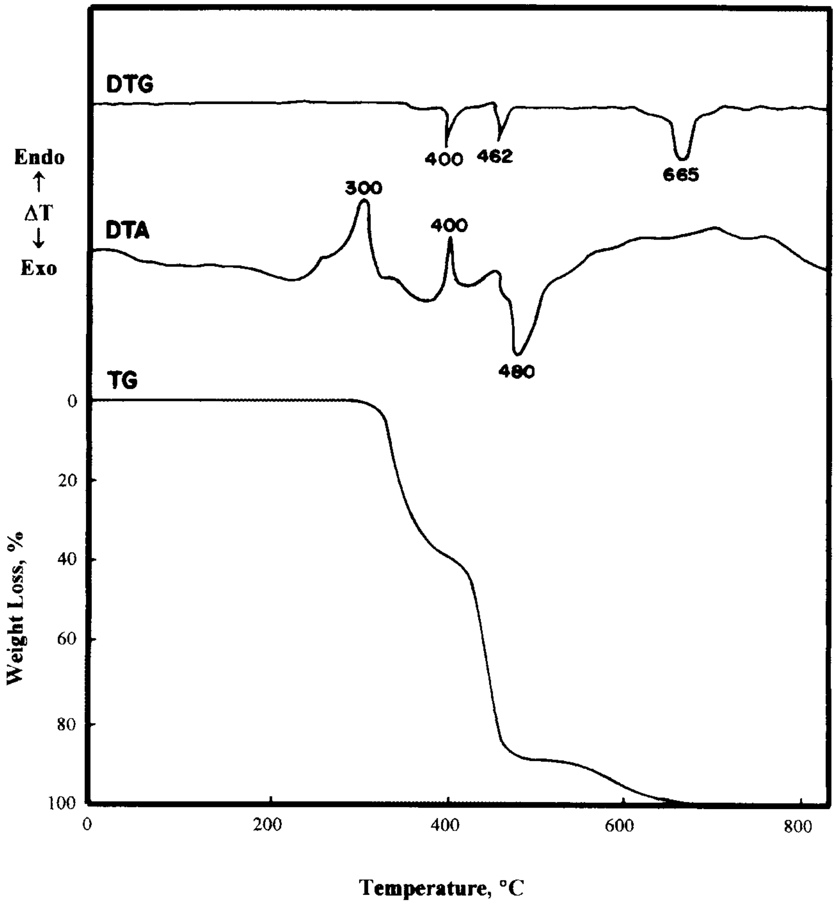

Fig. 1. Thermoanalytical (TG, DTG and DTA) curves of $CH_2(CH_2NC_5H_{10})_2$ in air atmosphere.

mixture was left overnight to get piperidinium bromide crystals of 80% yield.

2.3. Preparation of ligand solution

The ligand was dissolved in minimum amount of methanol, to which a calculated amount of alcoholic potassium hydroxide was added and filtered to remove potassium bromide as precipitate. The filtrate was used as ligand solution.

2.4. Synthesis of solid complexes

All the complexes were synthesized by using similar general method. Approximately 10 mmol of partially dehydrated salt was dissolved in minimum amount of anhydrous solvent. Methanol was used as solvent for the preparation of $CoC1_2$ and $NiC1_2$ complexes and ethanol for the synthesis of the rest of the complexes. The ligand DPP, an excess over 1:2 metal to ligand 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 30 min, then cooled for about 20 min. The metal complexes precipitated either immediately or on cooling. The product obtained was filtered through sintered glass crucible, washed several times with ether and dried under vacuum at 50°C. The complexes were recrystallized from suitable solvent.

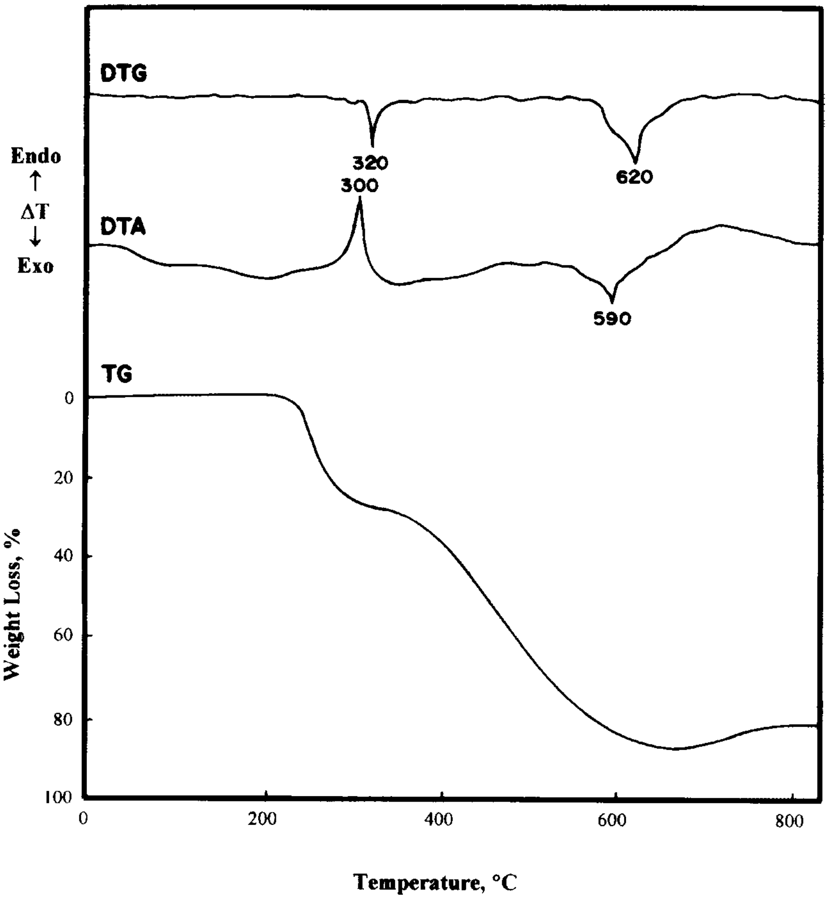

Fig. 2. Thermoanalytical (TG, DTG and DTA) curves of $Co(CH_2(CH_2NC_5H_{10})_2)Br_2$ in air atmosphere.

2.5. Physicochemical techniques

Elemental analysis was performed on CHN analyzer, Carloerba Mod. 1106. The metal contents were determined by EDTA complexometric titration after decomposing a known amount of the complexes with concentrated nitric acid by published methods [20–21]. The molar conductance of the prepared complexes in DMSO was measured using the conductivity bridge, made by Mullard, England. The room temperature magnetic measurements were carried out by Gouy method using Hg[Co-(SCN)$_4$] as the calibrant. Diamagnetic corrections were applied using Pascal's constants [22]. Electronic spectra were recorded on a Jasco DEC-1 spectrophotometer with 1 cm matched quartz cells in the range of 200–900 nm using various solvents. IR spectra of prepared complexes and intermediate products of their thermal decomposition were recorded on a PYE UNICAM IR spectrophotometer, FTIR, Shimadzu using KBr discs in the range 4000–400 cm^{-1}. A NETZSCH simultaneous thermal analyzer STA 429 was used to carry out the thermoanalytical analyses. The thermal experiments were performed in air from ambient temperature to 700°C with a heating rate of 10° min^{-1}. Platinum crucibles were used to hold 30–55 mg samples for analyses.

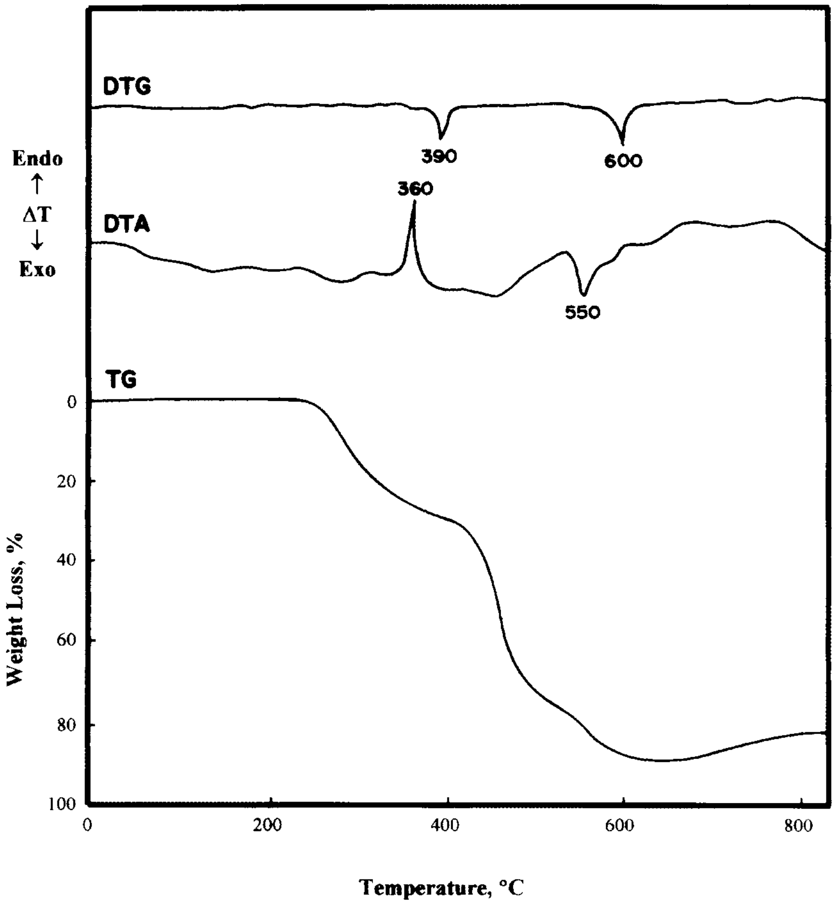

Fig. 3. Thermoanalytical (TG, DTG and DTA) curves of Ni(CH$_2$(CH$_2$NC$_5$H$_{10}$)$_2$)Br$_2$ in air atmosphere.

3. Results and discussion

The compositions of ligand and prepared complexes are summarized in Table 1. The proton NMR spectrum of ligand in D_2O with TMS as external standard shows five signals indicating the presence of five environmentally different types of hydrogen atoms. A singlet at 1.61 ppm for four terminal hydrogens, a broad singlet at 1.80 ppm for eight hydrogens attached to ring carbon atoms, a sharp multiplet at 2.22 ppm for two protons of central methylene group, a triplet at 3.21 ppm for four ethyl hydrogens and a broad singlet at 3.25 ppm for eight hydrogen attached to ring carbons adjacent to nitrogen atoms have been observed. The IR spectrum of ligand showed bands in the range 2965–2870 and 1225–1085 cm^{-1}, which are due to the C–H and C–N stretching and bending vibrations, respectively. A mass peak of moderate intensity at *m*/*Z* 210, corresponding to the molecular ion $(C_{13}H_{26}N_2)^+$ was observed in the spectrum of 1,3-dipiperidinopropane. The base peak of *m*/*Z* 98 is due to the formation of *N*-methylpiperidine cation radical, while signals at *m*/*Z* 112, 126 and 84 could be assigned to *N*-ethylpiperidine, *N*-propylpiperidine and piperidine, respectively. The Co(II) and Ni(II) complexes are soluble in DMSO; Cu(II) complex is soluble in nitromethane, while Zn(II), Cd(II) and Hg(II) complexes are soluble in acetone. Their molar conductance (Table 2) in respective solvents lie in the range of 3.92–8.29 mS mol^{-1}. The conductance values are in

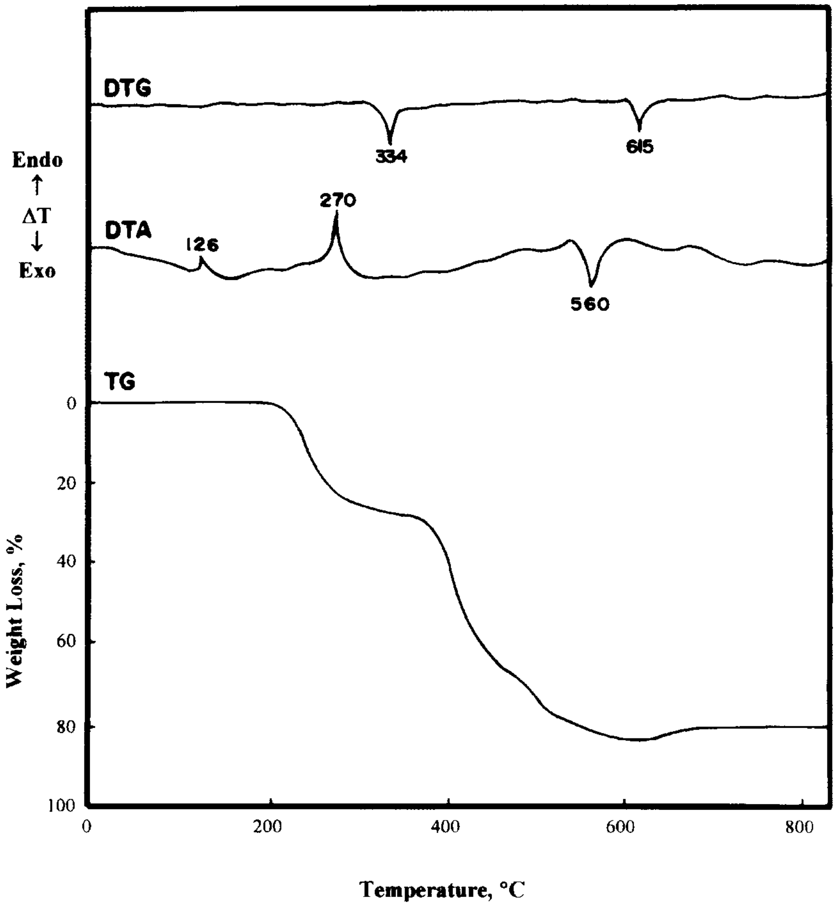

Fig. 4. Thermoanalytical (TG, DTG and DTA) curves of $Cu(CH_2(CH_2NC_5H_{10})_2)Br_2$ in air atmosphere.

accordance with the non-electrolytic nature of the complexes, which clearly indicates that anions are coordinated with the metal atom. The magnetic moments and electronic spectral values are also listed in Table 2. The position of bands in the spectra of complexes together with their magnetic moments suggest that metal ions are in distorted tetrahedral environment [23–29]. IR spectra of metal complexes clearly indicate that C–N stretching frequencies are shifted to lower and some to higher frequencies with changes in sharpness and intensities. This is caused by the withdrawal of electron density from C–N bond where nitrogen atom, is believed to have coordinated to the metal ion. Thus DPP behaves as bidentate ligand like substituted propylenediamine coordinating through nitrogen atoms. The far IR spectra of the complexes show multiple bands in the regions 350–370 and 225–295 cm^{-1}. The former bands are due to ν(M–X) vibrations and latter bands are assigned to ν(M–N) stretching vibrations [30]. Thermal analysis was carried out systematically for all the complexes in air atmosphere. The actual weight losses reported in Table 3, for the decomposition processes of the complexes appeared to be comparable with the calculated values. Figs. 1–6 illustrate the TG, DTA and DTG curves of ligand complexes heated from ambient to 700°C. The TG and DTA curves reveal that the ligand, 1,3-dipiperidinopropane decomposes in three stages in the temperature range 280–680°C. In the first step, the ligand loses piperidine, by the breakage of C–C

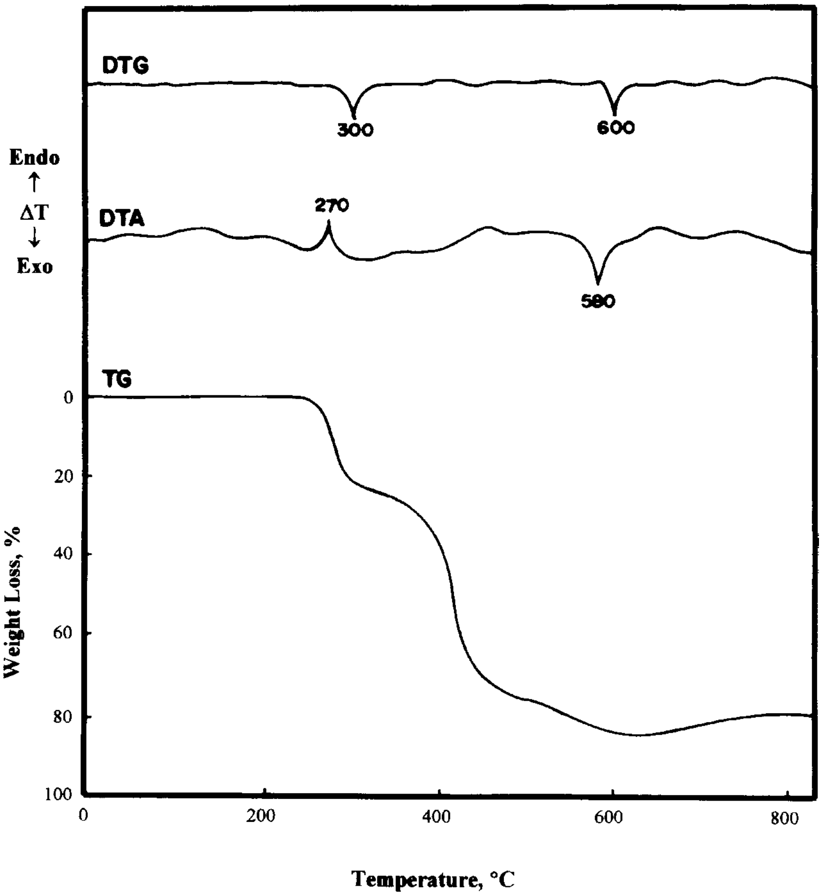

Fig. 5. Thermoanalytical (TG, DTG and DTA) curves of $Zn(CH_2(CH_2NC_5H_{10})_2)Br_2$ in air atmosphere.

bond around 280–410°C with an accompanying strong endothermic effect and the intermediate is then decomposed endothermally in the temperature range 410–470°C liberating *N*-methylenepiperidine. Third step is slower one and corresponds to oxidation and vaporization of ethylene group. This last stage is exothermic in nature. Heating of sample above 680°C leaves no final residue. The sequence of loss is comparable with the mass spectrum [1]. It can be seen that the complex III melts endothermally at 126°C, followed by degradation at about 190°C (first step), with beginning of the decomposition of the ligand. The melting point was not observed in rest of the complexes, indicating that melting has been masked by the decomposition of the complexes. The decomposition of all the complexes are analogous and occur in two steps.

The DTA curves of the complexes show two peaks, endothermic and exothermic corresponding to the first and last step of the TG curves. First step in the decomposition of complexes (190–227°C) is accompanied by endothermic effects in the DTA curves with the evolution of one mole of *N*-ethylenepiperidine moiety from the complex. Last step in the thermal decomposition involves the decomposition of intermediates and oxidation of metal by atmospheric oxygen. The second moiety of *N*-methylenepiperidine is liberated followed by the evolution of halogen molecules in the final step. The combined effect of loss of two moieties corresponds to large exothermic effect as

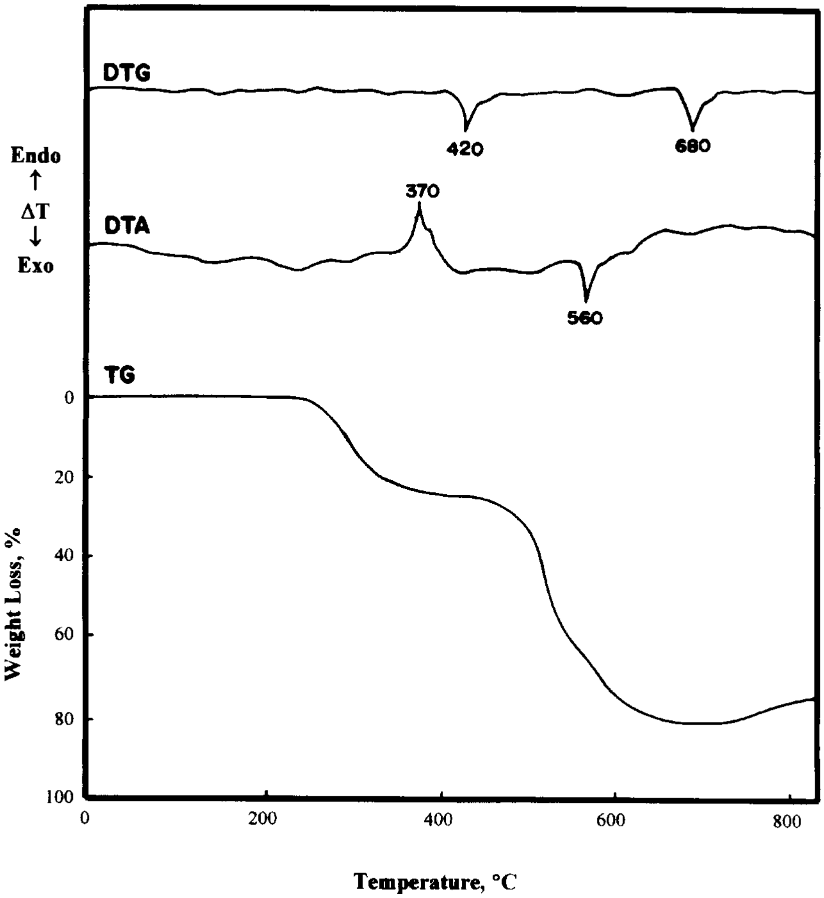

Fig. 6. Thermoanalytical (TG, DTG and DTA) curves of $Cd(CH_2(CH_2NC_5H_{10})_2)Br_2$ in air atmosphere.

indicated by DTA curves, accompanied by the oxidation of metal. The TG curves of all complexes also indicate the occurrence of processes causing an increase in the mass of residue of the expected product of the decomposition in air are the oxides [31–35], which are formed by the oxidation of the metals after heating up to 700°C. The TG, DTA and DTG curves permit the following conclusions: complex I is thermally stable up to 211°C, complex II to 225°C, complex III to 190°C, complex IV to 213°C and complex V to 227°C (according to the beginning of mass loss) [36,37]. The TG, DTA and DTG curves for the complexes I–V show that the release of volatile species occur in two-step process according to the following equation:

$$[\mathrm{MCH_2(CH_2NC_5H_{10})_2Br_2}] \rightarrow [\mathrm{M(CH_2NC_5H_{10})Br_2}] + \mathrm{CH_2CH_2NC_5H_{10}}$$

$$[\mathrm{M(CH_2NC_5H_{10})Br_2}] + (1/2)\mathrm{O_2} \rightarrow \mathrm{MO} + \mathrm{CH_2NC_5H_{10}} + \mathrm{Br_2}$$

where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

The final products of decomposition (to 620°C) are MO. The solid residue comprised 17–27% of the initial mass. The formation of metal oxides have been confirmed by chemical analysis and IR spectroscopy.

4. Conclusions

1. The present study reveals that co-ordination of metal ion to ligand causes weakening of the system. The complexes start losing weight at lower temperatures and also at faster rate.
2. Ligand appears to be more stable than the complexes as it exhibits higher decomposition temperature.
3. The decomposition of the complexes is completed earlier than that of pure ligand.
4. The complexes, which have distorted tetrahedral geometry, show similar mode of degradation and produce metal oxides as residue.
5. Two-step decomposition pattern is observed for all the complexes.
6. Only complex III melts during the course of heating whereas the rest of the complexes decompose without melting.
7. The increase in weight near the end TG curves for all the complexes clearly indicate the oxidation of metals to metal oxides.
8. Cadmium II forms the most thermally stable complex in the reported series.

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