J Therm Anal Calorim (2010) 102:715–722
DOI 10.1007/s10973-009-0184-3

Pyrolytical characterization of transition metal complexes of cobalt, nickel, copper and zinc with ethylenediamine-*N,N′*-diacetate

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Received: 19 March 2009 / Accepted: 22 April 2009 / Published online: 19 June 2009

Abstract A series of octahedral complexes, $[M(EDDA)(H_2O)_2] \cdot H_2O$ (where, $M^{+2} = Co(II)$, Cu(II), Ni(II) and Zn(II); EDDA, ethylenediamine-*N,N′*-diacetate), was prepared and studied by means of thermogravimetry (TG) and differential thermal analysis (DTA). Their compositions were investigated by elemental analysis in order to ensure their purity and structural elucidation was based on spectral and magnetic properties. Thermal decomposition of these distorted octahedral complexes, $[Ni(EDDA)(H_2O)_2]$, $[Co(EDDA)(H_2O)_2] \cdot H_2O$, $[Cu(EDDA)(H_2O)_2] \cdot H_2O$ and $[Zn(EDDA)(H_2O)_2] \cdot H_2O$ came of in one, two, three and four steps, respectively, upon heating to 800 °C, with the loss of organic and inorganic fragments. Ligand decomposed in three steps. The thermal degradation of all the complexes in static air atmosphere started at temperatures lower than those observed for the free ligand degradation (Ni-complex being the only exception). The composition of intermediates formed during degradation was confirmed by microanalysis and IR spectroscopy. The residues corresponded to metal oxide except for Ni(II) and Zn(II) complexes. It was found that thermal stability of the complexes increased in the following sequence:

$Cu(II) \sim Co(II) < Zn(II) < Ni(II)$

Keywords EDDA · Transition metals · Octahedral complexes · Pyrolytic study · Thermal stability

Introduction

In studies on the physical and chemical properties and the structures of solid complexes of transition metal ions with organic ligands, it is customary to investigate the thermal decomposition of these complexes so as to obtain useful data on the metal-ligand bonds [1–3] and stability trends. The thermal investigations on some derivatives of amines [4], sulfonamides [5], substituted thiourea salts [6], and complexes of bidentate ligands and others [7–11], have already been published.

As an extension of our previous studies [12–22], the present paper deals with pyrolysis of $M(EDDA)(H_2O)_2$ of the same type of complexes with nitrogen-coordinating ligand in order to understand the mechanism of disintegration and the nature of degradation products. The characterization of complexes was effected through elemental analysis, spectral, magnetic, TG, DTG and DTA studies. Attempts were also made to estimate the kinetic parameters from thermal studies employing Horowitz–Metzger method [23].

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Experimental

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 around 80–100 °C.

Preparation of the ligand

Ethylenediamine-*N,N′*-diacetic acid (H_2EDDA) was procured from market (Merck) and used without further purification.

Preparation of complexes of ethylenediamine-*N,N′*-diacetate (EDDA)

The complexes were synthesized as per reported method [24].

Ethylenediamine-*N,N′*-diacetato(diaquo)Co(II) hydrate

The reaction was carried out in a three-necked flask using deaerated water. The flask was flushed with nitrogen throughout the reaction. During filtration, nitrogen was drawn through the filter having a sealed connection. These measures did not completely prevent contact with air but were sufficient to block oxidation of the cobalt(II) complex as evidenced by darkening of the product when these precautions were not taken. To a stirred slurry of 1.3 g of $CoCO_3$ (0.01 mol) in 30 mL of water, 1.76 g of H_2EDDA was added. The reaction vessel was heated (60 °C) until evolution of CO_2 was complete (10 min), and the mixture was then filtered rapidly through a medium-fritted disk. The solution was placed in a vacuum-desiccator which was evacuated until a large crop of pink crystals formed. The product was filtered and washed with two 5-mL portions of ice-cold water, alcohol and acetone. After drying in the filter with nitrogen flush, the yield of $[Co(EDDA)(H_2O)_2] \cdot H_2O$ was recorded as 0.272 g, 68%. The dried product appeared to be stable in air.

Ethylenediamine-*N,N′*-diacetato(diaquo)Ni(II)

To slurry of 1.76 g (0.01 mol) of H_2EDDA in 40 mL of deaerated water on a steam bath, were added 2.62 g (0.01 mol) of $NiCl_2 \cdot 6H_2O$ and 0.8 g (0.2 mol) of NaOH with stirring. The solution was evaporated to about 10 mL, cooled and filtered. The crude product was washed with ethanol, which weighed 1.30 g. This was dissolved in a minimum amount of water (20 mL) at 70 °C. After cooling, filtering and washing as before, 1 g of light blue crystals was obtained. The air-dried yield was 68%.

Ethylenediamine-*N,N′*-diacetato(diaquo)Cu(II) hydrate

To a slurry of 1.21 g (0.0025 mol) of $CuCO_3$, $Cu(OH)_2$ in 25 mL of deaerated water on a steam bath, was added 1.76 g (0.01 mol) of H_2EDDA. The mixture was heated until the evolution of CO_2 ceased, filtered and evaporated to about 5 mL. The viscous mixture was filtered and the resultant deep blue precipitate was washed with ethanol and air dried; yield 0.4 g (40%).

Ethylenediamine-*N,N′*-diacetato(diaquo)Zn(II) hydrate

To slurry of 0.2 g (0.016 mol) of $ZnCO_3$ in 6 mL of deaerated water on a steam bath, was added 0.32 g (0.0018 mol) of H_2EDDA dissolved in 4 mL of water. The mixture was heated to 60 °C in nitrogen atmosphere and evaporated to 2 mL. The viscous mixture was filtered and white precipitate was washed with ethanol. Yield was 0.082 g (40%).

Physicochemical techniques

The microanalyses of C, H and N were performed with a CHN analyzer, Carlo Erba Model 1106. Metal ions and residues were determined with an XRF-500 link system England. Ultraviolet and visible absorption spectra of complexes (4×10^{-2} M solution) were recorded with a Cary Model 14 spectrophotometer in the range of 200–900 nm using various solvents. The degradation products (including gases) were identified through ATI Mattson, Infinity Series FTIR, Model No. 9495, USA. The magnetic susceptibility data on the complexes were determined by the Gouy's method at room temperature [25]. The thermoanalytical (TG-DTA-DTG) measurements were carried out with NETZSCH simultaneous Thermal Analyzer STA 429. Samples were contained in an alumina crucible Al_2O_3 (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 mass-loss of sample against temperature. Studies were made in static atmosphere of air using 20–35 mg samples at a heating rate of 10 °C/min. The activation energy (E°) and order of reaction (n) were evaluated using the Horowitz–Metzger method. A plot of Ln Ln $W_o - W_f/W - W_f$ against θ resulted in a straight line. The activation energy was calculated from its slope, which was equal to $E°/RT_s^2$, whereas order of reaction was determined by using the relation

Table 1 Kinetic parameters of thermal decomposition of ligand and metal complexes of H_2EDDA

Complex	Temperature range (°C)	Activation energy (E°, KJ/mol)	Order of reaction (n)
H_2EDDA	210–643	22.59	3
$C_6H_{16}N_2O_7Co$	50–460	5.57	1.5
$C_6H_{14}N_2O_6Ni$	284–340	11.2	2
$C_6H_{16}N_2O_7Cu$	50–495	5.22	1.5
$C_6H_{16}N_2O_7Zn$	80–450	6.80	0.5

Table 2 Analytical data of EDDA complexes

Complex	Color	Carbon (%) Found	Hydrogen (%) Found	Nitrogen (%) Found
$C_6H_{16}N_2O_7Co$	Pink	25.6 (25.1)[a]	5.87 (5.62)	9.61 (9.76)
$C_6H_{14}N_2O_6Ni$	Light blue	26.7 (26.8)	5.15 (5.25)	10.6 (10.4)
$C_6H_{16}N_2O_7Cu$	Dark blue	24.8 (24.7)	5.81 (5.53)	9.75 (9.60)
$C_6H_{16}N_2O_7Zn$	White	29.8 (29.9)	4.90 (4.98)	11.5 (11.6)

[a] Calculated values are given in parentheses

Table 3 Values of magnetic moment and electronic absorption spectra for EDDA complexes

Complex	μ_{eff} B.M.	ν (kK)	Assignment O_h
$C_6H_{16}N_2O_7Co$	5.0	8.95 (6.0)	${}^4T_{1g} \rightarrow {}^4T_{2g}$
		19.9 (11.7)	${}^4T_{1g} \rightarrow {}^4T_{2g}(P)$
$C_6H_{14}N_2O_6Ni$	3.21	9.90 (12.6)[b]	${}^3A_{2g} \rightarrow {}^3T_{2g}$
		13.2 (1.9)	$\rightarrow {}^1E_g$
		16.4 (4.2)	$\rightarrow {}^3T_{1g}(F)$
		27.2 (7.2)	$\rightarrow {}^3T_{1g}(P)$
$C_6H_{16}N_2O_7Cu$	1.76	14.9 (11.8)[a]	–
$C_6H_{16}N_2O_7Zn$	Diamagnetic	–	–

[a] Molar extinction coefficient

[b] Molar absorptivity (ε)

between reaction order and concentration at maximum slope (Table 1).

Results and discussion

Composition and structure

The results of the elemental analyses are presented in Table 2, which indicated the expected composition of the complexes. The EDDA afforded a standard by which deviations from an octahedral arrangement of ligand may be determined. The data from electronic absorption spectra of complexes are summarized in Table 3. The spectrochemical behavior of nickel complex is believed to reflect the average coordination geometry. $[Ni(EDDA)(H_2O)_2]$ is demonstrated by the calculation of energies of the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (p) transition from the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition which has an energy of 10Dq [26]. The close agreement (within 2%) between the observed and the calculated values (Table 3) gives strong support for the expected octahedral geometry of the complex [27]. The electronic absorption spectrum of pink $[Co(EDDA)(H_2O)_2] \cdot H_2O$ is characteristic of those observed for Co(II) octahedral complexes [28]. The band assignments are awarded on the basis of O_h symmetry (Table 3) and the effective magnetic moment, 5.0 BM, is typical of octahedral cobalt(II) complexes [27]. The blue complex of Cu(II) with EDDA exhibits single, symmetric absorption bands in the red region (Table 3). The Cu(II)-EDDA complex exhibits a μ_{eff} of 1.76 BM. In the case of $[Cu(EDDA)(H_2O)_2] \cdot H_2O$, the chelate structure tends to constrain the acetate oxygen along the z^2 orbital; or, alternately, if the chelate were planar, the acetate would tend to be pulled away from the metal ion due to the expected strain in the framework analogous to that found for the in-plane acetate of $Co(EDDA)^-$ [29] and the energy of the $x^2 - y^2$ orbital would, therefore, be lowered. In case of complex,

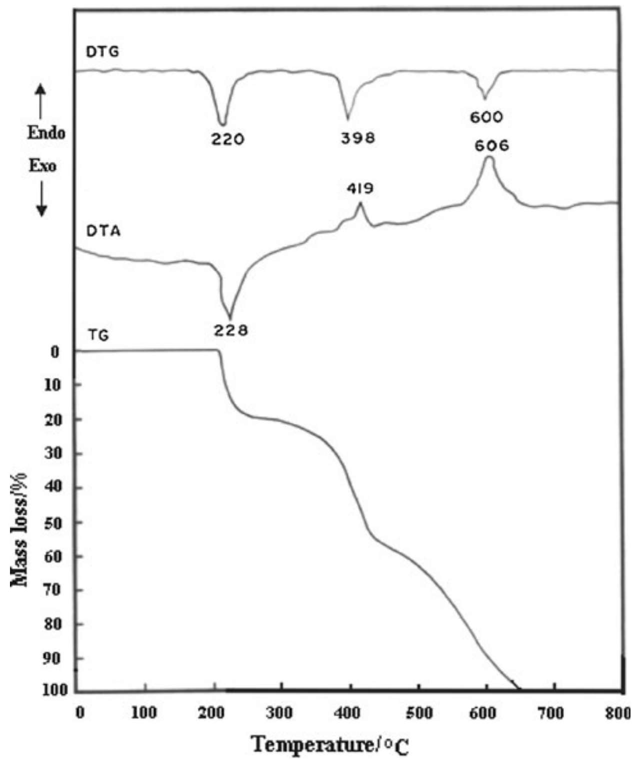

Fig. 1 Thermal curves of EDDA

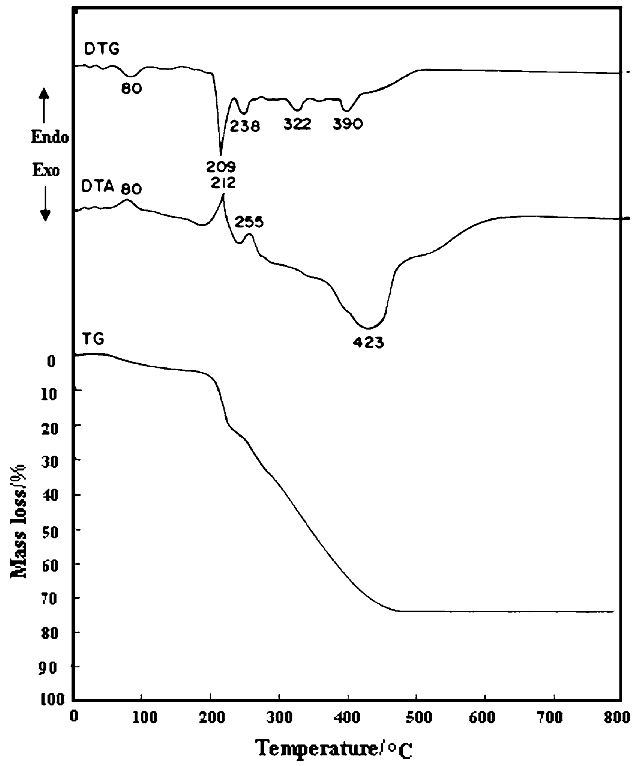

Fig. 2 Thermal curves of $[Co(EDDA)(H_2O)_2] \cdot H_2O$

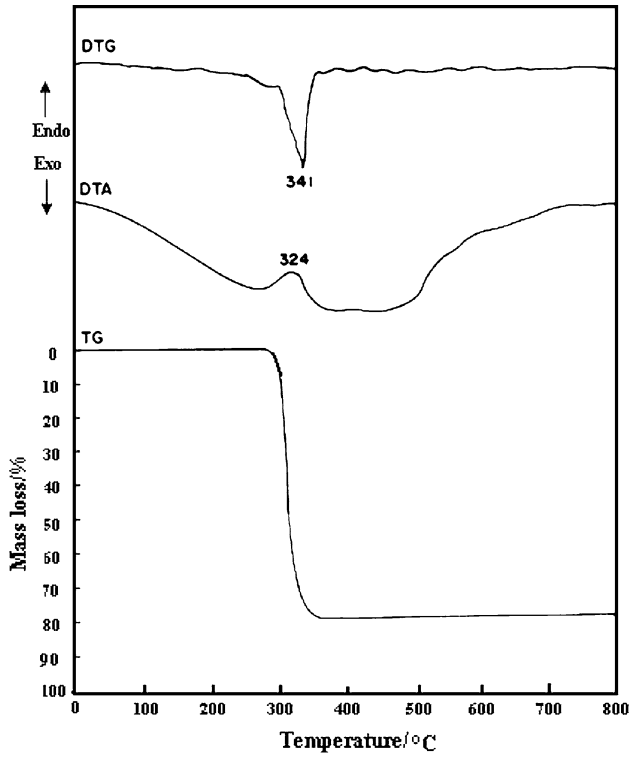

Fig. 3 Thermal curves of $[Ni(EDDA)(H_2O)_2]$

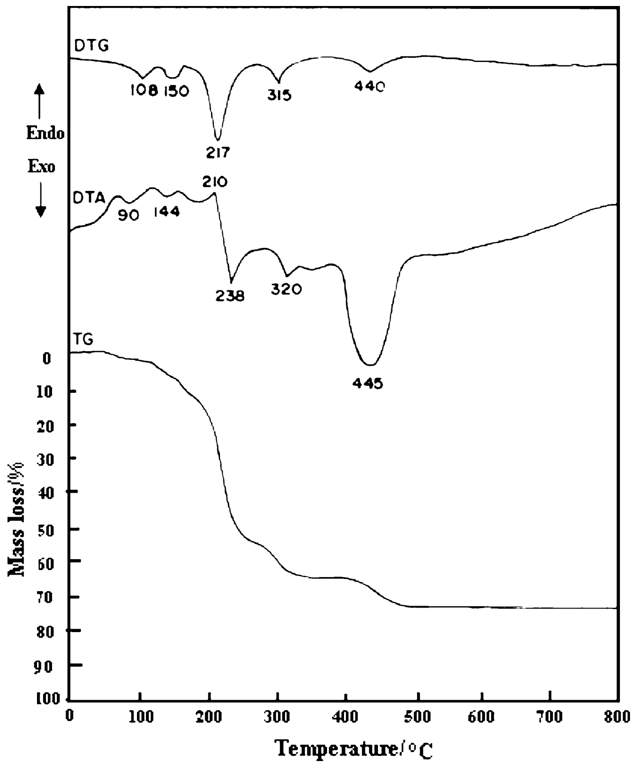

Fig. 4 Thermal curves of $[Cu(EDDA)(H_2O)_2] \cdot H_2O$

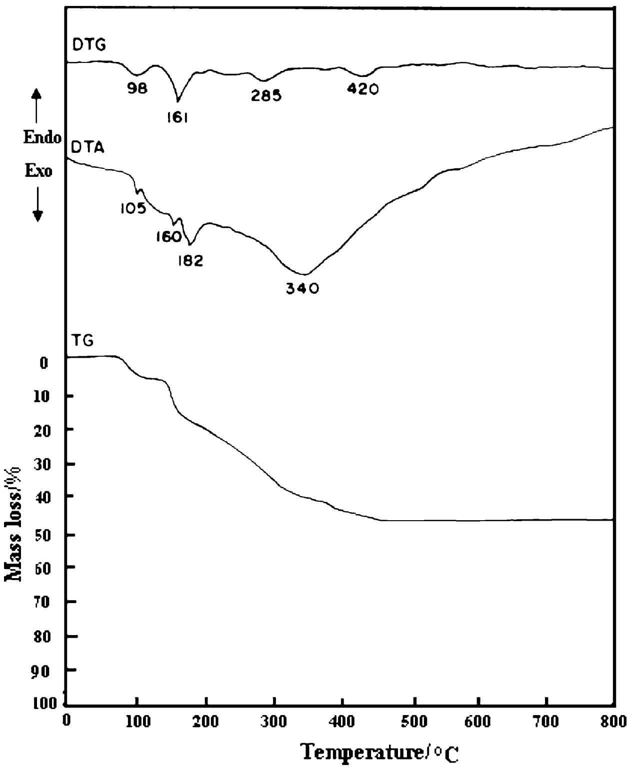

Fig. 5 Thermal curves of $[Zn(EDDA)(H_2O)_2] \cdot H_2O$

$[Zn(EDDA)(H_2O)_2] \cdot H_2O$, conductance data indicate presence of non-ionic species. The IR data show the attachment through the same sites as those found for Ni, Cu and Co complexes. Considering the analytical, IR and conductance data, the octahedral geometry is assigned, where EDDA is acting as a tetradentate ligand [24]. Water molecules are the part of octahedral structure.

Thermal properties

The thermal decomposition curves (TG, DTG and DTA) are given in Figs. 1, 2, 3, 4, 5, while the TG mass-loss data, DTG and DTA peak temperatures are presented in Table 4. The ligand (H_2EDDA) shows a three-step pyrolysis. The first stage starts around 210 °C and terminates at 258 °C. For this stage DTG and DTA peaks appear at 220 °C and 228 °C, respectively. Two species evolve, i.e., carbon monoxide (1 mole) and hydrogen (3 moles). This stage accounts for 20% mass-loss. The intermediate, formed at the completion of first step, resists further degradation (the conjugated system exhibits resonance stabilization) to some extent. The rate of slow decomposition from 258 °C to 372 °C (5% mass-loss) confirms this observation. The second stage comes to an end around 440 °C. The overall mass-loss is 35%. One mole each of carbon dioxide and

Table 4 Thermoanalytical results for the ligand and complexes, $[M(EDDA)(H_2O)_2]$

Complex	TG, Temperature range (°C)	Stage	Mass loss (%)		DTA	DTG	Evolved moiety
			Calc.	Found			
H_2EDDA	210–258	I	19.3	20	(−)228	220, 398, 600	CO, $3H_2$
	258–440	II	35.2	35	(+)419		CO_2, H_2O
	440–643	III	45.4	45	(+)606		2HCN, C_2H_2
$C_6H_{16}N_2O_7Co$	50–200	I	7	6.3	(−)80	80	H_2O
	200–460	II	68	67.6	(−)212, (−)255, (+)423	209, 238, 322, 390	$3H_2O$, C_2H_2, HCN, H_2, CO, NH_3
	>460	Res.	25	26.1	–	–	CoO
$C_6H_{14}N_2O_6Ni$	284–340	I	79.2	78.2	(−)324	341	CO_2, H_2O, C_2H_4, C_2H_6,
	>340	Res.	20.8	21.8	–	–	H_2, N_2 Ni
$C_6H_{16}N_2O_7Cu$	50–250	I	52	52.1	(+)90, (+)144, (−)210, (+)238	108, 150, 217	$3H_2O$, CO_2, CO, C_2H_2
	250–325	II	10	9.9	(+)320	315	H_2, HCN
	325–495	III	11	10.6	(+)445	440	CH_3NH_2
	>495	Res.	27	27.3	–	–	CuO
$C_6H_{16}N_2O_7Zn$	80–140	I	6	6.1	(+)105	98	H_2O
	140–180	II	12	12.2	(+)160	161	$2H_2O$
	180–315	III	18	18.2	(+)182	285	C_2H_2, CO
	315–450	IV	9.3	9.1	(+)340	420	HCN,
	>450	Res.	54.7	54.4	–	–	$ZnO_3H_7C_2N$

Res. residue, *calc.* calculated

(−) = Endothermic, (+) = Exothermic

water is given off. DTG peak is found at 398 °C while DTA peak is noted at 419 °C. The intermediate produced between second and final stage does not manifest any stability and disintegrates to hydrogen cyanide (two moles) and acetylene (one mole). The third stage ends at 643 °C accompanied by 45% mass-loss. There is one DTG peak (600 °C) and one DTA peak (606 °C) for this stage. The whole degradation process leaves no residue. The pyrolysis of the ligand proceeds in the following way:

$$C_6N_2O_4H_{12} \rightarrow CO\uparrow + 3H_2\uparrow + C_5N_2O_3H_6 \quad \text{I stage}$$

$$C_5N_2O_3H_6 \rightarrow CO_2\uparrow + H_2O\uparrow + C_4N_2H_4 \quad \text{II stage}$$

$$C_4N_2H_4 \rightarrow 2HCN\uparrow + C_2H_2\uparrow \quad \text{III stage}$$

The complex, $[Co(EDDA)(H_2O)_2]\cdot H_2O$, starts to lose mass around 50 °C. The first stage which accounts for 6.3% mass-loss is attributed to the loss of water (outside the coordination sphere) leaving behind the non-hydrated complex. A single peak each for DTG and DTA in this region (both at 80 °C) substantiates the TG results. The remaining complex begins decomposing from 200 °C and up to 460 °C the whole structure is destroyed. In this stage, many small molecules (as a result of the pyrolysis) are released such as H_2O, C_2H_2, HCN, CO, NH_3. For this step, three DTA peaks (212, 255, 423 °C) and four DTG peaks (209, 238, 322 and 390 °C) are observed which clearly show that at least three highly unstable intermediates are also formed during this degradation stage. This stage accounts for 67.6% mass-loss. The residue that is stable after 460 °C is identified as CoO. The two-stage degradation is summarized as under:

$$C_6H_{16}N_2O_7Co \rightarrow H_2O\uparrow + C_6H_{14}N_2O_6Co \quad \text{I stage}$$

$$C_6H_{14}N_2O_6Co \rightarrow CO_2\uparrow + 3H_2O\uparrow + 2C_2H_2\uparrow + HCN\uparrow + NH_3\uparrow + CoO\ \text{(residue)} \quad \text{II stage}$$

The complex, $[Ni(EDDA)(H_2O)_2]$, starts losing mass around 284 °C and shows a single-step decomposition. The ligand framework splits in unusual fashion and gives out O_2, CO, CO_2, ethylene, ethane, hydrogen, nitrogen and water leaving behind nickel as residue. This stage exhibits a mass-loss of 78.2%. This result is also supported by DTG and DTA curves (single peaks). It is interesting to note that in complexation with nickel, the ligand decomposes in a single step, however, when degraded alone, it pyrolyzed in three stages. The route, this complex follows, is:

$$C_6H_{14}N_2O_6Ni \rightarrow H_2O\uparrow + CO_2\uparrow + CO\uparrow + C_2H_4\uparrow + C_2H_6\uparrow + H_2\uparrow + N_2\uparrow + O_2\uparrow + Ni\ \text{(residue)I stage}$$

The complex, $[Cu(EDDA)(H_2O)_2]\cdot H_2O$, begins losing mass around 50 °C. The first step shows a mass-loss of 52.1% ascribed to the elimination of 3 moles of H_2O, one mole each of acetylene, CO and CO_2. This stage ends around 250 °C and is marked by three DTG peaks (108, 150, 217 °C) which suggest that although in TG there is only one fall but the elimination of certain entities from the complex occurs along with the formation of very unstable intermediates. Four peaks for DTA in this region (50–250 °C) support above-drawn conclusion. The second step which commences at 250 °C and terminates at 325 °C, shows a mass-loss of 9.9%. The mainframe of complex, which broke down in the first step, experiences elimination of H_2 and HCN. Single peaks, each for DTG and DTA, are found in this region. The third stage exhibits a mass-loss of 10.6% in the temperature zone of 325–495 °C. A mole of methylamine breaks up from the already destroyed framework of the complex. Single peaks for DTG (440 °C) and DTA (445 °C) are observed for this stage. Above 495 °C, the residue is identified as CuO and was stable. The equations for the degradation stages are as follows:

$$C_6H_{16}N_2O_7Cu \rightarrow 3H_2O\uparrow + CO_2\uparrow + CO\uparrow + C_2H_2\uparrow + C_2H_8N_2OCu \quad \text{I stage}$$

$$C_2H_8N_2OCu \rightarrow H_2\uparrow + HCN\uparrow + CH_5NOCu \quad \text{II stage}$$

$$CH_5NOCu \rightarrow CH_3NH_2\uparrow + CuO \quad \text{III stage}$$

The decomposition for the complex, $[Zn(EDDA)(H_2O)_2]\cdot H_2O$, commences around 80 °C and first step accounts for 6.1% mass-loss which is attributed to the elimination of H_2O (outside coordination sphere). The second stage starts around 140 °C and shows a mass-loss of 12.2%. Two moles of water detach and leave the octahedral complex. Single peaks for DTA and DTG are observed (160 and 161 °C) as was the case for first step (105 and 98 °C, respectively). The third step which starts from 180 °C and ends at 315 °C, exhibits a mass-loss of 18.2% which is marked with the elimination of acetylene and carbon monoxide. Single peaks for DTG and DTA are observed (285 and 182 °C, respectively). The fourth stage begins around 315 °C and loss of 9.1% mass is observed. HCN is eliminated. As was the case with above three stages, single peaks for DTA and DTG were noticed (340 and 420 °C, respectively). The residue was stable above 450 °C and it is evident that a part of the overall framework of the complex remains intact. The results obtained are in accordance with the literature [30–36]. The path of decomposition may be given as:

$$C_6H_{16}N_2O_7Zn \rightarrow H_2O\uparrow + C_6H_{14}N_2O_6Zn \quad \text{I stage}$$

$$C_6H_{14}N_2O_6Zn \rightarrow 2H_2O\uparrow + C_6H_{10}N_2O_4Zn \quad \text{II stage}$$

$$C_6H_{10}N_2O_4Zn \rightarrow C_3H_8N_2O_3Zn + C_2H_2\uparrow + CO\uparrow \quad \text{III stage}$$

$$C_3H_8N_2O_3Zn \rightarrow HCN\uparrow + ZnO_3H_7C_2N \text{ (Residue)}$$
$$\text{IV stage}$$

Conclusions

1. Ligand decomposes in three steps whereas complexes $[Zn(EDDA)(H_2O)_2] \cdot H_2O$, $[Cu(EDDA)(H_2O)_2] \cdot H_2O$, $[Co(EDDA)(H_2O)_2] \cdot H_2O$ and $[Ni(EDDA)(H_2O)_2]$ degrade in four, three, two and one step, respectively.
2. Ligand is more stable than $[Zn(EDDA)(H_2O)_2] \cdot H_2O$, $[Cu(EDDA)(H_2O)_2] \cdot H_2O$, and $[Co(EDDA)(H_2O)_2] \cdot H_2O$ but less stable than $[Ni(EDDA)(H_2O)_2]$ when their Ti's (temperature corresponding to the detection of first mass-loss) are compared.
3. HCN gas was detected in the pyrolysis of $[Zn(EDDA)(H_2O)_2] \cdot H_2O$, $[Cu(EDDA)(H_2O)_2] \cdot H_2O$, and $[Co(EDDA)(H_2O)_2] \cdot H_2O$ whereas it could not be found in the degradation of $[Ni(EDDA)(H_2O)_2]$.
4. For complexes, Ni was the residue in case of $[Ni(EDDA)(H_2O)_2]$ whereas CuO and CoO were found as residue for $[Cu(EDDA)(H_2O)_2] \cdot H_2O$ and $[Co(EDDA)(H_2O)_2] \cdot H_2O$, respectively. In case of $[Zn(EDDA)(H_2O)_2] \cdot H_2O$, part of the main framework of the complex remained intact as residue. For oxide residues, oxygen was taken from degrading complexes.
5. The complexes show the following order of thermal stability: $[Cu(EDDA)(H_2O)_2] \cdot H_2O \sim [Co(EDDA)(H_2O)_2] \cdot H_2O < [Zn(EDDA)(H_2O)_2] \cdot H_2O < [Ni(EDDA)(H_2O)_2]$.
6. The geometries of $[Cu(EDDA)(H_2O)_2] \cdot H_2O$ and $[Co(EDDA)(H_2O)_2] \cdot H_2O$ appear strained which is believed to be the cause of their thermal instability.
7. The ligand, despite being organic in nature, unfolds remarkable stability when judged from the temperature range of its complete degradation, i.e., 210–643 °C. This may be attributed to the formation of one of the intermediates which is considered to be resonance-stabilized and seems to impart thermal stability as well.
8. There was no residue in case of ligand.
9. The activation energies of complexes show that $[Ni(EDDA)(H_2O)_2]$ possesses the highiest thermal stability whereas $[Cu(EDDA)(H_2O)_2] \cdot H_2O$ is the least thermally stable among these complexes.

Acknowledgment The authors are indebted to PINSTECH, Nilore Islamabad for providing the facility of thermonalytical techniques. Messrs Nadeem Ahmad, Adeel Khattak (CD, PINSTECH) and Nehad Ali (Sr. Tech. IAD, PINSTECH) are acknowledged for extending technical assistance.

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