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Investigation of thermal stability and kinetics of thermal degradation of *meridional* isomers of aminocarboxylato cobalt(III) complexes

S.R. Grgurić-Šipka [a], T.J. Sabo [a], S.R. Trifunović [b], D.M. Minić [c,*]

[a] *Faculty of Chemistry, University of Belgrade, P.O. Box 158, 11000 Belgrade, Yugoslavia*
[b] *Faculty of Science, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Yugoslavia*
[c] *Faculty of Physical Chemistry, University of Belgrade, P.O. Box 173, 11000 Belgrade, Yugoslavia*

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Abstract

The thermal properties of some mixed complexes of cobalt(III) containing tetradentate ethylenediamine-*N*,*N*′-di-3-propionate (eddp) ligand and several amino acids were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal stability derived from decomposition temperatures was discussed in terms of amino acid present. It was shown that the processes of thermal decomposition of these complexes are multi-step degradation processes. Some of these can be separated into individual steps.

The corresponding kinetic and thermodynamic parameters of these processes were determined, and the possible mechanisms were discussed.

Keywords: Cobalt(III) complexes; Thermal analysis; Kinetic studies

1. Introduction

Cobalt(III) complexes with the ethylenediamine-*N*,*N*′-di-3-propionate (eddp) ligand have been investigated in the past few years [1–5]. The eddp is a tetradentate ligand with two nitrogen and two oxygen atoms as donors and, as well as edda, can take two different configurations in the six-coordinate metal complexes, s-*cis* and uns-*cis* (Fig. 1a) [6]. It was noted that complexes containing eddp which forms a six-membered aminocarboxylato backbone, prefer the uns-*cis* configuration, suggesting that the size of the chelate ring has a profound effect on the distribution of geometric isomers. In the case of octahedral edda-type-Co(III) complexes with additional unsymmetrical bidentate ligand (as amino acids) a further isomerism in the uns-*cis* geometry arises, *facial* uns-*cis* and *meridional* uns-*cis* (Fig. 1b). These compounds, as well as the others previously synthesized compounds are attracting the attention because of their importance in studying biological systems. In the last period there has been an increased interest in Co(III) complexes with ligands similar to eddp, because of their possible hydrolytic activity on DNA molecule [7]. Also these compounds are very interesting in the view of studying their chirality, optical resolution, isomerization reactions, photochemistry and other various aspects [8–10].

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[*] Corresponding author. Fax: +381-11-187-133.
E-mail address: dminic@ffh.bg.ac.yu (D.M. Minić).

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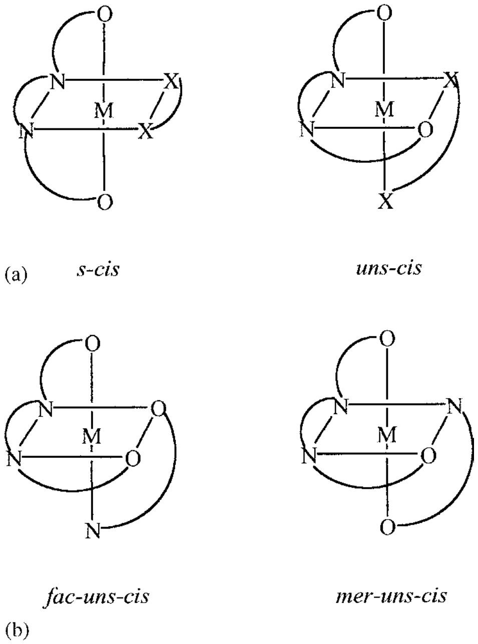

Fig. 1. Possible geometrical isomers of [M(eddp)L] complexes: (a) L-symmetrical bidentate ligand; (b) L-unsymmetrical N,O-bidentate ligand.

This paper investigates the thermal behavior of a series of *meridional* isomers of uns-*cis*-[Co(eddp)Am] complexes (Am: anion of alanine (ala), valine (val), nor-valine (n-val), leucine (leu), isoleucine (ile)), whereas the thermal studies of both *facial* and *meridional* isomers of uns-*cis*-[Co(eddp)gly] (gly: anion of glycine) has already been published [11]. It was shown that the stepwise degradation of the *facial* isomer proceeded with the individual steps overlapping that prevented analysis of each step individually, unlike degradation of the *meridional* isomer where the detailed analyses was carried out. The purpose of this investigation is to investigate the thermal decomposition pathways of these complexes and to elucidate kinetic parameters derived from their TG curves.

2. Experimental

2.1. Material preparation

The investigated complexes were prepared by the reaction of uns-*cis*-Na[Co(eddp)CO_3] and corresponding amino acid, as described earlier [12,13]. The complexes were fully characterized by elemental analysis, infrared and electronic absorption spectra.

2.2. Thermal analyses

Thermal analyses were performed on a DuPont 1090 thermal analyzer, using a DSC cell and a TG cell. The TG and DSC curves were obtained at a heating rate of 5 and 20 °C min^{-1} in N_2 atmosphere. The masses of the samples used in TG and DSC measurements were in the range 3.50–9.40 mg.

2.3. Mass spectra

Mass spectra were recorded on a double focusing reverse geometry Funnigan-MAT 8230 mass spectrometer at a resolution of 1000, using a combined EI–CI source at a source temperature of 200 °C, as described earlier [11].

2.4. X-ray analysis

X-ray analysis was carried out on a Philips Analytical PW710 Diffractometer, using Cu Kα radiation (0.15405 nm).

3. Results and discussion

3.1. Thermal studies

Thermal investigation of the synthesized complexes in the temperature interval from room temperature to 600 °C reveals a series of degradation stages (Fig. 2). From the DSC curves, it can be seen that stepwise degradation of all investigated complexes proceeded with the individual steps overlapping which prevented analysis of each step individually. In all compounds can be observed first the loss of both water of crystallization and trace of hygroscopic water. The mass loss for the freshly prepared samples agrees with the composition given by elemental analysis. However, the water content of the older samples, as can be seen in Table 1, is somewhat higher (the complexes [Co(eddp)leu] and [Co(eddp)ile]). The expected endothermic behavior for such processes has been observed in the DSC curves over the 90–160 °C temperature range for all complexes. The anhydrous

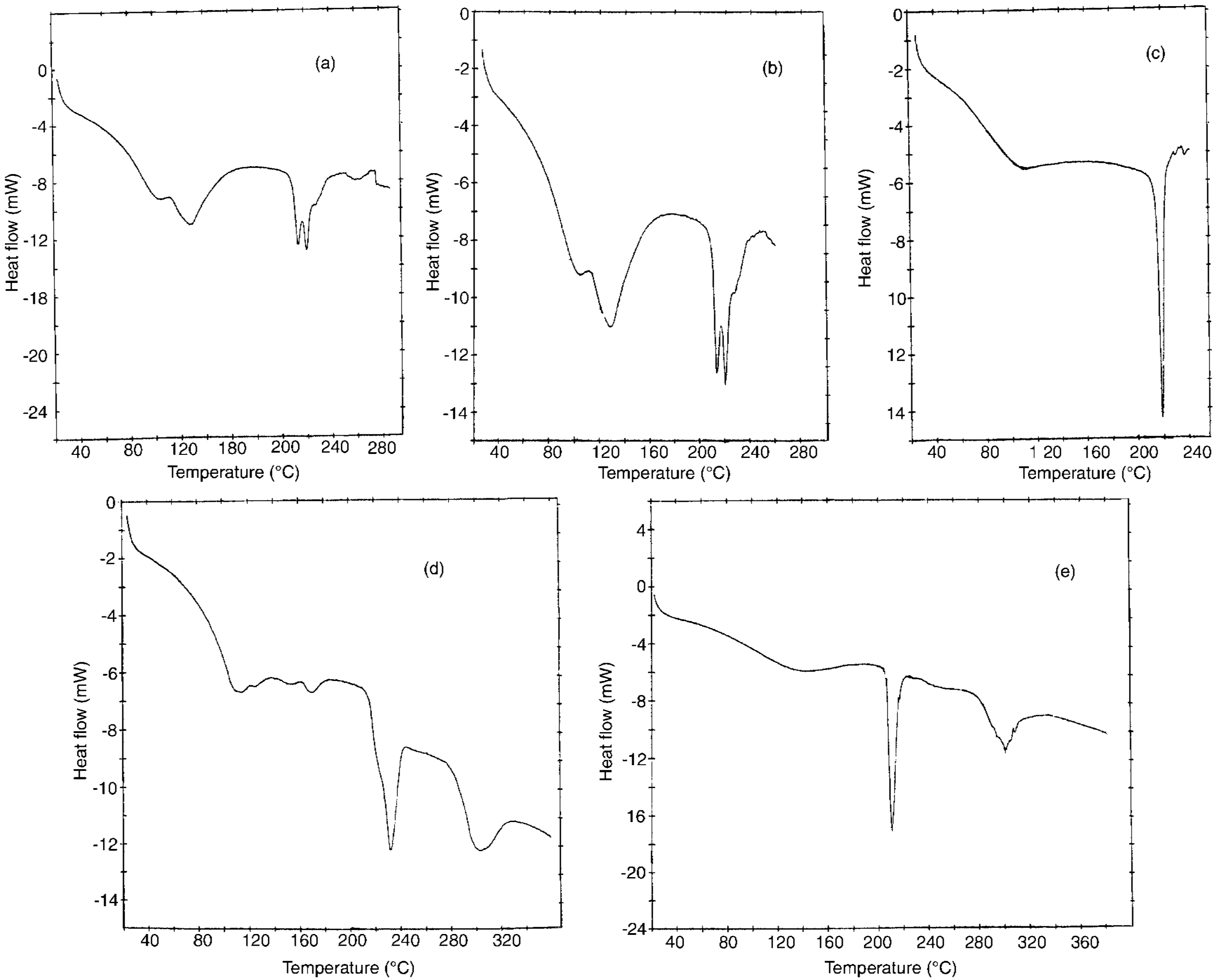

Fig. 2. DSC curves of the *mer*-uns-*cis*-[Co(eddp)Am]: (a) *mer*-uns-*cis*-[Co(eddp)ala]; (b) *mer*-uns-*cis*-[Co(eddp)val]; (c) *mer*-uns-*cis*-[Co(eddp)n-val]; (d) *mer*-uns-*cis*-[Co(eddp)-leu]; (e) *mer*-uns-*cis*-[Co(eddp)ile].
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Table 1
TG data and products of stepwise thermal degradation of the complexes

Complex	Step 1		Step 2		Step 3		Step 4		Step 5	
	T (°C)	Mass loss found/calcd (%)	*T* (°C)	Mass loss found/calcd (%)	*T* (°C)	Mass loss found/calcd (%)	*T* (°C)	Mass loss found/calcd (%)	*T* (°C)	Mass loss found/calcd (%)
[Co(eddp)ala]·0.5H_2O	80–130	2.70/2.51 ($0.5H_2O$)	210–260	12.90/12.29 (CH_4, CO)	260–330	7.95/7.26 ($0.5C_2N_2$)	330–480	15.96/15.64 (C_2H_4, CO)		
[Co(eddp)val]·1.5H_2O	90–130	6.95/6.92 ($1.5H_2O$)	200–240	14.40/13.85 (C_2H_4, CO)	240–310	14.00/13.33 (C_2H_2, $0.5C_2N_2$)	310–500	18.00/18.46 (C_2H_4, CO)		
[Co(eddp)n-val]·0.5H_2O	80–130	2.53/2.42 ($0.5H_2O$)	205–230	15.20/15.05 (C_2H_2, CO)	230–270	5.00/4.30 (CH_4)	270–330	14.88/14.52 (C_2H_4, C_2N_2)	330–500	15.45/15.05 (C_2H_4, CO)
[Co(eddp)leu]·H_2O	90–150	7.05[a]/4.40 (H_2O)	210–250	17.06/17.60 (C_3H_8, CO)	250–310	9.80/10.27 (CH_4, $0.5C_2N_2$)	310–420	19.40/20.00 (C_2H_4, C_2N_2)	420–600	32.60/33.70 (C_2H_4, $2CO_2$, H_2O, $2H_2$)
[Co(eddp)ile]·0.5H_2O	80–140	5.90[a]/2.25 (H_2O)	220–230	10.25/11.00 (CH_4, CO)	230–315	23.83/24.00 (C_3H_8, C_2N_2)	315–450	21.38/22.00 (C_2H_4, CH_4, CO_2)	450–600	25.05/26.00 ($0.5C_2N_2$, CO,CO_2 $3H_2$)

[a] Loss of both hygroscopic and crystal water.

complexes are stable until about 200 °C, but after that thermal decomposition is observed. The temperature at which the anhydrous complexes begin to decompose varies with the amino acid ligand.

However, the TG curves of the investigated complexes showed the better separated stepwise degradation, which permitted determination of mass losses of each of the individual steps (Fig. 3). From the observed weight losses, possible products of degradation were proposed and compared with those calculated from given formulae as reported in Table 1. The first step corresponds to the loss of both crystal and trace of hygroscopic water, the second and third steps are attributed to the fragmentation of the coordinated amino acids, and after that starts the decomposition of eddp ligand. The presence of different products of degradation is a consequence of change of present amino acid chain (Table 1). It could be assumed that complexes on heating undergo decomposition that starts with the fragmentation of the amino acid molecule, followed by oxidation of the remaining coordinated eddp. The result is appearance of numerous products in a gaseous phase. The greater stability of coordinated eddp ligand comparing with the amino acid is due to three chelate rings forming by tetradentate eddp. By heating the complexes over 600 °C it was determined using X-ray analyses that final residue of decomposition is Co. Taking into account this fact, it could be suggest that decomposition proceeds with reduction of central metal ion and oxidation of the remaining ligands.

Similar thermal degradation pathways that were observed are consistent with their very similar structure derived from almost the same electronic absorption and infrared spectra [12,13]. Although the change of the hydrocarbon side chains of the amino acid could not affect the significant difference in the decomposition paths, it can be noticed that decrease in stability going from [Co(eddp)ala] to [Co(eddp)n-val]. The enlargement of the number of carbon atoms lead to decrease in stability. The longer side chains may be assumed to be responsible for a decrease in thermal stability, due to their vibrations or steric hindrance. The relatively high stability of [Co(eddp)leu] and [Co(eddp)ile] could be explained by $–CH(CH_3)–CH_2CH_3$ and $–CH_2–CH(CH_3)_2$ side chains which can take place in forming intermolecular bridges [14].

On the basis of the above results, i.e. taking into account the experimental (TG) and theoretical calculations based on mass losses, the processes of thermal decomposition of the complexes can be assumed to occur as general mechanism pathways:

Step 1 :

$$[\mathrm{Co(eddp)(Am)}]\cdot x\mathrm{H_2O} \rightarrow [\mathrm{Co(eddp)(Am)}] + x\mathrm{H_2O}$$

Step 2 :

$$[\mathrm{Co(eddp)(Am)}] \rightarrow [\mathrm{Co(eddp)(Am')}] + \mathrm{C}_n\mathrm{H}_n + \mathrm{CO}$$

Step 3 :[1]

$$[\mathrm{Co(eddp)(Am')}] \rightarrow [\mathrm{Co(eddp')}] + \mathrm{C}_n\mathrm{H}_n + \mathrm{C_2N_2}$$

Step 4 :

$$[\mathrm{Co(eddp')}] \rightarrow [\mathrm{Co(eddp'')}] + \mathrm{C}_n\mathrm{H}_n + \mathrm{C_2N_2}$$

Step 5 :

$$[\mathrm{Co(eddp'')}] \rightarrow \mathrm{Co} + \mathrm{C}_n\mathrm{H}_n + \mathrm{CO} + \mathrm{CO_2} + \mathrm{H_2} + \mathrm{H_2O}$$

For a more detailed analysis of these processes, the mass spectra of [Co(eddp)val] and [Co(eddp)n-val] were used. They show the presence of species that are proposed to be formed on sample decomposition. Degradation of the [Co(eddp)val] in the first phase of Step 3 gives rise to species C_2N_2 along with the formation of an ion with $m/z = 281$. The presence of ions with $m/z = 255, 228, 202$ results from the degradation according to the following reactions:

Step 3 :

$$\mathrm{CoC_9H_{18}N_3O_5} \rightarrow \underset{m/z=281}{\mathrm{CoC_8H_{18}N_2O_5}} + 0.5\mathrm{C_2N_2}$$

$$\underset{m/z=281}{\mathrm{CoC_8H_{18}N_2O_5}} \rightarrow \underset{m/z=255}{\mathrm{CoC_6H_{16}N_2O_5}} + \mathrm{C_2H_2}$$

Step 4 :

$$\underset{m/z=255}{\mathrm{CoC_6H_{16}N_2O_5}} \rightarrow \underset{m/z=228}{\mathrm{CoC_4H_{12}N_2O_5}} + \mathrm{C_2H_4} + \mathrm{H_2O}$$

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[1] In this step eddp starts to decompose on the way that depends on the complex.

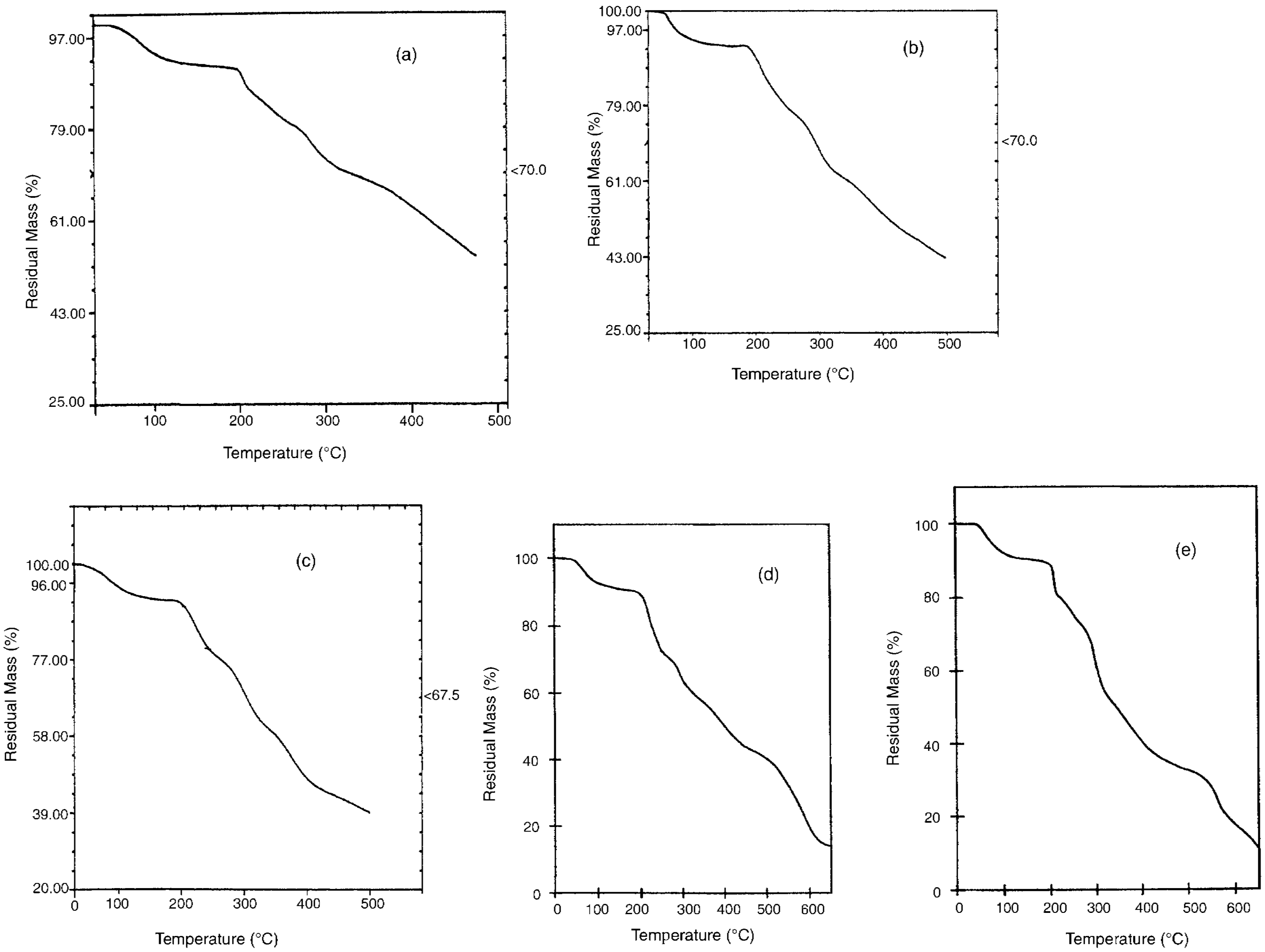

Fig. 3. TG curves of the *mer*-uns-*cis*-[Co(eddp)Am]: (a) *mer*-uns-*cis*-[Co(eddp)ala]; (b) *mer*-uns-*cis*-[Co(eddp)val]; (c) *mer*-uns-*cis*-[Co(eddp)n-val]; (d) *mer*-uns-*cis*-[Co(eddp)-leu]; (e) *mer*-uns-*cis*-[Co(eddp)ile].

$$\underset{m/z=228}{\mathrm{CoC_4H_{12}N_2O_5}} \rightarrow \underset{m/z=202}{\mathrm{CoC_3H_{12}NO_5}} + 0.5\mathrm{C_2N_2}$$

$$\underset{m/z=202}{\mathrm{CoC_3H_{12}NO_5}} \rightarrow \mathrm{CoC_3H_{10}NO_4} + \mathrm{H_2O}$$

It was noted that [Co(eddp)n-val] undergoes faster degradation, although its mass spectrum shows some molecular species proposed on the basis of the TG.

Step 2 :

$$\underset{m/z=362}{\mathrm{CoC_{12}H_{22}N_3O_6}} \rightarrow \underset{m/z=335}{\mathrm{CoC_{11}H_{22}N_3O_5}} + \mathrm{CO}$$

$$\underset{m/z=335}{\mathrm{CoC_{11}H_{22}N_3O_5}} \rightarrow \underset{m/z=310}{\mathrm{CoC_9H_{20}N_3O_5}} + \mathrm{C_2H_2}$$

Step 4 :

$$\mathrm{CoC_8H_{16}N_3O_5} \rightarrow \underset{m/z=276}{\mathrm{CoC_8H_{14}N_3O_4}} + \mathrm{H_2O}$$

$$\underset{m/z=276}{\mathrm{CoC_8H_{14}N_3O_4}} \rightarrow \underset{m/z=231}{\mathrm{CoC_7H_{14}N_3O_2}} + \mathrm{CO_2}$$

3.2. *Kinetic studies*

The thermal effects observed in the DSC curves are not suitable for kinetic analysis because the peaks are complex, asymmetric and overlapped. However, the TG curves display better separated processes, which allowed a kinetic analysis of individual steps. For this purpose were applied Newkirk [15], Freeman–Carroll

Table 2
The activation energy (kJ/mol) of individual steps of the decomposition of the complexes derived from TG curves[a]

Complex	Step 1	Step 2	Step 3	Step 4	Step 5
[Co(eddp)ala]·0.5H_2O	27.77	133.98	142.33	129.50	–
	35.50	94.77	132.11	100.70	–
	30.80	110.50	135.11	108.20	–
[Co(eddp)val]·1.5H_2O	–	85.69	117.40	81.30	–
	–	95.10	131.00	90.20	–
	–	90.20	125.82	88.64	–
[Co(eddp)n-val]·0.5H_2O	32.02	23.82	182.90	267.82	187.28
	47.13	18.82	197.04	250.80	159.12
	40.15	20.80	180.12	235.22	160.80
[Co(eddp)leu]·H_2O	71.72	194.72	81.95	54.49	66.99
	82.04	183.75	77.74	58.56	75.20
	80.40	190.72	75.50	50.43	70.81
[Co(eddp)ile]·0.5H_2O	47.50	132.08	151.08	85.04	98.85
	51.82	148.06	175.14	90.54	128.88
	50.76	141.05	160.04	100.18	108.10

[a] The first value for each complex represents data obtained by Newkirk's method, the second by Coats–Redfern's method and the third by Freeman–Carroll's method. The error of methods is 1%.

Table 3
The activation parameters relating to the rate constant calculated from TG curves by Newkirk's method for the first and second step of degradation of the complexes

Complex	Step 1			Step 2		
	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/mol K)	$\Delta G^{\#}$ (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/mol K)	$\Delta G^{\#}$ (kJ/mol)
[Co(eddp)ala]·0.5H_2O	24.92	−58.16	47.78	130.06	−109.10	188.22
[Co(eddp)val]·1.5H_2O	–	–	–	81.63	−104.06	132.96
[Co(eddp)n-val]·0.5H_2O	28.82	−184.68	101.39	20.23	−215.22	123.53
[Co(eddp)leu]·H_2O	67.52	−191.35	144.63	190.25	−142.10	261.77
[Co(eddp)ile]·0.5H_2O	44.02	−68.19	72.31	128.78	122.08	68.66

[16] and Coats–Redfern [17] methods. The reaction order $n = 1$ is typical for reactions of decomposition where the surface is decomposed by first-order kinetics. The obtained activation energies for these processes are listed in Table 2. The values for activation energies follow the assumption derived from consideration of thermal stability. It can be noticed that decrease in values of activation energies going from [Co(eddp)ala] to [Co(eddp)n-val], but higher values for the [Co(eddp)leu] and [Co(eddp)ile] what is consequence of longer side chains that can take place in forming intermolecular interactions, as assumed previously.

The activation parameters relating to the rate constant obtained from TG curves by Newkirk's method were calculated for the first and second steps of degradation of the complexes in the usual way [18] (Table 3).

4. Conclusion

On the basis of the results obtained from TG and DSC curves it could be concluded that investigated complexes have very similar thermal behavior, thermal stability and decomposition pathways. The effect of the different amino acid chain is reflected with the slight differences, i.e. the lower stability of the [Co(eddp)n-val] complex and the greater stability of the [Co(eddp)leu] complex. The activation energies of the reaction decomposition obtained from a few different methods are in good agreement. In addition, degradation pathways are proposed.

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