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Mixed cobalt(III) complexes with aromatic amino acids and diamine
Part V. Thermal investigation of (1,2-diaminoethane)*bis*(*S*-tyrosinato)cobalt(III) complex diastereomers

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Abstract

Thermal properties of (1,2-diaminoethane)*bis*(*S*-tyrosinato)cobalt(III) complex diastereomers are investigated by means of TG technique in 293–873 K temperature range. This is a first thermal study of $[Co(S\text{-aa})_2en]^+$ (*S*-aa = anion of *S*-amino acid; en = 1,2-diaminoethane) complex diastereomers. It is shown that thermal decompositions of these complexes are multi-step degradation processes, which in some cases can be satisfactory separated into individual steps, depending on the molecular symmetry. It is proposed that the degradation processes occur with cleavage of the side chain of one *S*-tyrosinato ligand, followed by the cleavage of the second side chain by further heating. The proposed pathways of decomposition are in accordance with results of thermal degradation of noncoordinated *S*-tyrosine [F. Rodante, G. Marrosu, G. Catalani, Thermochim. Acta 194 (1992) 197–213]. In the case of diastereomers which crystallize with water molecules, the departure of both hygroscopic and crystal water occurs before.

The corresponding kinetic and thermodynamic parameters of some processes were determined.

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Keywords: Cobalt(III) complexes; *S*-tyrosine; Thermal analysis

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1. Introduction

It has been well known that aromatic amino acids side chains have important role in many molecular recognitions in vivo: antibody–antigen [1–3], enzyme–substrate [4–7], protein–nucleic acid base [8,9], protein–oligosaccharide [10], etc. The processes of molecular recognition occur through various types of noncovalent interactions of aromatic side chains, such as hydrophobic, cation-π, aromatic ring stacking, hydrogen bonds (tyr and trp), etc. A strong interest has recently been shown to investigate these types of interactions, whereby the complexes of transition metals with aromatic amino acids have proved to be good model systems [11–15].

In order to study noncovalent interactions in which *S*-tyrosinato moiety takes part, we have recently synthesized five out of six theoretically possible diastereomers of (1,2-diaminoethane)*bis*(*S*-tyrosinato)cobalt(III) complex [16]. In this paper we have undertaken thermal analysis of diastereomers of this complex to obtain information about stereochemical effects on their thermal stability.

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2. Experimental

2.1. Material preparation

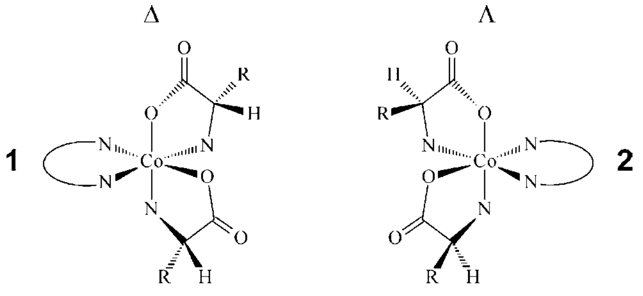
The diastereomers of [Co(*S*-tyr)$_2$en]Cl (*S*-tyr = *S*-tyrosinato ligand; en = 1,2-diaminoethane) complex (**1–4**, Fig. 1) were obtained by the reaction of *trans*-[CoCl$_2$(en)$_2$]Cl complex with *S*-tyrosine by the procedure described in literature [16].

2.2. Thermal analysis

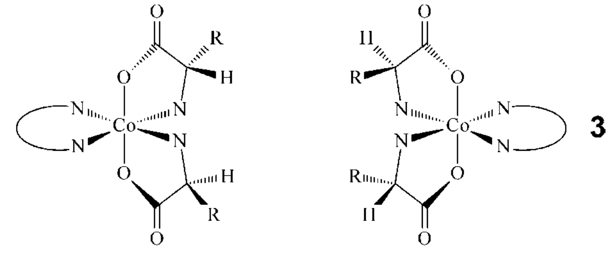
Thermogravimetric curves for complexes were recorded on DuPont 9900 thermo analyser in nitrogen atmosphere up to 873 K at heating rates of 5 and 10 K min^{-1}.

2.3. IR spectroscopy

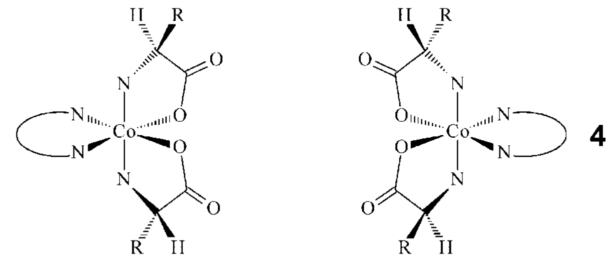
The IR spectra (KBr technique) were recorded on Perkin-Elmer FTIR 31725X spectrometer.



C$_1$-*cis*(o)



trans(o)



C$_2$-*cis*(o)

Fig. 1. Theoretically possible diastereomers of [Co(*S*-tyr)$_2$en]$^+$ complex ion (R = —CH$_2$—C$_6$H$_4$—OH).

3. Results

3.1. Thermal analysis

Thermal investigation of Δ-C$_1$-*cis*(O)-(**1**), Λ-C$_1$-*cis*(O)-(**2**), Λ-*trans*(O)-(**3**) and Λ-C$_2$-*cis*(O)-(**4**) diastereomers of [Co(*S*-tyr)$_2$en]Cl complex was carried out by TG technique, in the range from 293 to 873 K, in stream of nitrogen. The TG curves obtained at 5 and 10 K min^{-1} heating rates and corresponding DTG curves (at 5 K min^{-1}) are shown in Fig. 2.

The intervals of the temperature of individual degradation steps for each investigated diastereomer, as well as found and calculated mass losses, at rates of heating of 5 and 10 K min^{-1}, are presented in Tables 1 and 2, respectively.

3.2. IR spectra

IR spectra of complex **2** performed at room temperature and after isothermal treatments at 573 and 873 K in inert atmosphere were recorded and presented in Fig. 3.

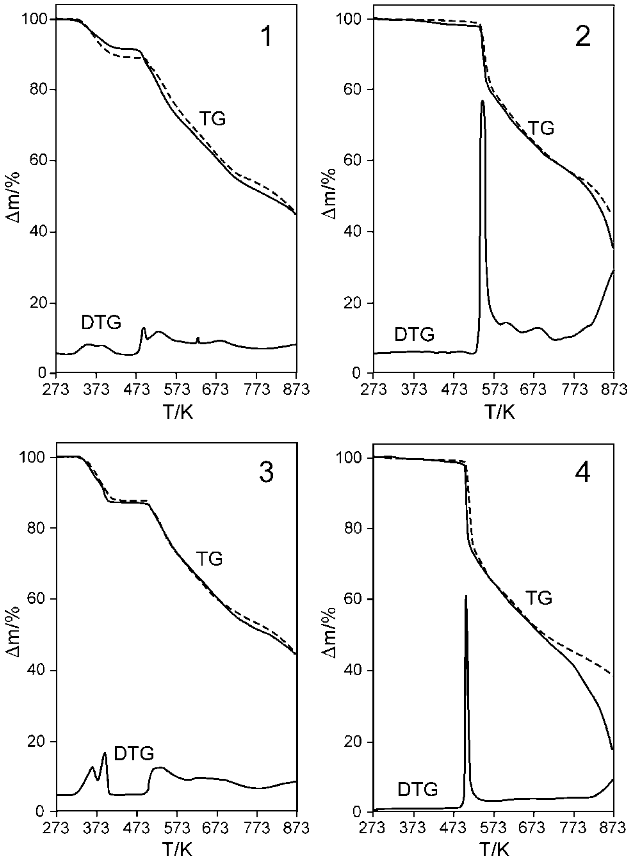


Fig. 2. TG curves of Δ-C$_1$-*cis*(O)-(**1**), Λ-C$_1$-*cis*(O)-(**2**), Λ-*trans*(O)-(**3**) and Λ-C$_2$-*cis*(O)-(**4**) diastereomers of [Co(*S*-tyr)$_2$en]Cl complex at heating rates of 5 K min^{-1} (—) and 10 K min^{-1} (- - -) and corresponding DTG curves (heating rate of 5 K min^{-1}).

Table 1
TG data (heating rate of 5 K min^{-1}) and products of stepwise thermal degradation of the complexes

Complex	Step 1 and 1′[a]		Step 2		Step 3		Residue	
	T (K)	Mass loss (found/calc (%))	T (K)	Mass loss (found/calc (%))	T (K)	Mass loss (found/calc (%))	T (K)	Found/calc (%)
1	325–409 483–493	1/8.00 1′/3.93 $\sum$11.93/10.92 (3.5H_2O)	493–753	35.62/36.68 (2-CH—Ar—OH)			753	52.45/52.40
2	–	–	539–556	19.32/20.61 (—CH—Ar—OH)	556–717	21.07/20.61 (—CH—Ar—OH)	717	59.61/58.78
3	339–401	12.51/12.28 (4H_2O)	503–770	35.98/36.16 (2-CH—Ar—OH)			770	51.51/51.56
4	–	–	503–690	48.07/48.53 (2-CH—Ar—OH + HCON$(CH_3)_2$)			690	51.93/51.47

[a] Loss of both hygroscopic and crystal water.

Table 2
TG data (heating rate of 10 K min^{-1}) and products of stepwise thermal degradation of the complexes

Complex	Step 1[a]		Step 2		Step 3		Residue	
	T (K)	Mass loss (found/calc (%))	T (K)	Mass loss (found/calc (%))	T (K)	Mass loss (found/calc (%))	T (K)	Found/calc (%)
1	330–417	10.65/10.92 (3.5H_2O)	493–748	35.44/36.68 (2-CH—Ar—OH)			748	54.10/52.40
2	–	–	538–561	20.59/20.61 (—CH—Ar—OH)	561–728	19.36/20.61 (—CH—Ar—OH)	728	60.05/58.78
3	345–413	12.35/12.28 (4H_2O)	501–793	35.91/36.16 (2 —CH—Ar—OH)			793	51.74/51.56
4	–	–	502–697	49.73/48.53 (2-CH—Ar—OH + HCON$(CH_3)_2$)			697	50.27/51.47

[a] Loss of both hygroscopic and crystal water.

3.3. Kinetic data

The results of kinetic analysis (activation energy values) of individual steps for isolated complexes (**1**–**4**) on the basis of Newkirk's [17], Freeman–Carroll's [18] and Coats–Redfern's methods [19] are shown in Table 3.

Table 3
The activation energy (kJ mol^{-1}) of individual steps of the decomposition of the complexes derived from TG curves[a] obtained at heating rate of 10 K min^{-1}

Complex	Step 1	Step 2	Step 3
1[b]	23.80 24.00 38.00		
2		101.30 103.00 105.80	64.64 66.00 66.76
3[b]	44.96 46.00 66.00		
4		210.50 210.00 212.20	

[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%.

[b] For complexes **1** and **3** Steps 2 and 3 are unresolved, and TG curves are not suitable for determination and calculation of E_a.

Table 4
The activation parameters relating to the rate constant calculated from TG curves (heating rate of 10 K min^{-1}) by Newkirk's method for the corresponding steps of degradation of the complexes

Complex/step	Z (s^{-1})	$\Delta^{\#}S^{\circ}$ (J/mol K)	$\Delta^{\#}H^{\circ}$ (kJ/mol)	$\Delta^{\#}G^{\circ}$ (kJ/mol)	$K^{\#}$
1/1	9.3×10^{1}	198.0	19.9	93.5	9.3×10^{-14}
2/2	4.3×10^{5}	65.4	96.4	132.3	1.8×10^{-13}
2/3	1.1×10^{4}	174.2	59.4	167.9	1.6×10^{-14}
3/1	1.2×10^{5}	174.5	41.6	111.1	4.0×10^{-14}
4/2 and 3	7.5×10^{19}	122.7	168.8	105.9	1.3×10^{-11}

The activation parameters relating to the rate constant obtained from TG curves by Newkirk's method, and calculated for the corresponding steps of degradation of the complexes in the usual way [20] are listed in Table 4.

4. Discussion

In [Co(S-tyr$)_2$en]Cl complex each S-tyrosinato ligand is coordinated as bidentate, through carboxylate oxygen atom and nitrogen atom from NH_2 group. The 1,2-diaminoethane (ethylenediamine) is coordinated via two nitrogen atoms in the bidentate manner.

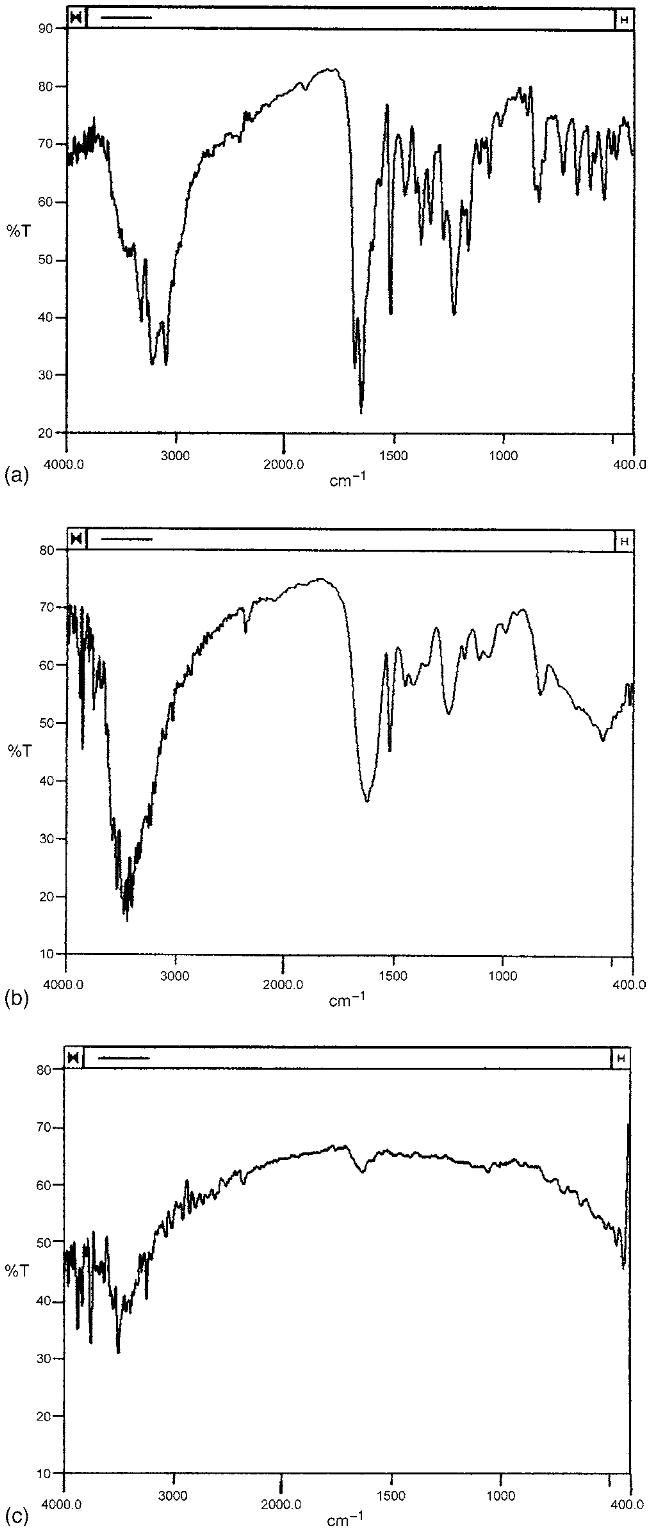


Fig. 3. IR spectra of complex **2** at room temperature (a), after heating and isothermal treatment at 573 K (b) and 873 K (c).

The complex ion of $[Co(S\text{-}tyr)_2en]^+$ composition can theoretically occurs in the form of six diastereomers (Fig. 1). According to the molecular pseudo-symmetry the investigated compound may be related to C_2 (Λ and Δ-*trans*(O) and Λ and Δ-C_2-*cis*(O)-diastereomers) and C_1 symmetry (Δ and Λ-C_1-*cis*(O)-diastereomers). TG curves of four investigated diastereomers: Δ-C_1-*cis*(O)-(**1**), Λ-C_1-*cis*(O)-(**2**), Λ-*trans*(O)-(**3**) and Λ-C_2-*cis*(O)-(**4**) are shown in Fig. 2. It is obvious that TG curves for any particular diastereomer obtained at heating rates of 5 and 10 K min^{-1} are very similar, especially in the region of proposed breaking of *S*-tyrosinato side chains (Tables 1 and 2).

Thermal investigation of the diastereomers in the temperature interval from 293 to 873 K exhibits a series of endothermic degradation steps starting for complexes **1** and **3** at about 330 and 345 K, respectively, and for complexes **2** and **4** at about 540 and 500 K, respectively (Tables 1 and 2). The complexes **1** and **3** contain structural water in solid state [16,21] and the first degradation step (in Tables 1 and 2 denoted as Step 1) is consistent with the loss of hygroscopic and crystallization water. From TG curves scanned at heating rate of 10 K min^{-1} it seems that loss of water occurs in one continuous step (Fig. 2). However, when the heating is performed slower (heating rate of 5 K min^{-1}), it is observed on the basis of TG, as well as the corresponding DTG curves, that this process occurs in at least two “sub-steps”. Although mentioned “sub-steps” are poorly resolved, these data suggest that each of complexes **1** and **3** contains two different kind of water bonded at two various ways.

The complexes **2** and **4** crystallize without water (Step 1 corresponding to loose of water is not included).

The first degradation step seen from TG curves for complex **2** (Step 2 in Tables 1 and 2) corresponds to the loss of one *S*-tyrosinato side chain and as a consequence the formation of chelate glycinato ring. This supposition is in accordance with literature data for thermal decomposition of noncoordinated *S*-tyrosine. Namely, during thermal degradation of *S*-tyrosine in nitrogen atmosphere at heating rate of 10 K min^{-1} the breakage between α- and β-carbon atoms occurs in temperature range of 566–596 K; the presence of aromatic ring favours the breakage of the side chain during thermal decomposition of amino acids [22]. Further, GC–MS spectroscopic data also indicate that the base peak (100%) during fragmentation of tyrosine is ion fragment $Ar\text{–}CH_2{}^+$, because of localisation of the positive charge on the β-carbon atom [23]. The fact that our complexes begin to lose side chains at lower temperatures than noncoordinated tyrosine could be caused by displacement of electron density toward central metal ion during coordination, and consequently more expressive localisation of the positive charge on the β-carbon atom of tyrosinato ligand.

As mentioned above, the complexes **1** and **2** have no symmetry elements (they belong to C_1-symmetry, Fig. 1). Because of that two *S*-tyrosinato ligand side chains have different chemical environments in the molecule. It has been noticed that amino-group avoids *trans* coordination toward another one [24], i.e., NH_2-group of *S*-tyrosinato ligand, which is in *trans* position to carboxylate oxygen atom, is electronically favoured. Because of that, we assume that the decomposition of the side group of *S*-tyrosinato ligand with

NH_2-group being *trans* to NH_2-group of diamine, occurs first. By further heating, decomposition of the second *S*-tyrosinato side chain occurs (Step 3). The mass residue of complex **2** at 728 K (Tables 1 and 2) is in agreement with the $[Co(gly)_2en]Cl$ complex composition. Unfortunately, the intermediate complex is not stable enough that could be investigated.

Very good correlation between TG data and IR data obtained by recording the spectra of complex **2** at room temperature, after heating and isothermal treating the sample at 573 and 873 K (Fig. 3). It is obvious that the complex undergoes structural changes during heating to 573 K but IR bands at 1514 and 825 cm^{-1} (assigned to aromatic ν(C=C) and γ(CH), respectively) suggest that one *S*-tyrosinato side chain is still present (Fig. 3b). By further heating occurs the breaking of coordination bonds with cobalt ion which leads to the decomposition of all ligands. Consequently, there are no bands for any functional groups in IR spectrum of complex **2** residue obtained after heating and isothermal treating the sample at 873 K (Fig. 3c).

The stepwise degradation of complexes **1** and **3** (after the loss of crystal water) proceeds the most probably also with cleavage of the *S*-tyrosinato side chains, but in these cases through the nonresolved degradation steps (Steps 2 and 3 occur simultaneously). In accordance to complex **2** the mass residues at approximately 723 K (Tables 1 and 2) are consistent with $[Co(gly)_2en]Cl$ complex composition.

We have recently performed X-ray crystal structures of complexes **1** and **3** [16,21], and these results exhibit that two different types of noncovalent interactions between two aromatic groups are present, i.e., $CH\cdots\pi$ (in complex **1**) and $\pi\cdots\pi$ (in complex **3**), respectively [21]. The breaking of these intermolecular noncovalent interactions, which occur during heating, may be the reason for nonresolved degradation steps for these complexes.

Thermal decomposition process for complex **2** (Step 2) starts at somewhat higher temperature (Tables 1 and 2) in comparison with thermal decomposition of other diastereomers (**1**, **3** and **4**, Table 1). We have recently established on the basis of NMR spectra the existence of intra- and interligand $NH\cdots\pi$ interactions in complex **2** in water solution [25]. It is reasonable to assume that $NH\cdots\pi$ interactions are also present in the crystal lattice of this diastereomer. Since $NH\cdots\pi$ interactions are energetically more favorable than $CH\cdots\pi$ and $\pi\cdots\pi$ ones [26] which were established in crystal lattices of complexes **1** and **3**, it could be the explanation for higher thermal stability of complex **2** in comparison with the others.

In the case of complex **4**, NMR spectrum of the complex in DMSO-d_6 solution shows that the complex crystallizes with 1 mol of dimethylformamide added to water solution of the sample to initiate crystallization. We suppose that the mass loss of 25% in the first degradation step (Step 2) corresponds to degradation through cleavage of one *S*-tyrosinato ligand side chain with the loss of 1 mol DMF simultaneously. The mass residue at 698 K (Tables 1 and 2) is also consistent with $[Co(gly)_2en]Cl$ complex composition.

The purpose of the TG analysis in this paper was not the determination of the final residue, but to establish a general mechanism of degradation. On the basis of the results presented above (i.e., taking into account the experimental data (TG) and calculated mass losses at chosen temperatures), the processes of thermal decomposition of the complexes **1–4** in 293–873 K temperature range can be assumed to occur as the following general mechanism:

- *Step* 1: $[Co(S\text{-tyr})_2en]Cl\cdot xH_2O \rightarrow [Co(S\text{-tyr})_2en]Cl + xH_2O$.
- *Step* 2: $[Co(S\text{-tyr})_2en]Cl \rightarrow [Co(S\text{-tyr})(gly)en]Cl$ + one *S*-tyrosinato side chain.
- *Step* 3: $[Co(S\text{-tyr})(gly)en]Cl \rightarrow [Co(gly)_2en]Cl$ + second *S*-tyrosinato side chain.

For the kinetic analysis of individual steps of isolated complexes (**1–4**) we applied three nonisothermal methods applicable to TG curves: Newkirk's [17], Freeman–Carroll's [18] and Coats–Redfern‘s methods [19]. The degradation steps with no well resolved TG curves were not suitable and consequently were not the object of this analysis. The plot of $\log k$ versus $1/T$ enabled us to obtain the activation energy E_a directly from the slope of the straight line. The resulting E_a values obtained by the three mentioned methods are in excellent agreement to each other, and are presented in Table 3.

Because two different methods (Newkirk's and Freeman–Carroll's) exhibit such a good agreement (Table 3) one of them is used for the calculation of kinetic data. The activation parameters relating to the rate constant obtained from TG curves by Newkirk's method were calculated for the corresponding steps of degradation of the complexes in the usual way [20]. Thermodynamic parameters that are the result of these calculations are listed in Table 4. It could be seen that activation enthalpies for Step 1 of complexes **1** ($\Delta^{\#}H^{\circ}$ = 19.9 kJ/mol) and 3 ($\Delta^{\#}H^{\circ}$ = 41.6 kJ/mol) differ from each other by factor of 2. One of the reasons for that (and also for differences in activation energies for Step 1, Table 3) could be the different number of significant H bonds in these complexes. That assumption is consistent with the fact that X-ray structure of complex **3** [21] imply on a much more significant H-bonds in comparison with **1** [25].

Results for activation enthalpies for Step 1 are in agreement with the activation enthalpies data obtained recently by Grgurić-Šipka et al. in investigation of cobalt(III) complexes with EDDP and various amino acids [27]. They obtained $\Delta^{\#}H^{\circ}$ values for the dehydration step in the range of 25–67 kJ mol^{-1}.

The positive sign of ΔS values is in agreement with the proposed general thermal degradation mechanism, because of the rising number of particles and having in mind that gaseous products could be also expected.

5. Conclusion

In this paper the first study of thermal degradation of $[Co(S\text{-aa})_2en]^+$ complex diastereomers (S-aa = anion of S-amino acid) is presented. This is also a first cobalt(III)complex with S-tyrosinato ligand which is investigated by means of TG analysis.

On the basis of the results obtained from TG curves it could be concluded that the investigated complex diastereomers exhibit very similar thermal behaviour and thermal stability in temperature range of 293–873 K. It is proposed that the degradation processes occur with cleavage of the side chain of one S-tyrosinato ligand, followed by the cleavage of the second side chain by further heating. The proposed pathways of decomposition are in accordance with results of thermal degradation of noncoordinated S-tyrosine. In the case of diastereomers which crystallize with water molecules, the departure of both hygroscopic and crystal water occurs before.

In addition, the activation energies of some of the thermal decomposition steps obtained from three different non-isothermal methods (from the TG curves) are in good agreement.

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