

THERMAL STUDY OF ZINC(II) 4-CHLOROSALICYLATE COMPLEX COMPOUNDS WITH BIOACTIVE LIGANDS

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Three new complex compounds of general formula $Zn\{4-ClC_6H_3-2-(OH)COO\}_2 \cdot L_2 \cdot nH_2O$ (where L =thiourea (tu), nicotinamide (nam), caffeine (caf), $n=2,3$), were prepared and characterized by chemical analysis, IR spectroscopy and their thermal properties were studied by TG/DTG, DTA methods. It was found that the thermal decomposition of hydrated compounds starts with the release of water molecules. During the thermal decomposition of anhydrous compounds the release of organic ligands take place followed by the decomposition of salicylate anion. Zinc oxide was found as the final product of the thermal decomposition performed up to 650°C. RTG powder diffraction method, IR spectra and chemical analysis were used for the determination of products of the thermal decomposition.

Keywords: caffeine, chlorosalicylate complexes, nicotinamide, thermal behaviour, thiourea, zinc

Introduction

Metal(II) carboxylate complexes with N- and O-donor ligands have been attracting a scientific interest for last decades and are interesting because of their potential biological activity [1, 2]. Nowadays, this attention is paid to salicylate- and halogenosalicylate-metal(II) complexes. Mojumdar *et al.* [3] describes an investigation of thermal and spectral properties of Cu(II) halogenosalicylates. Duran *et al.* reports in his paper crystallographic data of Zn(II) and Co(II) thio-salicylates [4]. Another crystallographic study was done by Tatar *et al.* [5], where the crystal structure of mixed Cu(II) and Zn(II) complex with salicylidine-1,3-propanediaminate ligand was described.

In our latest papers, we studied thermal and spectral properties of Zn(II) salicylate and 5-chlorosalicylate complex compounds with heterocyclic ligands such as thiourea, nicotinamide and caffeine [6, 7]. In comparison to our previous investigation, we decided to study thermal and spectral properties of 4-chlorosalicylates with thiourea, nicotinamide and caffeine, that are reported in this paper.

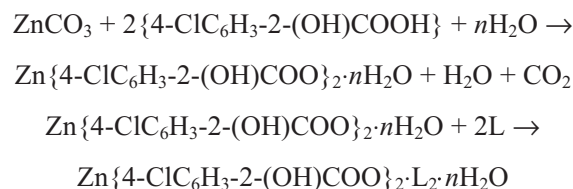
Experimental

Synthesis of the compounds

The following A. R. grade chemicals were used for the preparation of the studied compounds: $ZnCO_3$

(Lachema Neratovice), 4-chlorosalicylic acid (Aldrich), thiourea, nicotinamide, caffeine, (Merck).

The synthesis may be expressed by the following equation:



Preparation of $Zn\{4-ClC_6H_3-2-(OH)COO\}_2 \cdot 2H_2O$ (I)

3.44 g (0.02 mol) of 4-chlorosalicylic acid was added to water suspension of 1.25 g (0.01 mol) $ZnCO_3$ under continual stirring in hot water bath until it dissolved. In a few days white product precipitated. The formed compounds $Zn\{4-ClC_6H_3-2-(OH)COO\}_2 \cdot 2H_2O$ was filtered off, recrystallized from methanol and dried in air. The yield of the reaction was 45%.

Preparation of $Zn\{4-ClC_6H_3-2-(OH)COO\}_2 \cdot tu_2$ (II)

4.44 g (0.01 mol) of zinc 4-chlorosalicylate (I) was dissolved in hot water under continual stirring. Then 20 cm³ water solution of 1.52 g (0.02 mol) thiourea was added. In several hours white crystalline compound $Zn\{4-ClC_6H_3-2-(OH)COO\}_2 \cdot tu_2$ was formed, filtered off and dried in air. 40% yield of the reaction was achieved.

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Preparation of

Zn{4-ClC₆H₃-2-(OH)COO}₂·nam₂·3H₂O (**III**)

Hot water solution of 4.44 g (0.01 mol) zinc 4-chlorosalicylate (**I**) was treated with 30 cm³ water solution of 2.16 g (0.02 mol) nicotinamide under continual stirring. In a few hours white crystals precipitated. The formed complex was filtered off and dried in air. The yield of the reaction was 45%.

Preparation of

Zn{4-ClC₆H₃-2-(OH)COO}₂·caf₂·3H₂O (**IV**)

3.85 g (0.02 mol) of caffeine dissolved in 40 cm³ of water was added in small amounts to 4.44 g (0.01 mol) of hot water solution of zinc 4-chlorosalicylate (**I**). In several days white product Zn{4-ClC₆H₃-2-(OH)COO}₂·caf₂·3H₂O was formed which was filtered off and dried in air. 30% yield of the prepared compound was achieved.

Methods

The content of zinc was determined complexometrically using Complexone III as an agent and Eriochrome black T as an indicator.

Infrared spectra as well as of the solid decomposition intermediates were recorded with SPECORD IR M-80 (Zeiss Jena) using KBr pellets (5 mg/500 mg KBr) in the range 4000–400 cm⁻¹. The

gaseous products of thermal decomposition were collected into gaseous cuvette and identified by IR spectra.

The thermal properties (TG/DTG, DTA) were studied in air atmosphere in Pt crucibles (heating rate 9°C min⁻¹, 100 mg sample) under dynamic conditions on Derivatograph MOM OD 102 (Budapest, Hungary) and PerkinElmer DSC 7 and TGA 7 (heating rate 10°C min⁻¹, 10 mg sample).

Final solid product of thermal decomposition were identified by X-ray powder diffraction analysis with MIKROMETA 2 (Czech Republic) using Ni-filtered radiation CuK_α (λ=0.1518 nm).

Results and discussion

The compounds Zn{4-ClC₆H₃-2-(OH)COO}₂·2H₂O (**I**), Zn{4-ClC₆H₃-2-(OH)COO}₂·tu₂ (**II**) are light brown and brown in colour, compounds Zn{4-ClC₆H₃-2-(OH)COO}₂·nam₂·3H₂O (**III**) and Zn{4-ClC₆H₃-2-(OH)COO}₂·caf₂·3H₂O (**IV**) are white in colour, stable on air and light. They are soluble in water, methanol, ethanol, dimethylsulfoxide, dimethylformamide and 1,4-dioxane and insoluble in chloroform, carbon tetrachloride and benzene. The results of elemental analysis are in a good agreement with calculated ones. The observed absorption bands of prepared complexes are given in Table 1.

Table 1 Characteristic absorption bands (v/cm⁻¹) in infrared spectra

Assignment	(I)	(II)	(III)	(IV)
v(O-H)H ₂ O	3355 w	–	3456 w	3441 s
v(O-H)phe	3182 w	3200 m	3184 m	3132 m
v(C-H)phe	3078, 3020 w	3062, 3018 w	3044, 3012 w	3036, 3012 w
v(C-H)(CH ₃ -)caf	–	–	–	2960 m
v(C=O)nam, caf	–	–	1692 vs	1696 s
δ(O-H)H ₂ O	1620 s	–	1628 s	1648 s
δ(O-H)phe	1344 s	1360 s	1368 vs	1368 s
v(C-OH)phe	1236 s	1240 s	1240 s	1240 s
v _{as} (COO ⁻)	1584 vs	1588 vs	1565 vs	1558 s
v _s (COO ⁻)	1392 m	1376 s	1386 s	1396 m
v(C-C)phe	1488 s, 1472 vs	1480 m, 1468 s	1484 vs, 1464 s	1480 m, 1464 s
v(N-H)	–	3256 m, 3120 m	3164 m	–
δ(N-H)	–	1625 vs, 1435 s	1605 vs	–
v(C=S)	–	1416 s, 1088 m	–	–
δ(COO ⁻)	884 m	876 m	884 w	872 m
γ(C-H)phe	756 m	764 m	743 m	760 s
v(C-Cl)	704 w	708 m	716 m	718 w

vs – very strong; s – strong; m – medium; w – weak; phe – phenol; nam – nicotinamide; tu – thiourea; caf – caffeine;
 Zn{4-ClC₆H₃-2-(OH)COO}₂·2H₂O (**I**); Zn{4-ClC₆H₃-2-(OH)COO}₂·tu₂ (**II**); Zn{4-ClC₆H₃-2-(OH)COO}₂·nam₂·3H₂O (**III**);
 Zn{4-ClC₆H₃-2-(OH)COO}₂·caf₂·3H₂O (**IV**)

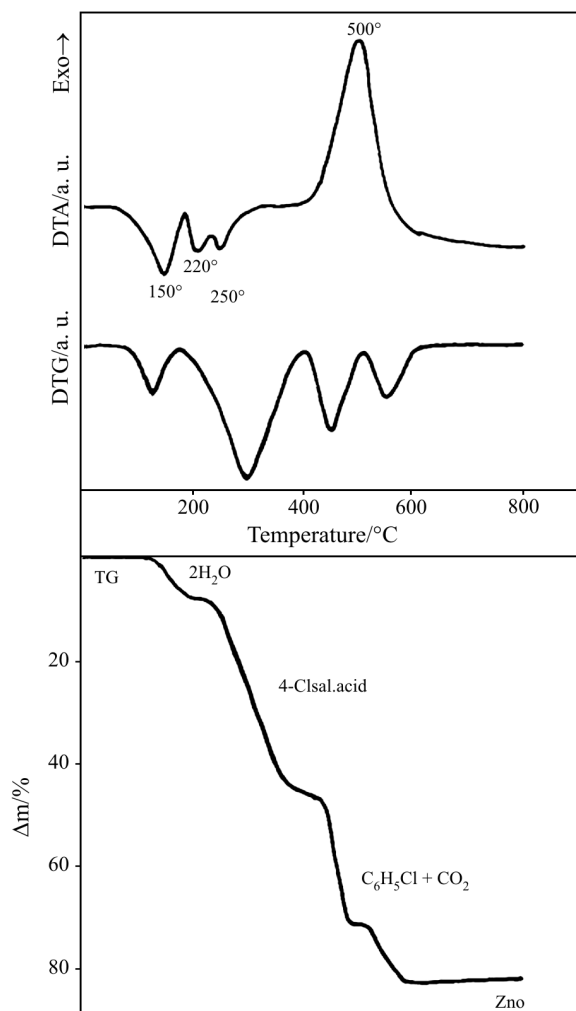


Fig. 1 Thermal decomposition of $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot 2\text{H}_2\text{O}$ (I)

Thermal behaviour

$\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot 2\text{H}_2\text{O}$ (I)

Compound $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot 2\text{H}_2\text{O}$ (I) starts to decompose at 110°C with the release of two water molecules in an endothermic effect at 150°C (Fig. 1) as shown on the DTA curve (experimental mass loss 7.8%, theoretical 8.1%). Next step of the thermal decomposition is the release of 4-Cl-salicylic acid and formation of solid intermediate product $\text{Zn}(4\text{-ClC}_6\text{H}_3\text{-2-(O)-COO})$. This is accompanied by an endothermic effect on the DTA curve at 220 and 250°C (experimental mass loss 38%, theoretical 38.8%). In the temperatures range $420\text{--}600^\circ\text{C}$ $\text{C}_6\text{H}_5\text{Cl}$ and CO_2 are released with an exothermic effect at 500°C (Table 2). The gaseous product of thermal decomposition $\text{C}_6\text{H}_5\text{Cl}$ was identified by IR spectra ($\text{C}_6\text{H}_5\text{Cl}$: $\nu(\text{C-H})$ $3025, 3050\text{ cm}^{-1}$, $\nu(\text{C-C})$ $1585, 1445\text{ cm}^{-1}$, $\gamma(\text{C-H})$ 750 cm^{-1} , $\nu(\text{C-Cl})$ 710 cm^{-1}) and CO_2 by reaction with $\text{Ba}(\text{OH})_2$ solution.

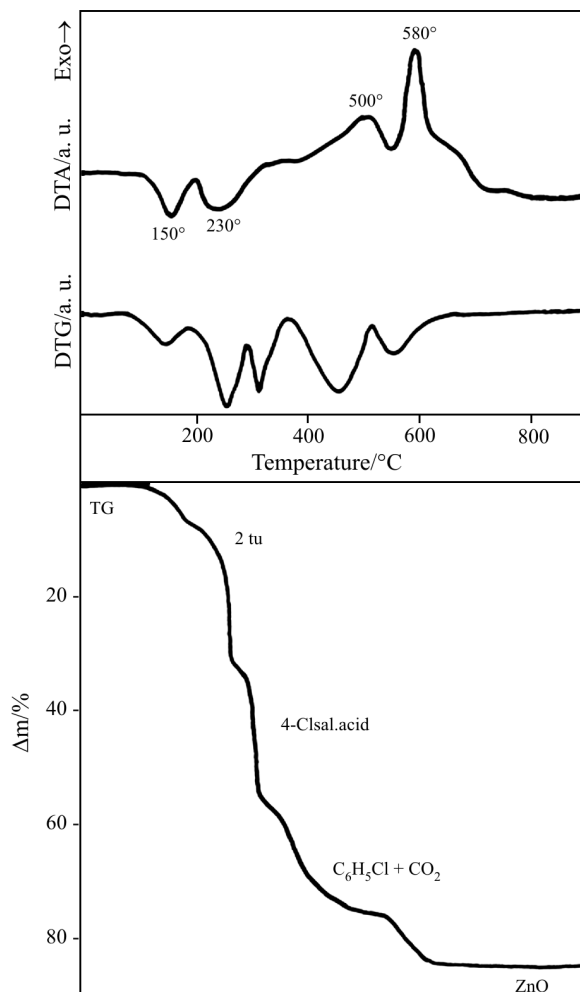
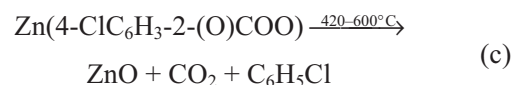
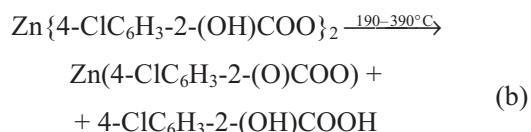


Fig. 2 Thermal decomposition of $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot \text{tu}_2$ (II)

The final solid product of the thermal decomposition is ZnO (experimental 18%, theoretical 18.31%). The following mechanism is proposed for the thermal decomposition:



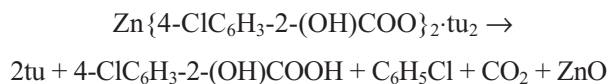
$\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot \text{tu}_2$ (II)

Thermal decomposition of $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2 \cdot \text{tu}_2$ starts at 90°C . Two thiourea molecules and one molecule of 4-Cl-salicylic acid are released in the temperature range $90\text{--}320^\circ\text{C}$

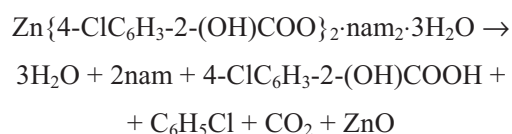
Table 2 Thermal decomposition of the prepared compounds

Compound	Temperature of decomposition/°C	Products of decomposition	Mass loss/%		DTA curve
			theor.	exp.	
Zn{4-ClC ₆ H ₃ -2-(OH)COO} ₂ ·2H ₂ O (I)	150	2H ₂ O	8.1	7.8	endo
	220, 250	4-Cl ₂ sal.acid	38.8	38	endo
	500	C ₆ H ₅ Cl+CO ₂	36.68	37	exo
	R ₆₀₀	ZnO	18.31	18	
Zn{4-ClC ₆ H ₃ -2-(OH)COO} ₂ ·tu ₂ (II)		2tu+	27.14	57	endo
	150, 230	4-Cl ₂ sal.acid	30.77	–	
			20.04	28	exo
	500, 580	C ₆ H ₅ Cl+CO ₂	7.84		
	R ₆₄₀	ZnO	14.51	15	
Zn{4-ClC ₆ H ₃ -2-(OH)COO} ₂ ·nam ₂ ·3H ₂ O (III)	90	3H ₂ O	8.5	7.95	endo
	120, 250	2nam+	57.2	56	endo
		4-Cl ₂ sal.acid			
	350				endo
	420	C ₆ H ₅ Cl+CO ₂	23.04	24	exo
	R ₅₅₀	ZnO	11.99	12	
Zn{4-ClC ₆ H ₃ -2-(OH)COO} ₂ ·caf ₂ ·3H ₂ O (IV)	100	3H ₂ O	6.37	7	endo
	270, 290	2caf+	65.41	65	endo
		4-Cl ₂ sal.acid	13.27	–	exo
	510	C ₆ H ₅ Cl+CO ₂	5.19	18	
	R ₆₅₀	ZnO	9.6	10	

shown as an endothermic effect at 150 and 230°C on the DTA curve (Fig. 2, Table 2). Zn(4-ClC₆H₃-2-(O)-COO) is formed (experimental mass loss 57%, theoretical 57.8%). Then thermal decomposition continues with maxima on DTA curve at 500 and 580°C and Zn(4-ClC₆H₃-2-(O)-COO) decomposes, C₆H₅Cl, CO₂ and ZnO are formed, as described above (Eq. (c)). The whole mass loss was 85%, theoretical 86.65%. The following reaction is proposed for the process of the thermal decomposition:



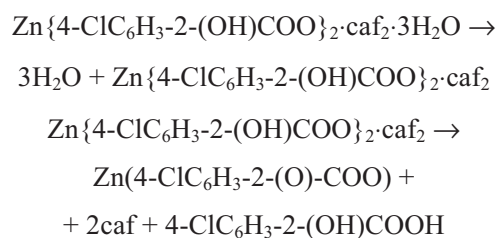
Three molecules of water are released in the first step of the thermal decomposition of this compound (Fig. 3) in the temperature range 60–110°C with a minimum on the DTA curve at 90°C. Experimental mass loss was 8.5% and theoretical 7.95%. Then two molecules of nicotinamide with 4-Cl-salicylic acid are gradually released at 120 and 250°C with experimental mass loss 56%, theoretical 57.2% and Zn(4-ClC₆H₃-2-(O)-COO) is formed. By further heating CO₂ and C₆H₅Cl are released in the temperature range 400–500°C as an exothermic process on the DTA curve at 420°C (experimental mass loss 24%, theoretical 23.04%):



Final solid product of the thermal decomposition is ZnO (experimental 12%, theoretical 11.99%).



The thermal decomposition of compound (**IV**) starts with the release of water molecules in the temperature range 65–130°C shown as a minimum on the DTA curve at 100°C (experimental mass loss 7%, theoretical 6.37%) (Fig. 4). Then two molecules of caffeine are gradually released in the temperature range 160–420°C with 4-Cl-salicylic acid depicted as endothermic effects on the DTA curve at 270 and 290°C and the solid intermediate product Zn(4-ClC₆H₃-2-(O)-COO) is formed (experimental mass loss 65%, theoretical 65.41%). The following equation for the thermal decomposition can be proposed:



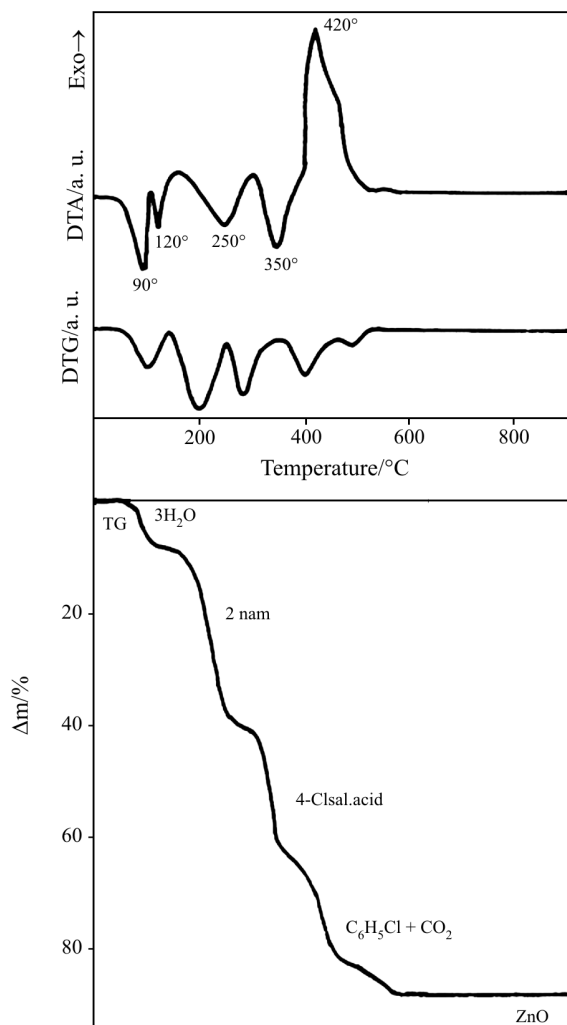
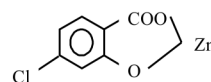


Fig. 3 Thermal decomposition of $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2\cdot\text{nam}_2\cdot 3\text{H}_2\text{O}$ (III)

Thermal decomposition continues in temperature range 420–650°C where CO_2 and $\text{C}_6\text{H}_5\text{Cl}$ are released shown as an exothermic effect at 510°C and ZnO is formed as the final solid product of the thermal decomposition of (IV) (experimental 10% ZnO, theoretical 9.6%).

Conclusions

The thermal behaviour of the newly synthesized compounds depends on the character of the organic ligand. Thermal decomposition of hydrated compounds starts with the release of water molecules in the temperature range 60–180°C. After dehydration, organic ligands are released in all compounds and then the release of 4-chlorosalicylic acid takes place. The solid intermediate compound



was proved by IR spectra where the absorption bands the phenolic group $\nu(\text{OH})$ ($3132\text{--}3200\text{ cm}^{-1}$) and $\delta(\text{OH})$ ($1344\text{--}1368\text{ cm}^{-1}$) are missing [8, 9]. Zinc oxide was found as the final solid product of the thermal decomposition of all studied complexes. Their thermal stability increases in the following order:

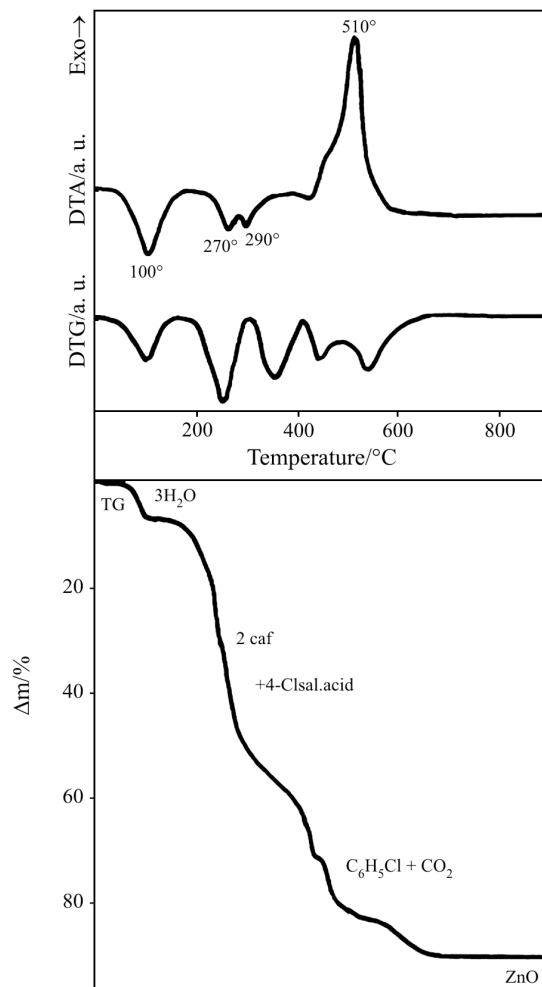
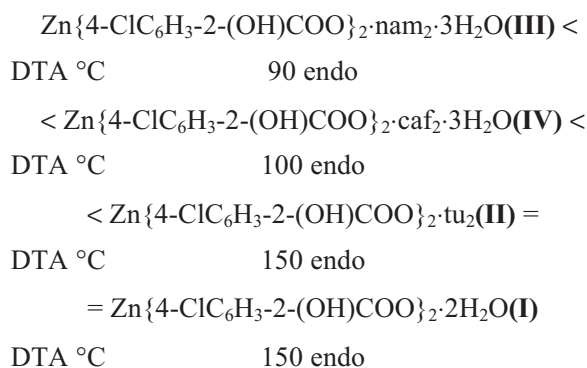


Fig. 4 Thermal decomposition of $\text{Zn}\{4\text{-ClC}_6\text{H}_3\text{-2-(OH)COO}\}_2\cdot\text{caf}_2\cdot 3\text{H}_2\text{O}$ (IV)

The similar sequence is ordered in previously studied 5-chlorosalicylates [7], where compound with nicotinamide starts to degrade thermally at the lowest temperature, then compound with caffeine is decomposed and at the highest temperature it is compound with thiourea. That means that the position of halogene atom has no influence to the temperature of the thermal degradation. The stoichiometry of the thermal decomposition is similar, too, but the shape and temperature of DTA curves is different in substituted 4,5-halogenosalicylates depending on the position of the substituent.

Acknowledgements

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