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THERMAL BEHAVIOUR OF ZINC(II) 5-CHLOROSALICYLATE COMPLEX COMPOUNDS

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Three new complex compounds of general formula $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot L_2\cdot nH_2O$ (where L=thiourea (*tu*), nicotinamide (*nam*), caffeine (*caf*), n=2–5), 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 800°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

Zinc is an essential element in human growth and it is the second most abundant transition element in human organism following iron. There are about 300 metaloenzymes, where zinc ion is presented in their active site or it plays structural role. Zinc is a component of 'zinc fingers' participating in the reliable transfer of genetic information [1, 2].

Zinc(II) carboxylate complex compounds with nitrogen donor organic ligands have attracted an increasing interest in the last decade [3, 4] and are interesting because of their potential biological activity. Mojumdar *et al.*[5] studied from this point of view copper(II) carboxylates and magnesium(II) carboxylates. Mészáros *et al.* studied Zn(II), Co(II), Mn(II) and Cu(II) complexes with pyrazole based ligands. The compounds were characterized by thermal methods and FTIR spectroscopy [6, 7]. The latest research in the field of thermal behaviour of Cu(II), Zn(II), Cd(II), Fe(III), Ni(II) and Co(II) complexes of 6-(2-pyridylazo)-3-acetamidophenol was done by Mohamed *et al.* [8]. They found out that thermal decomposition of these compounds is a stepwise process and metal oxide remained as a solid product.

In continuation to our previous papers which are dealing with the study of thermal, spectral and structural properties of aliphatic zinc(II) carboxylates and halogenocarboxylates [9–17] is this study devoted to properties of zinc(II)halogenosalicylate complexes with some selected organic ligands. Till now, zinc(II) salicylate dihydrate with organic ligands such as thiourea, caffeine, theobromine and nicotinamide [18] was prepared and studied together with nickel(II) salicylate, cobalt(II)salicylate and cadmium(II) salicylate [19, 20]. Nicotinamide is especially known for its biological activity and it is as an important component of the hydrogen-carrying co-enzymes, such as nicotinamide–adenine nucleotide and nicotinamide–adenine dinucleotide phosphate.

In this paper the thermal properties of new zinc 5-chlorosalicylate based complexes with thiourea, caffeine and nicotinamide are reported and IR spectra were used for confirmation of released products.

Synthesis of the compounds

The following A. R. grade chemicals were used for the preparation of the studied compounds: $ZnCO_3$ (Lachema Neratovice, Czech Republic), 5-chlorosalicylic acid (Aldrich), thiourea, nicotinamide, caffeine, (Merck).

The synthesis may be expressed by the following equation:

$$ZnCO_3+2[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COOH]+nH_2O \rightarrow Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot nH_2O+H_2O+CO_2$$

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot nH_2O+2L \rightarrow Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot L_2\cdot nH_2O$$

Preparation of $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot 2H_2O$ (**I**)

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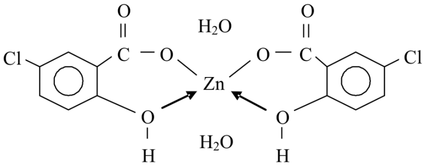
3.44 g (0.02 mol) of 5-chlorosalicylic acid was added to water suspension of 1.25 g (0.01 mol) $ZnCO_3$ under continual stirring in hot water bath until it dissolved. In a few days white crystals precipitated. The formed product $Zn[5\text{-}ClC_6H_3\text{-}2(OH)COO]_2{\cdot}2H_2O$ (Scheme 1) was filtered off and dried in air. The crude product was recrystallized from hot ethanol. The yield of the reaction was 40–45%.



Sceme 1

Preparation of
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}tu_2{\cdot}2H_2O$ (**II**)
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}nam_2{\cdot}3H_2O$ (**III**)
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2.caf_2{\cdot}5H_2O$ (**IV**)

Hot water solution of (0.01 mol) zinc 5-chlorosalicylate (**I**) was treated with water solution of (0.02 mol) organic ligand under continual stirring. After several hours white crystals precipitated. The formed complex was filtered off, washed with ethanol and dried over silicagel. The yield of the reaction were 30–48%.

Instrumentation

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

Infrared spectra of complex compounds as well as of the solid decomposition intermediates were recorded on SPECORD IR M–80 (Zeiss, Jena) using KBr pellets (5 mg/500 mg KBr) in the range of 4000–400 cm^{-1}. The gaseous products of thermal decomposition were collected into gaseous cuvette, or were absorbed in ethylalkohol and identified by IR spectra. CO_2 was also determined by reaction with $Ba(OH)_2$ solution.

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 Perkin Elmer DSC 7 and TGA 7 (heating rate 10°C min^{-1}, 10 mg sample).

The characteristic temperatures of decomposition of measured samples were evaluated from original TG curves as well as from their derivatives and DTA curves.

Final solid product of thermal decomposition was identified by X-Ray powder diffraction analysis with Micrometa 2 (Chirana, Czech Republic) using Ni-filtered radiation CuK_α (λ=0.1518 nm).

Results and discussion

The prepared compounds

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}2H_2O$ (**I**),
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}tu_2{\cdot}2H_2O$ (**II**)
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}nam_2{\cdot}3H_2O$ (**III**)
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}caf_2{\cdot}5H_2O$ (**IV**)

are white in colour, stable on air and light. They are soluble in water, methanol, ethanol, ammonia, acetic acid, dimethylformamide, 1,4-dioxane and insoluble in chloroform, carbon tetrachloride and benzene. The results of elemental analysis are in a good agreement with the calculated ones. The observed absorption bands of prepared complexes are given in Table 1.

Thermal behaviour

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}2H_2O$ (**I**)

Compound I loses the crystalline water in the temperature range 60–120°C as shown on the DTA curve as an endothermic effect at 100°C (Fig. 1) (experimental mass loss 8%, theoretical 8.09%). Next step of the thermal decomposition in the temperature range

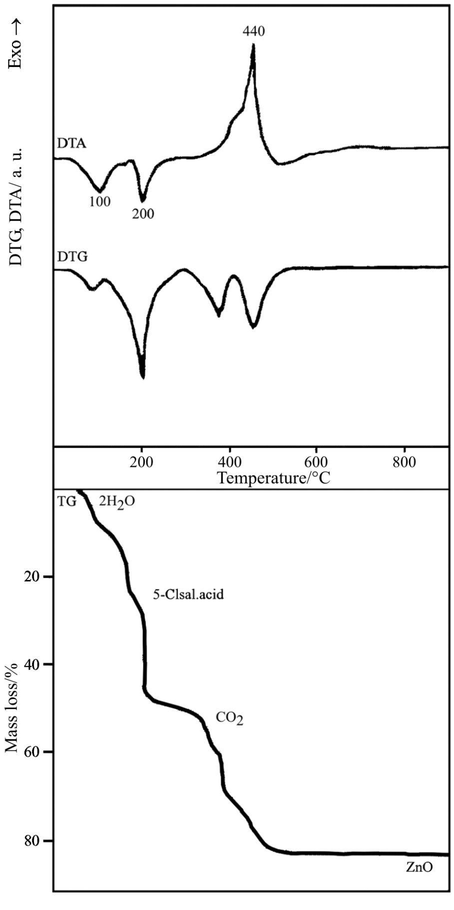


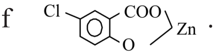
Fig. 1 Thermal decomposition of $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}2H_2O$ **(I)**

Table 1 Characteristic absorption bands (ν/cm^{-1}) in infrared spectra

Assignment	(I)	(II)	(III)	(IV)
$\nu(O–H)_{H_2O}$	3350 w	3432 w	3420 m	3448 w
$\nu(O–H)_{phe}$	3184 w	3200 m	3200 w	3100 w
$\nu(C–H)_{arom}$	3074, 3018 w	3054, 3014 w	3034, 3015 w	3021, 3010 w
$\nu(C–H)_{(–CH_3)caf}$	–	–	–	2920 w
$\nu(C=O)_{nam,\ caf}$	–	–	1688 vs	1696 s
$\delta(O–H)_{H_2O}$	1628 s	1626 sh	1630 s	1640 s
$\delta(O–H)_{phe}$	1348 m	1350 m	1352 m	1335 m
$\nu(C–OH)_{phe}$	1244 m	1236 m	1248 m	1244 m
$\nu_{as}(COO\text{-})$	1592 s	1580 s	1564 s	1560 s
$\nu_s(COO\text{-})$	1383 s	1380 s	1384 s	1385 s
$\nu(C–C)_{arom}$	1480 m	1485 m	1485 m	1485 m
	1461 s	1460 s	1467 s	1465 s
$\nu(N–H)$	–	3280 m	3180 m	–
		3165 m		
$\delta(N–H)$	–	1624 m	1624 m	–
$\nu(C=S)$	–	1430 m	–	–
		1418 m		
		1085 m		
$\delta(COO\text{-})$	888 s	860 m	890 w	872 m
$\gamma(C–H)_{arom}$	743 s	752 s	758 m	756 s
$\nu(C–Cl)$	728 m	704 m	712 m	712 m

vs – very strong, s – strong, m – medium, w – weak, sh – shoulder, *nam* – nicotinamide, *phe* – phenol, *tu* – thiourea, *caf* – caffeine

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}2H_2O$ **(I)**
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2.tu_2{\cdot}2H_2O$ **(II)**
$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}nam_2{+}3H_2O$ **(III)**
$Zn[5\text{-}ClC_6H_3\text{-}2(OH)COO]_2{\cdot}caf_2{\cdot}5H_2O$ **(IV)**

120–220°C is the release of 5-chlorosalicylic acid and formation of  .

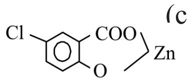
This is accompanied by endothermic effect on the DTA curve at 200°C (experimental mass loss 38%, theoretical 38.81%). Solid intermediate product $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ was confirmed by IR spectra, where the absorption bands of phenolic group ν(OH) at 3184 cm^{-1} and δ(OH) at 1348 cm^{-1} are missing, in accordance with literature data [21]. In the temperature range 220–480°C CO_2 and C_6H_5Cl are released with an exothermic effect at 440°C. The gaseous products of thermal decomposition were identified by IR spectra (C_6H_5Cl: ν(C–H) 3029, 3055 cm^{-1}, ν(C–C) 1580, 1445 cm^{-1}, γ(C–H) 756 cm^{-1}, ν(C–Cl) 712 cm^{-1}; CO_2: δ_{CO_2} 669, $\nu_{asym\,CO_2}$ 2352 cm^{-1}) and also by chemical analysis (for CO_2 the reaction with $Ba(OH)_2$ solution).

The final solid product of the thermal decomposition is ZnO (experimental 18%, theoretical 18.3%). The following mechanism is proposed for the thermal decomposition:

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}2H_2O \xrightarrow{60\text{–}120°C} Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{+}2H_2O \qquad (a)$$

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2 \xrightarrow{120\text{–}220°C} Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO){+}5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COOH \qquad (b)$$

$$Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO) \xrightarrow{220\text{–}480°C} ZnO{+}CO_2{+}C_6H_5Cl \qquad (c)$$

where $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ is 

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}tu_2{\cdot}2H_2O$ (II)

Thermal decomposition of $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2{\cdot}tu_2{\cdot}2H_2O$ (**II**) starts at 80°C with the release of two water molecule with endothermic process at 140°C on the DTA curve. Two thiourea molecules and one molecule of salicylic acid are released in the temperature range 125–270°C shown as an endothermic effect at 175, 220 and 260°C on the DTA curve (Fig. 2). $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ is formed (experimental mass loss 55%, theoretical 54.41%). Then thermal decomposition continues with maxima on DTA curve at 460 and 560°C. $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ decomposes and CO_2,

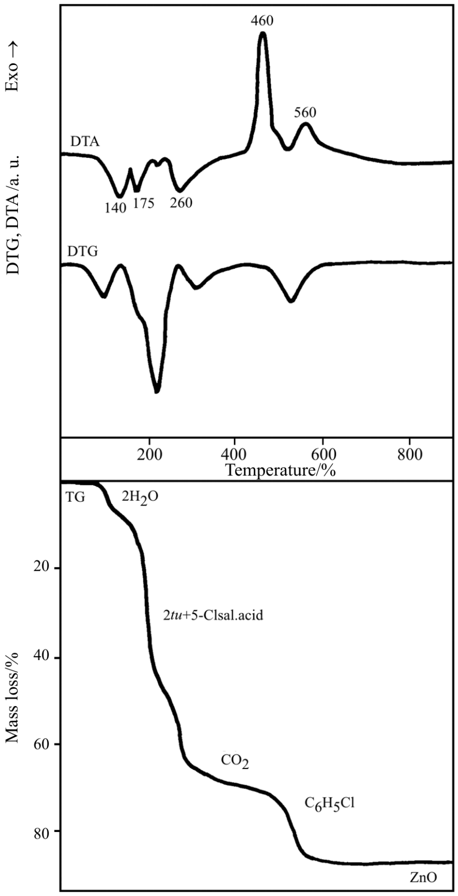


Fig. 2 Thermal decomposition of $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO_2]\cdot \mathit{tu}_2\cdot 2H_2O$ **(II)**

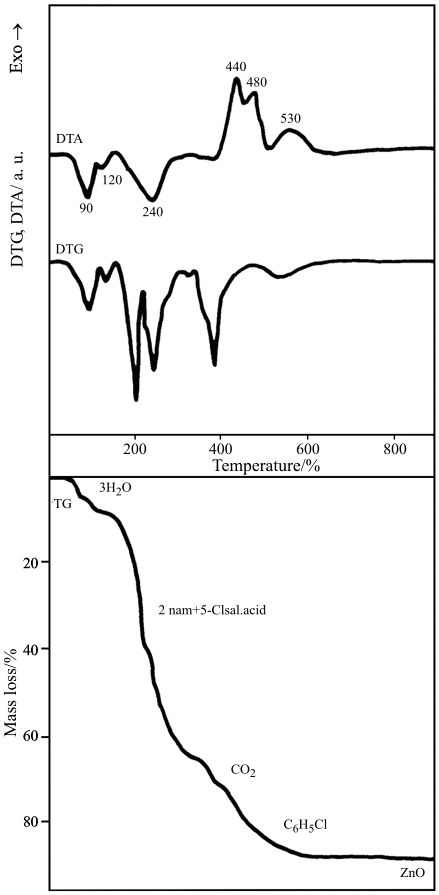


Fig. 3 Thermal decomposition of $Zn[5ClC_6\ H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{nam}_2\cdot 3H_2O$ **(III)**

C_6H_5Cl and ZnO are formed, as described above in Eq. 3c. The whole mass loss was 87%, theoretical 86.6%. The following reaction is proposed for the whole process of the thermal decomposition:

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{tu}_2\cdot 2H_2O \rightarrow$$
$$2H_2O+2\mathit{tu}+5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COOH+C_6H_5Cl+CO_2+ZnO$$

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{nam}_2\cdot 3H_2O$ (**III**)

Three molecules of water are released in the first step of the thermal decomposition of this compound (Fig. 3) in the temperature range 60–130°C with a minimum on the DTA curve at 90 and 120°C. Experimental mass loss was 8% and theoretical 7.95%. Then two molecules of nicotinamide with 5-chlorosalicylic acid are gradually released at 240°C with experimental mass loss 57%, theoretical 57.27% and $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ is formed. By further heating CO_2 and C_6H_5Cl are released in the temperature range 300–600°C as an exothermic process on the DTA curve at 440, 480°C (experimental mass loss 23%, theoretical 23.05%):

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{nam}_2\cdot 3H_2O \rightarrow 3H_2O+$$
$$+2\mathit{nam}+5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COOH+C_6H_5Cl+CO_2+ZnO$$

Final solid product of the thermal decomposition is ZnO (experimental mass loss 88%, theoretical 88.27%).

$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot caf_2\cdot 5H_2O$ (**IV**)

The thermal decomposition of compound (**IV**) starts with the release of five water molecules in the temperature range 70–140°C shown as a minimum on the DTA curve at 100°C (experimental mass loss 10%, theoretical 10.22%) (Fig. 4). Then two molecules of caffeine are gradually released in the temperature range 140–350°C with 5-chlorosalicylic acid depicted as endothermic effect on the DTA curve at 260°C and the solid intermediate product $Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)COO)$ is formed (experimental mass loss 63%, theoretical 63.09%). The following equation for the thermal decomposition can be proposed:

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{caf}_2\cdot 5H_2O \rightarrow$$
$$5H_2O+Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot \mathit{caf}_2$$

$$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot caf_2 \rightarrow$$
$$Zn(5\text{-}ClC_6H_3\text{-}2\text{-}(O)\text{-}COO)+2\mathit{caf}+5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COOH$$

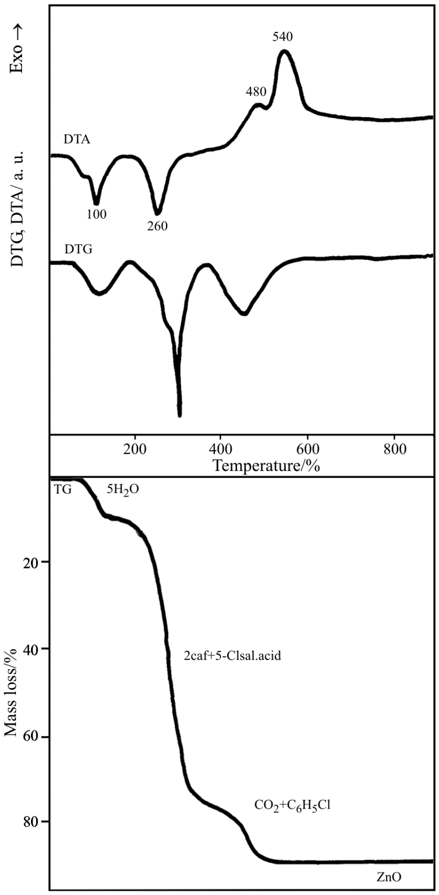
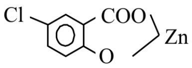


Fig. 4 Thermal decomposition of $Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot caf_2\cdot 5H_2O$ **(IV)**

Thermal decomposition continues in temperature range 350–550°C where CO_2 and C_6H_5Cl are released shown as an exothermic effect at 480 and 540°C and ZnO is formed as the final solid product of the thermal decomposition of (**IV**) (experimental 9% ZnO, theoretical 9.21%).

Conclusion

The thermal behaviour of the new compounds described in this paper is depending on the character of the organic ligand. The first step of thermal decomposition – the dehydration – started in the temperature range 60–140°C. After dehydration the organic ligands were released in all compounds and then the release of 5-chlorosalicylic acid took place.
The following intermediate compound



was formed while the phenolic group was deprotonated. We could see it from the IR spectra where the absorption bands ν(OH) at 3184 cm^{-1} and δ(OH) at 1348 cm^{-1} are missing [20, 21]. Subsequently, the pyrolysis of the intermediate products took place, being accompanied by the release of CO_2 a C_6H_5Cl. Zinc oxide was found as the final solid product of the thermal decomposition of all complex compounds studied in this paper.

When comparing the thermal stability of the new synthesized chlorosalicylate compounds described in this paper, the thiourea complex was relatively most stable, whereas the nicotinamide complex possessed a lowest thermal stability. The thermal stability increases in the following order:

	$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot nam_2\cdot 3H_2O$	<	$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot 2H_2O$	=
	(**III**)		(**I**)	
DTA/°C	90, 120 endo		100 endo	
=	$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO\}_2\cdot caf_2\cdot 5H_2O$	<	$Zn[5\text{-}ClC_6H_3\text{-}2\text{-}(OH)COO]_2\cdot tu_2\cdot 2H_2O$	
	(**IV**)		(**II**)	
DTA/°C	100 endo		140 endo	

A similar tendency was observed earlier in the thermal stability of non-substituted zinc(II) salicylates that contained organic molecules (nicotinamide, thiourea and caffeine) (*nam*<*caf*<*tu*) [18]. We assume that it is related to the molecular structure of the compound.

Acknowledgements

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