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# THERMAL STUDY OF ZINC(II) SALICYLATE COMPLEX COMPOUNDS WITH BIOACTIVE LIGANDS

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## Abstract

Five new complex compounds of general formula $Zn(Hsal)_2\ L_2\ nH_2O$ (where *Hsal*=$OHC_6H_4COO^-$, *L*=thiourea (tu), nicotinamide (nam), caffeine (caf), theobromine (tbr), *n*=2–4), were prepared and characterized by chemical analysis, IR spectroscopy and studied by methods of thermal analysis (TG/DTG, DTA). 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 heated 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, nicotinamide, salicylate complexes, theobromine, thermal and spectral properties, thiourea, zinc

## Introduction

Zinc is one of the most abundant trace elements in the body. It is an important component of many proteins. Up to now more than 300 metalloenzymes have been described [1]. $Zn^{2+}$ ion strongly interacts with electronegative sulphur, nitrogen, oxygen and yet it is not redox active, it does not promote the formation of toxic free radicals [2].

Zinc(II) carboxylates with organic ligands are interesting because of their potential biological activity. Mojumdar *et al*. [3] 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 FT-IR spectroscopy [4, 5]. The latest research at the field of the 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*. [6]. They

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found out that thermal decomposition of these compounds is a few-step 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 [7–14] and halogen-carboxylates [15, 16] is this study devoted to properties of zinc(II) salicylate complexes with organic ligands such as thiourea, nicotinamide, caffeine and theobromine.

Till now, zinc(II) salicylate dihydrate was prepared and studied together with nickel(II) salicylate, cobalt(II) salicylate and cadmium(II) salicylate [17, 18]. In this paper the thermal and spectral properties of new zinc salicylate based complexes are reported.

## Experimental

*Synthesis of the compounds*

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

The synthesis may be expressed by the following equation:

$$ZnCO_3+2OHC_6H_4COOH+nH_2O \quad Zn(OHC_6H_4COO)_2\ nH_2O+H_2O+CO_2$$

$$Zn(OHC_6H_4COO)_2\ nH_2O+2L \quad Zn(OHC_6H_4COO)_2\ L_2\ nH_2O$$

*Preparation of $Zn(Hsal)_2 4H_2O$ (**I**)*

2.76 g (0.02 mol) of salicylic acid was added to water suspension of 1.23 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 $Zn(Hsal)_2\ 4H_2O$ was filtered off and dried in air. The yield of the reaction was 35%.

*Preparation of $Zn(Hsal)_2 tu_2$ (**II**)*

4.11 g (0.01 mol) of zinc salicylate (**I**) was dissolved in hot water under continual stirring. Then 20 $cm^3$ water solution of 1.4 g (0.02 mol) thiourea was added. In several hours white crystaline compound $Zn(Hsal)_2\ tu_2$ was formed, filtered off and dried in air. The yield of the reaction was 29%.

*Preparation of $Zn(Hsal)_2 nam_2 3H_2O$ (**III**)*

Hot water solution of 4.11 g (0.01 mol) zinc salicylate (**I**) was treated with 30 $cm^3$ water solution of 2.44 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 31%.

*Preparation of $Zn(Hsal)_2 caf_2 3H_2O$ (**IV**)*

3.98 g (0.02 mol) of caffeine dissolved in 40 $cm^3$ of water was added in small amounts to 4.11 g (0.01 mol) of hot water solution of zinc salicylate (**I**). In several days white product $Zn(Hsal)_2$ $caf_2$ $3H_2O$ was formed which was filtered off and dried in air. The yield of the reaction was 27%.

*Preparation of $Zn(Hsal)_2 tbr_2 3H_2O$ (**V**)*

4.11 g (0.01 mol) of zinc salicylate (**I**) was dissolved in hot water and 50 $cm^3$ water solution of 3.60 g (0.02 mol) theobromine was added. The mixture was kept under continual stirring. In a few days white crystals precipitated. The product was filtered off and dried in air. The yield of the reaction was 33%.

## Instrumentation

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

Infrared spectra were recorded with Specord IR M – 80 (Zeiss Jena) using KBr pellets (5 mg/500 mg KBr) in the region 4000–400 $cm^{-1}$.

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 (Hungary) and Perkin Elmer DSC7 and TGA7 (heating rate 10°C $min^{-1}$, 10 mg sample).

Volatile products of thermal decomposition were determined by IR spectra and methods of chemical analysis.

Final solid product of thermal decomposition were identifed by X-ray powder diffraction analysis with Mikrometa 2 (Czech Republic).

## Results and discussion

The prepared compounds $Zn(Hsal)_2 4H_2O$, $Zn(Hsal)_2 tu_2$, $Zn(Hsal)_2 nam_2 3H_2O$, $Zn(Hsal)_2 caf_2 2H_2O$, $Zn(Hsal)_2 tbr_2 3H_2O$ 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 experimental data of chemical analysis are in good accordance with theoretical data.

*Thermal behaviour*

$Zn(Hsal)_2$ 4 $H_2O$ (**I**)

Compound $Zn(Hsal)_2 4H_2O$ starts to decompose at 80°C with the release of two water molecules in the temperature range 80–110°C shown on the DTA curve as an endothermic effect at 110°C (Fig. 1). Next two molecules of water are released in the temperature range 110–180°C with an endothermic peak at 170°C (experimental

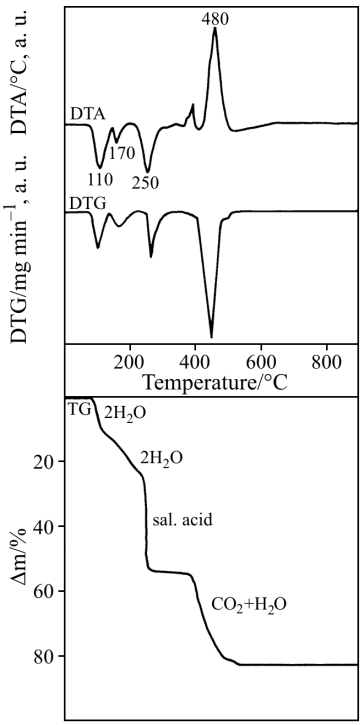


**Fig. 1** Thermal decomposition of $Zn(Hsal)_2\ 4H_2O$

mass loss 9%, theoretical 8.75%). Next step of the thermal decomposition in the temperature range 235–275°C is the release of salicylic acid and formation of $Zn(OC_6H_4COO)$. This is accompanied by endothermic effect on the DTA curve at 250°C (experimental mass loss 35%, theoretical 33.6%).The absence of salicylic acid was confirmed by IR spectra of the solid intermediate product where the absorption bands of phenolic group (OH) at 3184 cm$^{-1}$ and (OH) at 1348 cm$^{-1}$ are missing, in accordance with literature data [18]. In the temperature range 390–500°C $CO_2$ and $H_2O$ are released with an exothermic effect at 480°C .The final solid product of the thermal decomposition is ZnO (experimental 18.2%, theoretical 19.3%). The following mechanism is proposed for the thermal decomposition:

$$Zn(OHC_6H_4COO)_2\ 4H_2O \xrightarrow{80–110\,C} Zn(OHC_6H_4COO)_2\ 2H_2O+2H_2O \quad (a)$$

$$Zn(OHC_6H_4COO)_2\ 2H_2O \xrightarrow{110–180\,C} Zn(OHC_6H_4COO)_2+2H_2O \quad (b)$$

$$Zn(OHC_6H_4COO)_2 \xrightarrow{235–275\,C} Zn(OC_6H_4COO)+C_6H_4(OH)COOH \quad (c)$$

$$Zn(OC_6H_4COO) \xrightarrow{390–500\,C\ 7O_2} ZnO+7CO_2+2H_2O \quad (d)$$

$Zn(Hsal)_2\ tu_2$ (**II**)

Thermal decomposition of $Zn(Hsal)_2\ tu_2$ starts at 120°C with the release of two thiourea molecules and one molecule of salicylic acid in the temperature range 120–310°C shown as an endothermic effect at 180 and 220°C on the DTA curve (Fig. 2). $Zn(OC_6H_4COO)$ is formed (experimental mass loss 63%, theoretical 60%). Then thermal decomposition continues with maxima on DTA curve at 460, 520 and 620°C. $Zn(OC_6H_4COO)$ decomposes and $CO_2$, $H_2O$ and ZnO are formed, as described above (Eq. (d)). The whole mass loss was 85%, theoretical 83.5%. The following reaction is proposed for the process of the thermal decomposition:

$$Zn(OHC_6H_4COO)_2\ tu_2 \quad 2tu+C_6H_4(OH)COOH+ZnO+CO_2+H_2O$$

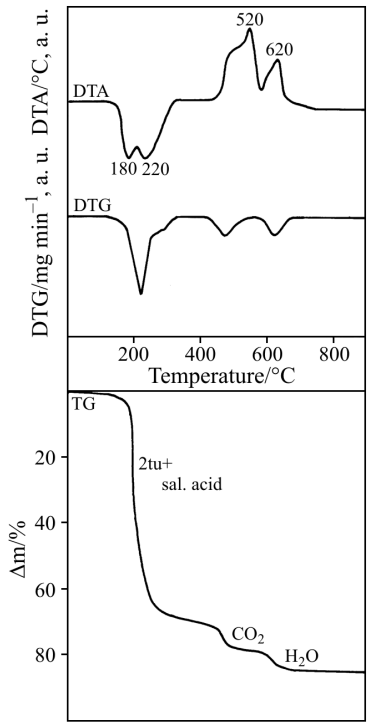


**Fig. 2** Thermal decomposition of $Zn(Hsal)_2\ tu_2$

$Zn(Hsal)_2\ nam_2\ 3H_2O$ (**III**)

Two molecules of water are released in the first step of the thermal decomposition of this compound (Fig. 3) in the temperature range 60–90°C with a minimum on the DTA curve at 80°C. Experimental mass loss was 7% and theoretical 5.69%. The third water molecule is released in the temperature range 90–160°C with an endothermic peak at 120°C. Experimental mass loss was 4% and theoretical 3.2%. Then two molecules of nicotinamide are gradually released at 200 and 260°C with experimental mass loss 39%,

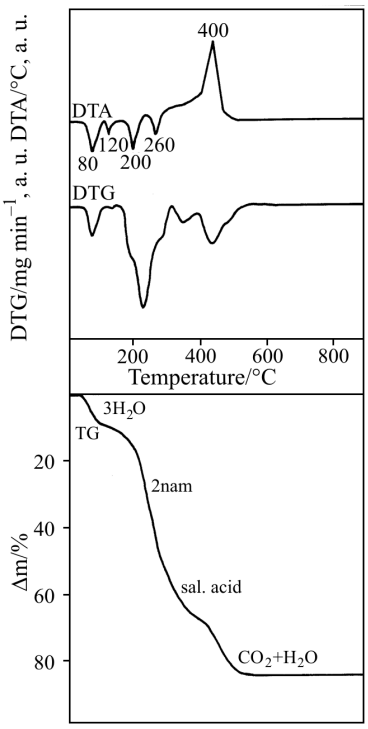


**Fig. 3** Thermal decomposition of $Zn(Hsal)_2\ nam_2\ 3H_2O$

theoretical 38.2%. By further heating molecule of salicylic acid is released in the temperature range 300–410°C as an exothermic process on the DTA at 400°C (experimental mass loss 18%, theoretical 21%):

$$Zn(OHC_6H_4COO)_2\ nam_2\ 3H_2O \quad 3H_2O+2nam+C_6H_4(OH)COOH+$$
$$+Zn(OC_6H_4COO)_2$$

Final solid product of the thermal decomposition is ZnO (experimental mass loss 85.5%, theoretical 87.2%).

$Zn(Hsal)_2\ caf_2\ 3H_2O$ (**IV**)

The thermal decomposition of compound **IV** starts with the release of three water molecules in the temperature range 70–115°C shown as a minimum on the DTA curve at 100°C (experimental mass loss 7.5%, theoretical 6.9%) (Fig. 4). Then two molecules of caffeine are gradually released in the temperature ranges 170–280 and 280–320°C depicted as endothermic effects on the DTA curve at 250 and 310°C. The following equation for the thermal decomposition can be proposed:

$$Zn(OHC_6H_4COO)_2\ caf_2\ 3H_2O \quad 3H_2O+Zn(OHC_6H_4COO)_2\ caf_2$$
$$Zn(OHC_6H_4COO)_2\ caf_2 \quad Zn(OHC_6H_4COO)_2+2\ caf$$

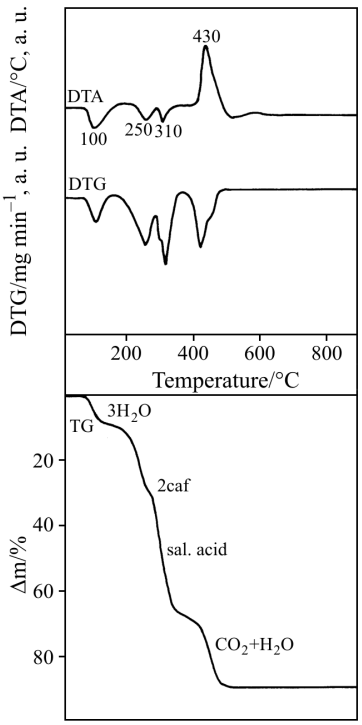


**Fig. 4** Thermal decomposition of $Zn(Hsal)_2$ caf$_2$ $3H_2O$

At 350°C one molecule of salicylic acid is released and $Zn(OC_6H_4COO)$ is formed (experimental mass loss 60%, theoretical 67.2%). Thermal decomposition continues in temperature range 380–500°C where $CO_2$ and $H_2O$ are released and ZnO is formed as the solid final product of the thermal decomposition (Eqs (c) and (d)).

$Zn(Hsal)_2$ tbr$_2$ $3H_2O$ (**V**)

In the first step of the thermal decomposition of $Zn(Hsal)_2$ tbr$_2$ $3H_2O$ three molecules of water are released in the temperature range 90–155°C with an endothermic peak at 120°C (Fig. 5), (experimental mass loss was 6.8% and theoretical 7.1%). This decomposition is followed by the release of one theobromine molecule in the temperature range 160–210°C with an endothermic peak at 200°C. The next step of the thermal decomposition is the release of the second molecule of theobromine in the temperature range 210–330°C shown as an endotherm on the DTA curve at 320°C (experimental mass loss 45%, theoretical 47.8%). Then one molecule of salicylic acid is released at 350°C (experimental mass loss 19%, theoretical 18.3%) and $Zn(OC_6H_4COO)$ is formed:

$$Zn(OHC_6H_4COO)_2\ tbr_2\ 3H_2O \quad 3H_2O+2tbr+C_6H_4(OH)COOH+Zn(OC_6H_4COO)$$

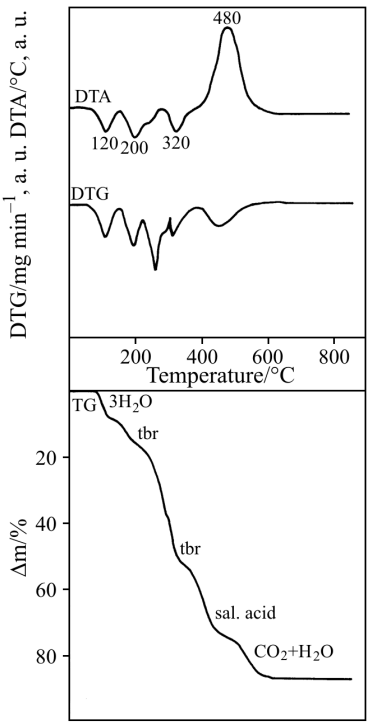


**Fig. 5** Thermal decomposition of $Zn(Hsal)_2$ $tbr_2$ $3H_2O$

After this, $Zn(OC_6H_4COO)$ decomposes and $CO_2$ and $H_2O$ are released. ZnO is the final solid product of the thermal decomposition (experimental mass loss 12.1%, theoretical 10.8%).

## Conclusions

The thermal behaviour of the newly synthetized 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 80–120°C. In comparison to thermal decomposition of Co(II) and Ni(II) salicylate tetrahydrates, where all four molecules of water are released in one step [18], we can assume that water molecules of zinc(II) salicylate tetrahydrate are coordinated in a different way. Zinc atom is probably octahedrally coordinated and salicylate groups are coordinated bidentately. After dehydration, organic ligands are released in all compounds and then the release of salicylic acid molecule takes place and zinc monosalicylate is formed while phenolic group is deprotonized. We can see it from IR spectra where the absorption bands (OH) at 3184 cm$^{-1}$ and (OH) at 1341 cm$^{-1}$ are missing [17, 18]. Zinc oxide was found as the final solid product of the thermal decomposition of all studied complexes. The thermal stability is increasing in the following order:

$Zn(Hsal)_2\ nam_2\ 3H_2O$ (**III**, DTA 80°C endo)<

$Zn(Hsal)_2\ caf_2\ 2H_2O$ (**IV,** DTA 100°C endo)<

$Zn(Hsal)_2\ 4H_2O$ (**I,** DTA 110°C endo)<

$Zn(Hsal)_2\ tbr_2\ 3H_2O$ (**V**, DTA 120°C endo)<

$Zn(Hsal)_2\ tu_2$ (**II**, DTA 180°C endo)

In comparison to aliphatic zinc(II) monocarboxylates and halogencarboxylates with the same organic ligands [9–16] we have found out that the initial temperature of the thermal decomposition of zinc(II) salicylate based complexes is lower by about 100°C.

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