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THERMAL PROPERTIES OF ZINC BUTYRATE COMPLEX COMPOUNDS
II. Caffeine, nicotinamide and theobromine

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Abstract

The new zinc(II) complexes of general formula $Zn(CH_3CH_2CH_2COO)_2 \cdot nL$ (where L = caffeine, nicotinamide, theobromine; $n = 1$ or 2) were prepared and identified.

Thermal properties of these compounds were investigated by thermal analysis (TG/DTG, DTA, DSC/DDSC).

Gaseous products of thermal decomposition were detected by IR spectroscopy and Mass spectroscopy. Final products of thermal decomposition were determined by X-ray powder diffraction patterns.

Keywords: caffeine, nicotinamide, theobromine, thermal properties, zinc butyrate

Introduction

The zinc complex compounds with organic ligands, such as urea, thiourea, caffeine, nicotinamide, etc. have been identified as biological active compounds [1]. It is of interest for the practical and theoretical reasons to know their solubilities in different solution and their thermal properties.

In the Part I of this series of papers [2] thermal properties of zinc butyrate complexes with urea and thiourea ligands were described.

In this paper the solubilities and thermal properties of zinc butyrate complexes with caffeine, nicotinamide and theobromine are described. Nicotinamide is especially known for it biological activity. Many authors have already paid attention to nicotinamide and examined it as a ligand in the coordination compounds of several central atoms [3, 4]. Nicotinamide is known as an important component of the hydrogen-carrying co-enzymes, such as nicotinamide-adenine nucleotide and nicotinamide-adenine dinucleotide phosphate.

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Experimental

Chemicals and synthesis

In the synthesis of zinc butyrate compounds the following chemicals of p. a. grade were used: $ZnCl_2$, $(NH_4)_2CO_3$ and caffeine (Lachema Brno); butyric acid, nicotinamide and theobromine (Aldrich). The $ZnCO_3$ reagent was prepared starting from $ZnCl_2$ and $(NH_4)_2CO_3$.

The zinc butyrate was formed by the reaction of aqueous suspension of zinc carbonate and butyric acid in stoichiometric ratio by following equation:

$$ZnCO_3 + 2C_3H_7COOH \rightarrow Zn(C_3H_7COO)_2 + H_2CO_3$$

The product of this reaction represents the white pine crystals. In order to prepare the complex compounds containing selected ligands, the aqueous solution of zinc butyrate was mixed with equimolar amount of aqueous solution of organic ligand *L* by reaction:

$$Zn(C_3H_7COO)_2 + nL \rightarrow Zn(C_3H_7COO)_2 \cdot nL$$

where: $n=1, 2$; C_3H_7COO=but

White crystalline or powder products of complex compounds with the following composition were obtained after filtration and crystallization:

$Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$
$Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$
$Zn(but)_2 \cdot 2theobromine$.

Instrumentation

The prepared solid substances were identified by elemental analysis on the Hewlet Packard CHN Analyser, Model 185. Zinc was determined complexometrically using eriochrome black as indicator. The presence of the individual groups was checked by measuring the IR spectra of solid substances, intermediates of thermal decomposition (using KBr disc 5 mg/500 mg KBr) and gaseous products on Specord IR M-80, Zeiss Jena in the range 4000–200 cm^{-1}.

The TG, DTG and DTA analysis were carried out using the Derivatograph MOM, Hungary and by Netzsch Thermoanalyser under dynamic conditions in an argon atmosphere (heating rate 9°C min^{-1}, in Pt crucibles, 100 mg sample).

The enthalpy changes were studied by Netzsch Simultaneous Thermoanalyser STA 409 in air under dynamic conditions, using reference material Al_2O_3. The Mass spectroscopy of gaseous products released at various temperatures was carried out by the Spectrophotometer MS 5988 and QMG 420 (Balzers GmbH).

The X-ray diffraction pattern were obtained using the Micrometa (Chirana CSFR).

Results and discussion

The prepared compounds were stable in air and light. Their solubility in various solvents is given in Table 1. The chemical composition of the compounds was determined by elemental analysis (Table 2) and IR spectra (Table 3). The results were in a good agreement with the theoretical amount [5].

Thermal properties of complex compounds

$Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$

As it follows from TG curve in Fig. 1, this hydrated compound losses the crystal water when heated above 70°C. The release of 2 water molecules is accompanied by an endothermic effect with the maximum at 90°C. From the TG curve (Fig. 1) it follows that the thermal decomposition of anhydrous complex compound $Zn(but)_2 \cdot 2caffeine$ starts at 160°C. From DTA curve in Fig. 1 it follows, that the thermal decomposition is a complex process, characterized by two endothermic effects by 240 and 340°C.

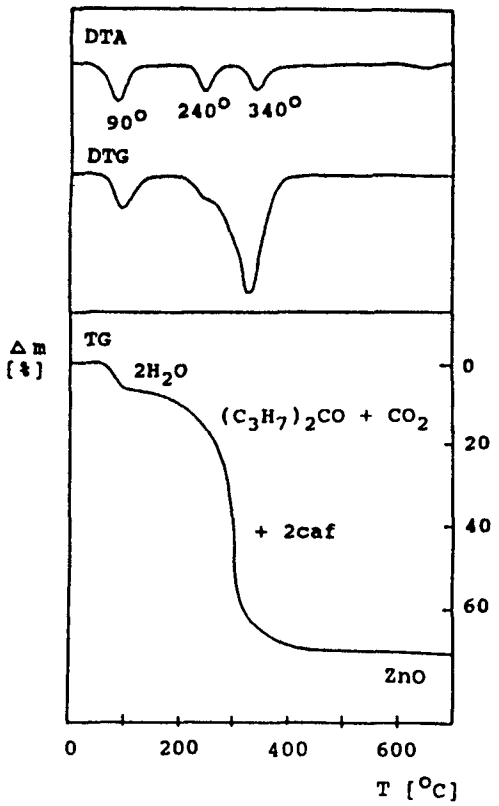

Fig. 1 TG/DTG and DTA curves of $Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$

Table 1 The solubilities of zinc butyrates in various solvents

Compound	Solvent							
	H_2O	CH_3OH	C_2H_5OH	$(CH_3)_2CO$	$CHCl_3$	CCl_4	$(C_2H_5)_2O$	C_6H_6
$Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$	sol heat	insol	insol	sol	sol	insol	insol	sol
$Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$	insol	sol	insol	sol heat	sol	sol	sol	sol
$Zn(but)_2 \cdot 2theobromine$	insol	sol	insol	sol	sol heat	sol heat	sol	sol

sol = soluble at 20°C
insol = insoluble even when heated to 80°C
sol heat = soluble by heating to 80°C

Table 2 Results of elemental analysis of zinc butyrate complexes

Compound		%C	%H	%N	%Zn
$Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$	experimental	43.45	5.31	19.5	9.95
	theoretical	44.61	6.53	17.3	10.12
$Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$	experimental	44.90	5.72	6.54	16.61
	theoretical	44.52	5.33	7.42	17.23
$Zn(but)_2 \cdot 2theobromine$	experimental	44.56	4.60	22.85	10.57
	theoretical	44.76	4.61	22.97	10.58

Table 3 IR spectra of zinc butyrate complexes [cm^{-1}]

Assignment	Compound		
	$Zn(but)_2 \cdot 2caf \cdot 2H_2O$	$Zn(but)_2 \cdot 1nam \cdot 2H_2O$	$Zn(but)_2 \cdot 2theo$
$\nu_{as}(COO^-)$	1552, 1540	1552	1564, 1548
$\nu_s(COO^-)$	1360	1384	1368
$\nu_{O-H}(H_2O)$	3500	3500	–
$\delta_{O-H}(H_2O)$	1600	1616	–
$\nu_{N-H}(-NH_2)$	–	3328, 3170	–
$\delta_{N-H}(-NH_2)$	–	1648	–
$\nu_{C-H}(-CH_3)$	2968, 2920, 2860	2976, 2950, 2890	2856, 2820
$\delta_{C-H}(-CH_3)$	1483	1472, 1428	1484
ν_{C-H}(arom)	3120	3100	3160, 3112
γ_{C-H}(arom)	744	735	750
δ_{C-H}(arom)	1288	1208	1252, 1140
$\nu_{C-N}(CONH_2)$	–	1280	–
$\nu_{C=O}(=C=O)$	1692	1690	1704

Figure 2 shows DSC curve measured during the thermal decomposition process of $Zn(but)_2 \cdot 2caffeine$ when heated in air. Following enthalpy changes were determined: for the effect with the maximum at 245°C $\Delta H = 69.5$ J g^{-1}, for the effect with the maximum at 321°C $\Delta H = 162$ J g^{-1} and for the effect with maximum at 480°C $\Delta H = 79.5$ J g^{-1}.

It was proved by IR-spectra that ketone, CO_2 and caffeine molecule are released during the thermal decomposition of the complex compound. In Fig. 3 the Mass

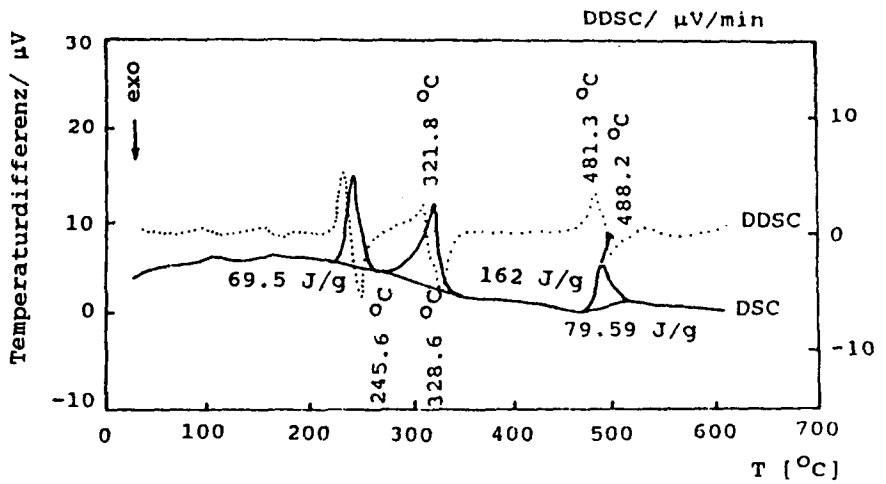

Fig. 2 DSC/DDSC curves of $Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$

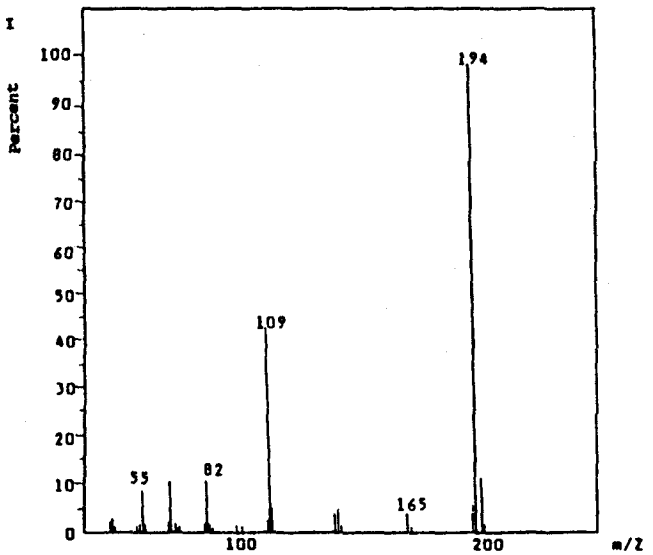

Fig. 3 Mass spectrum of volatile products of $Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$ heated at 340°C

spectrum of volatile product releases from sample at 340°C is demonstrated. It corresponds to the caffeine (m/z=194, 109, 82, 67, 55).

The final product of thermal decomposition after heating the complex compound to 600°C in air is ZnO.

$Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$

From the TG curve in Fig. 4 onset of the release of crystal water was determined at 60°C. The dehydration is also characterized by an endothermic effect at 110°C. The thermal decomposition of the anhydrous complex compounds $Zn(but)_2 \cdot 1$nicotinamide begins at 170°C. This decomposition is characterized by two endothermic effects at the temperatures of 250 and 340°C. The release of ketone, CO_2 and nicotinamide was determined by IR spectra. In Fig. 5 the Mass spectrum of volatile product releases at 250°C is demonstrated. It corresponds to the nicotinamide (m/z=122, 106, 78). The exothermic effect observed at 440°C on the DTA curve Fig. 4 is not yet interpreted. The final product of thermal decomposition of the complex compound after heating to 500°C is ZnO.

$Zn(but)_2 \cdot 2$theobromine

This anhydrous compound starts to decompose at the temperature of 180°C (TG curve, Fig. 6). This decomposition process is characterized on the DTA curve by an endothermic effect at 320°C and two exothermic effects at 440 and 540°C. The DTG curve proved this character of decomposition, where ketone, CO_2 and theobromine molecules are released.

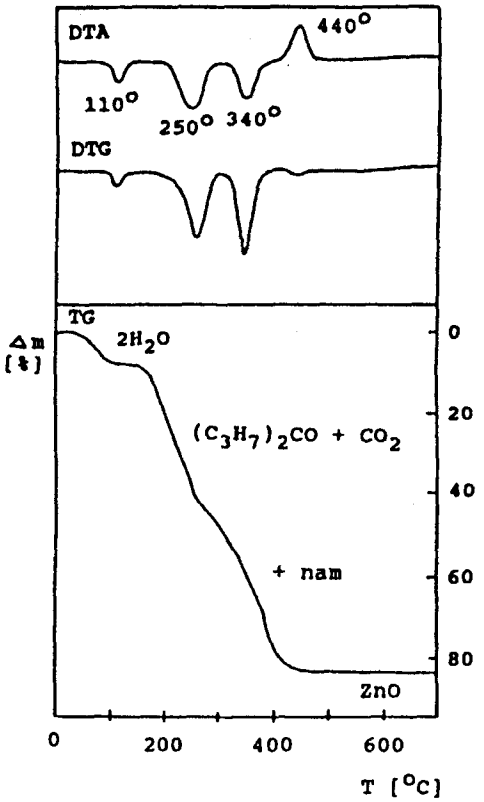

Fig. 4 TG/DTG and DTA curves of $Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$

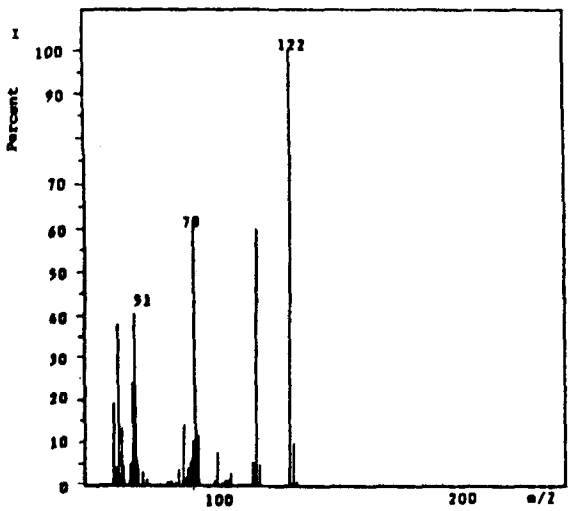

Fig. 5 Mass spectrum of $Zn(but)_2 \cdot 1nicotinamide$ heated at 250°C

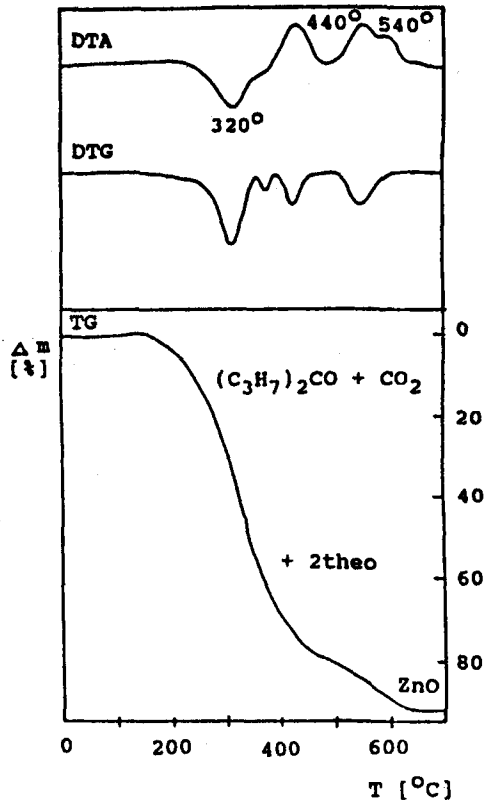

Fig. 6 TG/DTG and DTA curves of $Zn(but)_2 \cdot 2$theobromine

The IR spectra of the volatile products released corresponded to the presence of ketone, CO_2. Release of theobromine was confirmed by Mass spectrum ($m/z = 180$, 137, 109, 82). The decomposition terminated at 660°C ZnO was found by X-ray diffraction patterns.

Conclusion

It was found, that the thermal decomposition of the zinc butyrate complexes with caffeine, nicotinamide, theobromine depends of the organic molecule present as ligand.

The thermal decomposition of all studied hydrated Zn-butyrate complex compounds starts by the release of water above 60°C.

The thermal stability of anhydrous compounds increases in the following order:

$$Zn(but)_2 \cdot 2\text{caffeine} < Zn(but)_2 \cdot 1\text{nicotinamide} < Zn(but)_2 \cdot 2\text{theobromine}$$

160°C 170°C 180°C

As the result of the experimental study we have found:

– the thermal stability of $Zn(but)_2 \cdot 2caffeine$ and $Zn(but)_2 \cdot 2theobromine$ complex compounds is lower than the thermal stability of the organic compounds used as their ligands

– $Zn(but)_2 \cdot 1nicotinamide$ is decomposed at higher temperature than nicotinamide itself

– the thermal stability of the compounds

$Zn(but)_2 \cdot 2caffeine \cdot 2H_2O$

$Zn(but)_2 \cdot 1nicotinamide \cdot 2H_2O$

$Zn(but)_2 \cdot 2theobromine$

is higher than the thermal stability of the single zinc(II) butyrate. This is caused by the presence of the organic ligands, representing five and six membered aromatic rings.

* * *

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