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NOVEL ZINC(II) BENZOATE COMPLEX COMPOUNDS WITH CAFFEINE AND UREA
Synthesis and characterization

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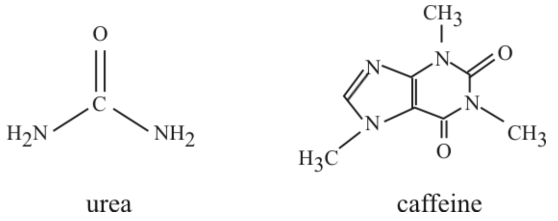
Novel zinc(II) complex compounds of general formula $Zn(C_6H_5COO)_2 \cdot L_2$ (where L=caffeine (caf) and urea (u)) were synthesized and characterized by elemental analysis and IR spectroscopy. The thermal behaviour of the complexes was studied during heating in air by thermogravimetry. It was found that the thermal decomposition of the anhydrous Zn(II) benzoate compounds with bioactive ligands was initiated by the release of organic ligands at various temperatures. On further heating of the compounds up to 400°C the thermal degradation of the benzoate anions took place. Zinc oxide was found as the final product of the thermal decomposition of all zinc(II) benzoate complex compounds heated to 600°C. Results of elemental analysis, infrared spectroscopy, mass spectroscopy and thermogravimetry are presented.

Keywords: *caffeine, IR spectroscopy, thermal stability, thermogravimetry, urea, zinc(II) benzoate complexes*

Introduction

Zinc is structural and catalytic component of proteins and enzymes. It was found that zinc forms chelates with ligands containing O- and N-donors [1]. Heterocyclic compounds play a significant role in many biological systems, e.g. N-donor compounds with hexagonal (six-membered) ring being a component of several vitamins and drugs. Moreover, some of the aromatic carboxylic acids (benzoic acid and salicylic acid) are known to have anti-bacterial and anti-fungal properties. Benzoic acid is used in combination with salicylic acid in dermatology as the agent for a fungicidal treatment (Whitfield's ointment) in the case of fungal skin diseases (ringworm) [2, 3]. Benzoate compounds of bivalent cations such as calcium and zinc also offer possibilities for corrosion inhibition. Their application is of particular interest because of their safe use and high solubility in water [4–9]. Moreover, it has been found that benzoates of metallic elements can be used to reduce 'flash rusting' in water-borne paints [10]. It has been our interest to study zinc(II) benzoates with bioactive ligands. In our previous works we described the preparation, thermal and spectral properties of zinc(II) acetates [11], salicylates [12] and halogenosalicylates [13] with bioactive organic ligands. In this study, novel complex compounds of zinc(II) benzoates with organic ligands such as caffeine and urea (Scheme 1) were synthesized and characterized by elemental analysis and infrared spectroscopy. Thermal behavior of the newly prepared zinc(II) benzoate complex compounds was investigated by thermogravimetry.



Scheme 1 Molecular formula of urea and caffeine

Experimental

Synthesis of the complex compounds

For the preparation of the Zn(II) benzoate complex compounds following A. R. grade chemicals were used: $ZnCO_3$ (Lachema Neratovice), benzoic acid (Aldrich), urea and caffeine (Merck).

The synthesis of the compounds is expressed by following equations:

$$ZnCl_2+Na_2CO_3 \rightarrow ZnCO_3+2NaCl \quad (1)$$

$$ZnCO_3+2C_6H_5COOH \rightarrow Zn(C_6H_5COO)_2+H_2CO_3 \quad (2)$$

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$$Zn(C_6H_5COO)_2+2L\rightarrow Zn(C_6H_5COO)_2\cdot L_2 \qquad (3)$$

$ZnCO_3$ was prepared by using solutions of the stoichiometric amounts of $ZnCl_2$ and Na_2CO_3 as described in Eq. (1). The water–alcohol solution of carboxylic acid was added to the water suspension of $ZnCO_3$ under continual stirring in hot water at 70°C. After 1 h, the solution of zinc(II) benzoate was filtered off and the aqueous solution of a ligand (caffeine, urea) was added to the filtrate. The reaction mixture was stirred for 3 h, then filtered off and left to stand to crystallize at room temperature. After several days white crystals were formed as a precipitate. The precipitates of the formed Zn(II) benzoate complex compounds were filtered off, washed with water and dried over silicagel. The compounds of the following formula were prepared:

$Zn(C_6H_5COO)_2$ **(I)**
$Zn(C_6H_5COO)_2\cdot caf_2$ **(II)**
$Zn(C_6H_5COO)_2\cdot u_2$ **(III)**

The yield of the reaction was 82% for the compound denoted **(I)**, 92% for the compound denoted **(II)** and 78% for the compound **(III)**.

Methods

Infrared spectra were recorded on Perkin Elmer Spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets and on Bruker Vertex 70 FTIR Spectrophotometer in the range 1100–200 cm^{-1} using CsI technique.

The content of C, H, N in prepared compounds was determined by means Perkin Elmer 2400 CHN analyzer and zinc content complexometrically using Complexone III as an agent and Eriochrome black as an indicator.

The thermal properties were studied in air atmosphere in ceramic crucibles (heating rate 9°C min^{-1}, the sample amount 100 mg) under dynamic conditions by Derivatograph MOM OD 102 (Hungary) and in nitrogen atmosphere by Perkin Elmer TGA7.

Mass spectra of the evolved gases were measured by mass spectrometer MS 5988.

Results and discussion

The prepared compounds are anhydrous, white, lightproof and stable in air. The results of elemental analysis are presented in Table 1. They are in good agreement with the theoretical calculated data. The solubility of the compounds are presented in Table 2.

Infrared spectra characterization

The studied Zn(II) benzoate compounds were characterized by IR spectroscopy. The most important IR absorption bands of the Zn(II) benzoate compounds are summarized in Table 3. The observed absorption bands were identified in accordance with the literature data [14]. The stretching vibrations $\nu_{C\text{–}H}$ of methyl groups of caffeine are at 2949 cm^{-1}. The presence of caffeine and urea is evident from presence of absorption bands of carbonyl $\nu_{C=O}$ vibration at 1704 and 1647 cm^{-1}, respectively. By using stretching vibrations of the carboxylate group COO^- the type of coordination of the compounds was evaluated by using the value of $\Delta\{\Delta=\nu_{asCOO^-}-\nu_{sCOO^-}\}$ calculated as a difference between the frequencies of ν_{asCOO^-} and ν_{sCOO^-}. Calculations for the prepared zinc(II) benzoates with organic ligands gave values of $\Delta\nu$ in the range 222–225 cm^{-1} and for sodium benzoate $\Delta\nu=138$ cm^{-1} [15]. Taking into account that for

Table 1 Results of elemental analysis of prepared compounds

Compound		C/%		H/%		N/%		Zn/%	
		calc.	found	calc.	found	calc.	found	calc.	found
$Zn(C_6H_5COO)_2$	**(I)**	54.67	54.48	3.28	3.07	–	–	21.36	20.87
$Zn(C_6H_5COO)_2\cdot caf_2$	**(II)**	51.77	50.64	4.34	4.07	16.10	15.77	9.40	9.30
$Zn(C_6H_5COO)_2\cdot u_2$	**(III)**	44.93	44.47	4.24	4.04	13.10	13.85	15.29	15.03

Table 2 Solubility of prepared compounds

Compound	Solvent						
	H_2O	CH_3OH	C_2H_5OH	$(C_2H_5)_2O$	$(CH_3)_2CO$	$CHCl_3$	CCl_4
$Zn(C_6H_5COO)_2$	s.s	s.s	ins.	ins.	ins.	ins.	ins.
$Zn(C_6H_5COO)_2\cdot caf_2$	s.s	s	ins.	v.s	ins.	v.s	ins.
$Zn(C_6H_5COO)_2\cdot u_2$	s	v.s	ins.	ins.	ins.	ins.	ins.

v.s=very soluble, s=soluble, s.s=slightly soluble, ins.=insoluble

Table 3 Characteristic absorption bands (ν/cm^{-1}) of prepared compounds in infrared spectra

Assignement	$\nu_{(C-H)_{ph}}$	$\nu_{C-H(-CH_3)caf}$	$\nu_{(C=O)_{caf,u}}$	$\nu_{(C=N)_{caf}}$	ν_{asCOO^-}	ν_{sCOO^-}	Δ	$\nu_{(C-C)_{ph}}$	$\nu_{(N-H)_u}$	δ_{COO^-}	$\gamma_{(C-H)_{ph}}$	ν_{Zn-O}
(I)	3060 w 3025 w	–	–	–	1638 s	1416 vs	222	1492 s	–	872 w	717 vs	498–376 w 352, 326, 302 m 279, 246, 226 s
(II)	3120 w 3063 w	2949 w	1704 m	1657 s	1632 m	1409 s	223	1489 w	–	872 w	717 vs	484–375 w 352, 326, 303 m 280, 246, 227 s
(III)	3055 w 3022 w	–	1647 m	–	1638 w	1413 vs	225	1506 s	3404 s 3316 w	869 w	720 vs	561, 534 s 443–375 w 352, 325, 303 m 280, 247, 226 s

vs – very strong; s – strong; m – medium; w – weak; ph – phenyl; caf – caffeine; u – urea; $Zn(C_6H_5COO)_2$ **(I)**; $Zn(C_6H_5COO)_2 \cdot caf_2$ **(II)**; $Zn(C_6H_5COO)_2 \cdot u_2$ **(III)** monodentate geometry of the carboxylate group the value of $\Delta_{\text{studied complex}}$ is larger more than the value of $\Delta_{\text{sodium salt}}$ [14] it can be supposed that the carboxylate ions in all the prepared Zn(II) benzoate compounds are monodentate [16–18]. In accordance with literature data the stretching vibrations $\nu_{Zn–O}$ were in the range 226–561 cm^{-1} in all prepared compound [19].

Thermal behaviour

Compound **(I)** of chemical composition $Zn(C_6H_5COO)_2$

As it follows from Fig. 1, the sample is thermally stable up to 185°C. On heating above this temperature thermal decomposition takes place as indicated by the TG results in Fig. 1. The release of $(C_6H_5)_2CO$ and CO_2 (experimental mass loss value 72%, calculated mass loss 73.55%) in the temperature range 185–400°C were observed by TG/DTG curves and confirmed by IR spectra and by mass spectroscopy results. It was found that after heating the sample to 330°C, the absorption band of carboxylate group ν_{asCOO^-} at 1638 cm^{-1} was missing. The mass spectra of the evolved gases from the sample heated up to 300°C confirmed the presence of the ions $C_6H_5CO^+$ (*m*/*z*=105) and $C_6H_5^+$ (*m*/*z*=77). The release of CO_2 (*m*/*z*=44) was confirmed in temperature range 361–532°C by mass spectra [20]. The final solid product of the thermal decomposition is ZnO (experimental mass loss 28%, calculated mass loss 26.46%). The following mechanism is proposed for the thermal decomposition:

$$Zn(C_6H_5COO)_2\xrightarrow{185–400°C}(C_6H_5)_2CO+CO_2+ZnO$$

Compound **(II)** of chemical composition $Zn(C_6H_5COO)_2\cdot caf_2$

The $Zn(C_6H_5COO)_2\cdot caf_2$ compound starts to decompose at 150°C (Fig. 2) with the release of two caffeine molecules in the temperature range 150–250°C (experimentally found mass loss 56%, calculated mass loss 55.80%). The release of caffeine in the first step of the thermal decomposition was confirmed by mass spectra (*m*/*z*=194) measured up to 240°C and by IR spectra of solid intermediates measured up to 290°C, where the characteristic bands of caffeine $\nu_{C=O}$ at 1704 cm^{-1}, $\nu_{C=N}$ at 1657 cm^{-1} and $\nu_{C–H(CH_3^-)caff}$ at 2949 cm^{-1} were missing. Then thermal decomposition continued with the release of $(C_6H_5)_2CO$ and CO_2 in the range 250–340°C (experimental value of mass loss 28%, calculated mass loss 32.50%). The intermediate products $(C_6H_5)_2CO$ and CO_2 were confirmed by mass spectra. The CO_2 starts release at 256°C (*m*/*z*=44) and $C_6H_5^+$ starts release at 306°C (*m*/*z*=77). ZnO resulted as the solid final product of the thermal decomposition (experimental mass loss 16%, calculated mass loss 11.69%). The following reaction is proposed for the thermal decomposition of the compound $Zn(C_6H_5COO)_2\cdot caf_2$:

$$Zn(C_6H_5COO)_2\cdot caf_2\xrightarrow{150–340°C}$$
$$2caf+CO_2+(C_6H_5)_2CO+ZnO$$

Compound **(III)** of chemical composition $Zn(C_6H_5COO)_2\cdot u_2$

From Fig. 3 it followed that the thermal decomposition of $Zn(C_6H_5COO)_2\cdot u_2$ takes place in two steps. The compound is stable up to 120°C. In the first step

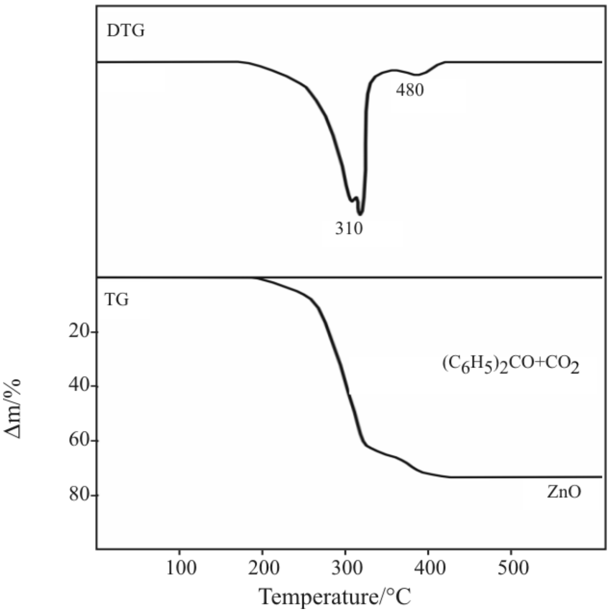

Fig. 1 TG/DTG curves of $Zn(C_6H_5COO)_2$ **(I)**

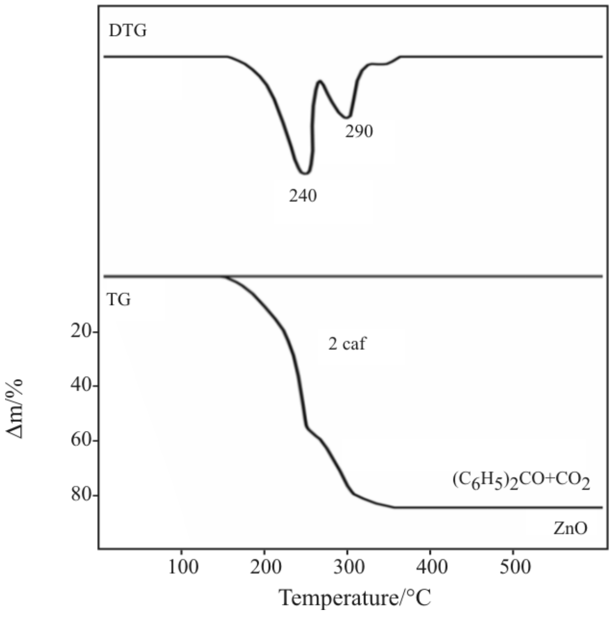

Fig. 2 TG/DTG curves of $Zn(C_6H_5COO)_2\cdot caf_2$ **(II)**

Table 4 Thermal decomposition of Zn(II) benzoate complexes prepared in this study

Compound		Temperature range of decomposition/°C	Products of thermal decomposition	Mass loss/ %	
				exp.	calc.
$Zn(C_6H_5COO)_2$	**(I)**	185–400	$(C_6H_5)_2CO+CO_2$	72	73.55
		R_{400}	ZnO	28	26.46
$Zn(C_6H_5COO)_2 \cdot caf_2$	**(II)**	150–250	2caf	56	55.80
		250–340	$(C_6H_5)_2CO+CO_2$	28	32.50
		R_{340}	ZnO	16	11.69
$Zn(C_6H_5COO)_2 \cdot u_2$	**(III)**	120–190	$2u+CO_2$	39	38.34
		190–340	$(C_6H_5)_2CO$	39	42.60
		R_{340}	ZnO	22	19.03

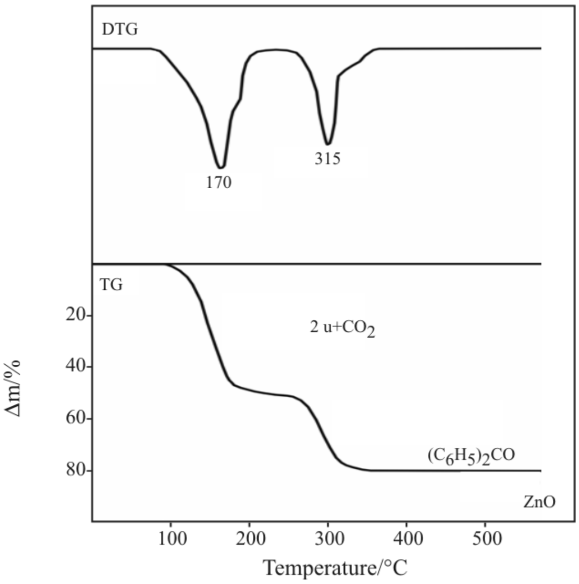

Fig. 3 TG/DTG curves of $Zn(C_6H_5COO)_2 \cdot u_2$ **(III)**

in temperature range 120–190°C two urea molecules and one molecule of CO_2 are released (experimental mass loss 39%, calculated mass loss 38.34%). The release of urea in the first step was confirmed by IR spectra of solid intermediates measured up to 160°C, where the characteristic absorption bands $\nu_{as(N-H)_u}$ at 3404 cm^{-1}, $\nu_{s(N-H)_u}$ at 3316 cm^{-1} and $\nu_{C=O}$ at 1647 cm^{-1} were missing. In the second step the $(C_6H_5)_2CO$ decomposed to the ions $C_6H_5CO^+$ (*m*/*z*=105) and $C_6H_5^+$ (*m*/*z*=77) in the temperature range 190–340°C (experimental mass loss 39%, calculated mass loss 42.60%). The final product of thermal decomposition is ZnO. The following mechanism is proposed for the thermal decomposition of the $Zn(C_6H_5COO)_2 \cdot u_2$ compound:

$$Zn(C_6H_5COO)_2 \cdot u_2 \xrightarrow{120\text{–}340^\circ C} 2u+CO_2+(C_6H_5)_2CO+ZnO$$

Conclusions

Anhydrous compounds of zinc(II) benzoate complexes with caffeine and urea, respectively, were synthesized. The values of the separation of the carboxylate stretches (Δ) in the IR spectra of the compounds show that carboxylate in all three zinc(II) benzoate complex compounds appeared to be monodentate.

Thermal decomposition of the compound **(I)** is a one step process and the compounds **(II)** and **(III)** are multistep processes. The thermal stability of the compounds decreases as follows:

$$\underset{185^\circ C}{Zn(C_6H_5COO)_2} > \underset{150^\circ C}{Zn(C_6H_5COO)_2 \cdot caf_2} > \underset{120^\circ C}{Zn(C_6H_5COO)_2 \cdot u_2}$$

During the thermal decomposition of the prepared zinc(II) benzoate complex compounds the release of the organic bioactive ligands takes place in the first step of the decomposition and it is followed by the thermal degradation of the benzoate anion (Table 4).

By comparison of thermal stability of zinc(II) benzoate-based compounds containing various ligands it was found that in the case of the compound $Zn(C_6H_5COO)_2 \cdot caf_2$ **(II)** the temperature of the release of caffeine (150°C) is lower than the decomposition temperature of the caffeine itself (200°C). The complex compound containing urea $Zn(C_6H_5COO)_2 \cdot u_2$ **(III)** decomposed at 120°C, which is by 10°C higher than with urea itself (110°C). It was found that the presence of bioactive ligands in the complex compounds influences the mechanism of thermal decomposition of the benzoate anion. In all the studied compounds zinc oxide was found as the final product of the thermal decomposition.

Acknowledgements

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