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THE STUDY OF NEW ZINC(II) ALIPHATIC CARBOXYLATE COMPLEX COMPOUNDS BY METHODS OF THERMAL ANALYSIS

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Abstract

Four new complex compounds were prepared by the reaction of zinc bromobutyrate and organic ligands. The general formula of the synthetized complex compounds are $(2\text{-Brbut})_2Zn{\cdot}L$ and $(4\text{-Brbut})_2Zn{\cdot}L_2{\cdot}nH_2O$ (*but*=butyrate, *L*=theobromine (tbr), theophylline (tph), methyl-3-pyridyl carbamate (mpc), *n*=0–1). The compounds were characterized by chemical analysis and IR spectroscopy. The thermal behaviour of the zinc(II) complexes was studied by thermal analysis. Thermal decomposition in the case of hydrated compounds starts with the release of water molecules. Then molecules of organic ligands and the bromobutyrate anion are released and decomposed. $CH_3CH_2CH{=}O$, CO, $CH_2{=}CHCH{=}O$, CH_2O and $ZnBr_2$ were found as gaseous products of thermal decomposition during heating up to 700°C. IR, mass spectroscopy, X-ray powder diffraction and chemical analysis were used for the determination of solid and gaseous intermediates and products of the thermal decomposition.

Keywords: methyl-3-pyridyl carbamate, theobromine, theophylline, thermal analysis, zinc(II) carboxylates

Introduction

Zinc is one of the most important trace elements. It is essential for all the living systems, even for microorganisms. There are about 300 metalloenzymes, where zinc ion is presented in their active site or it plays a structural role [1, 2]. While zinc is a structural and catalytic co-factor of many metalloproteins, its deficit causes metabolism defects and growth inhibition in microorganisms [3]. On the other hand, zinc also has antimicrobial properties. This microelement inhibits the growth of *Escherichea coli*, *Streptococcus faecalis*, *Klebsiella pneumoniae*, *Staphylococcus aureus* and some soil bacteria [4, 5]. That is the reason why zinc(II) compounds are considered to have pharmaceutical effects. For example: zinc(II) picolinate $Zn(pic)_2$ and zinc(II) asparate $Zn(asp)_2$ are effective for the treatment of the diseases caused by the *Herpes*

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simplex virus. The zinc(II) complexes with 8-hydroxyquinoline and salicylic acid as well as cobalt(II) and zinc(II) complexes with indane-1, 3-dione-2-imine-N-CH_2COOH have antimicrobial activities against *Escherichea coli*, *Proteus mirabilis*, *Staphylococcus aureus* and *Streptococcus faecalis*. Zinc(II) complexes with porphyrine, 2-(3-benzoylphenyl)propionate and pyrithione have biological properties used in the treatment of skin disseases. Some of zinc(II) chelate macrocyclic compounds are very important as lipophilic carriers for anti-HIV substances [6].

Until now, we have developed synthesis of some zinc(II) aliphatic carboxylates with N- and O-donor ligands. We have studied spectral, thermal properties and also the crystal structures of some zinc(II) formates, acetates, propionates and their halogenoderivatives [7–16]. A few of our complex compunds with papaverine and phenazone were tested against two bacterial species *Staphylococcus aureus* and *Escherichia coli* and a specie of fungi *Candida albicans*. It was shown that these compounds had bactericidal activity [17] .

The present paper is dealing with the synthesis and the spectral and thermal behaviour of new zinc(II) halogenobutyrates with theobromine, theophylline and methyl-3-pyridylcarbamate which are potentially biologically active substances.

Experimental

Materials

The following A.R. grade chemicals were used: $Zn(OH)_2$ (freshly prepared from $ZnCl_2$ and NaOH – Lachema Neratovice), 2-BrbutCOOH 97, 4-BrbutCOOH 98% (Aldrich), theobromine, theophylline, methyl-3-pyridyl carbamate (Merck).

Synthesis of the compounds

The synthesis can be expressed by the following equation:

$$2RCOOH+Zn(OH)_2 \rightarrow (RCOO)_2Zn+2H_2O$$

$$(RCOO)_2Zn+nL \rightarrow (RCOO)_2Zn\cdot nL$$

where R=(2-Brbut)-, (4-Brbut)-, n=1–2

Preparation of $(2\text{-Brbut})_2Zn\cdot$tbr (I)

Zinc(II) 2-bromobutyrate was prepared by neutralization of 0.77 cm^3 97% 2-bromobutyric acid (0.00719 mol) and 0.35 g $Zn(OH)_2$ (0.00352 mol). The water solution of 0.62 g theobromine (0.00344 mol) was added to the water solution of zinc(II) 2-bromobutyrate, stirring continously. After 30 min, the compound was filtered, evaporated and left to stand. Yellow products (molecular mass: 578.67) precipitated within several days. The compound is soluble in water, methanol, ethanol and insoluble in diethylether and benzene. The yield of the reaction is 42%.

Preparation of $(2\text{-Brbut})_2Zn\cdot tph$ (II)

0.77 cm^3 97% 2-bromobutyric acid (0.00719 mol) was dissolved in water and added to a water suspension of 0.35 g $Zn(OH)_2$ (0.00352 mol) with continual stirring. The water solution of 0.62 g theophylline (0.00344 mol) was added to the reaction mixture of zinc(II) 2-bromobutyrate. The solution was filtered, evaporated and left to stand at room temperature. A yellow product (molecular mass: 578.67) crystallized after several days. The compound is soluble in water, methanol and insoluble in diethylether. The reaction yield is 38%.

Preparation of $(4\text{-Brbut})_2Zn\cdot tbr_2\cdot H_2O$ (III)

0.89 g 98% 4-bromobutyric acid (0.00533 mol) was neutralized with 0.26 g $Zn(OH)_2$ (0.00262 mol) under continual stirring and zinc(II) 4-bromobutyrate was formed. The water solution of 0.93 g theobromine (0.00936 mol) was added to the solution of zinc(II) 4-bromobutyrate. After 30 min the reaction mixture was filtered, evaporated and left to stand. Within a few days a yellow product precipitated (molecular mass: 776.86).

The compound is soluble in water and methanol and insoluble in diethylether. The reaction yield is 45%.

Preparation of $(4\text{-Brbut})_2Zn\cdot mpc_2$ (IV)

0.49 g 98% 4-bromobutyric acid (0.00293 mol) was added to methanolic suspension of 0.14 g $Zn(OH)_2$ (0.00141 mol). After forming zinc organic salt, 0.87 g methyl-3-pyridyl carbamate (0.00572 mol) dissolved in hot methanol, was added to the reaction mixture and refluxed for 4 h. The solution was filtered and left to stand at room temperature. After a few days white crystalls (molecular mass: 701.70) precipitated. The compound is soluble in hot methanol. The reaction yield is 55%.

Characterization

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

Infrared spectra were recorded with Specord IR M–80 spectrophotometer in the region 4000–400 cm^{-1} using KBr pellets (5 mg/500 mg KBr) and gaseous cuvette technique.

The thermal decomposition (TG/DTG, DTA) was 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 Netzsch STA 409 thermoanalyser (heating rate 9°C min^{-1}, 3 mg sample).

Gaseous products were determined by IR spectra, methods of qualitative and quantitative chemical analysis and by Mass spectrometer MS 5988 and QMG 420 (Balzers GmbH). Solid intermediate products of the thermal decomposition were analyzed by X-ray powder diffraction analysis with Micrometa (Chirana CSFR).

Results and discussion

The prepared complexes $(2\text{-Brbut})_2Zn{\cdot}tbr$ (I), $(2\text{-Brbut})_2Zn{\cdot}tph$ (II), $(4\text{-Brbut})_2Zn{\cdot}tbr_2{\cdot}H_2O$ (III) are yellow and the complex $(4\text{-Brbut})_2Zn{\cdot}mpc_2$ (IV) is white. They are all stable in air. The experimental results of chemical analysis are in good accordance with theoretical ones.

IR spectroscopy study

The characteristic absorption bands of IR spectra used for the identification of synthetized compounds are presented in Table 1. The observed absorption bands are adjusted in accordance with literature data [18].

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

Assignment	(I)	(II)	(III)	(IV)
$\nu(O–H)_{H_2O}$	–	–	3400m	–
$\nu(C–H)_{met}$	2970w	2970w	2960m	2975m
$\nu(C=O)$	1680s	1680s	1650s	1726s
$\nu(C=N)_{pyrimidine}$	1640m	1640m	1610m	–
$\delta(O–H)_{H_2O}$	–	–	1600m	–
$\nu_{as}(COO^-)$	1600s	1600s	1610s	1557s
$\nu_a(COO^-)$	1410s	1400s	1420s	1300s
$\Delta\nu_{COO}$	190	200	190	257
$\nu(C=C)_{pyrimidine}$	1550m	1560m	1560m	–
$\nu(C–C)_{pyrimidine}$	940m, 850w	910m, 810w	920m, 860w	–
$\delta(COO^-)$	680s	650s	680s	710s
$\nu(C–Br)$	650m	610m	650m	697m

s – strong, *m* – medium, *w* – weak; (I): $(2\text{-Brbut})_2Zn{\cdot}tbr$, (II): $(2\text{-Brbut})_2Zn{\cdot}tph$, (III): $(4\text{-Brbut})_2Zn{\cdot}tbr_2{\cdot}H_2O$, (IV): $(4\text{-Br but})_2Zn{\cdot}mpc_2$

The symmetric stretching vibration of C=O group of purine ring in methyl derivatives of xantines (theobromine, theophylline) (I, II, III) (Table 1) appears at 1680 cm^{-1} in spectra of compounds (I) and (II), and at 1650 cm^{-1} in compound (III). The stretching vibration (C=O) of C=O group of methyl-3-pyridyl carbamate occurs at 1726 cm^{-1} for compound (IV). The experimental values agree with data in literature [18].

The symmetric stretching vibration of the COO^- group for compounds (I) and (II) occurs at 1600, compound (III) at 1610 and compound (IV) at 1557 cm^{-1}. Symmetric stretching vibration $\nu_s(COO^-)$ is observed at 1410 for (I), at 1400 for (II), at 1420 for (III) and at 1300 cm^{-1} for (IV). The analysis of COO^- group band frequencies allowed the determination of $\Delta\nu_{COO}=\nu_{as}(COO^-)–\nu_s(COO^-)$ whose magnitude has been used as a criterion of the carboxylate binding with metal ions [19]. Calculated

from the IR spectra, values of $\Delta\nu_{COO}$ are in the range 257–190 cm^{-1} for the complexes (I)–(IV) and they are in good accordance with literature data for unidentately bonded carboxylate structures [19].

The presence of the crystal water in the compound (III) is demonstrated by a stretching vibration at 3400 cm^{-1} and by a bending vibration δ(O–H) at 1600 cm^{-1}. Other characteristic absorption bands of the prepared complex compounds are unchanged in comparison with basic zinc compounds and free organic ligands which agrees with literature data [18].

Thermal behaviour

$(2\text{-Brbut})_2Zn\cdot tbr$ (I)

This complex is stable up to 60°C (Fig. 1). Above this temperature the sample loses one molecule of theobromine, two molecules of propylaldehyde and two molecules of carbon monooxide (exp. 351.7, theor. 353.27 mg $mmol^{-1}$) by an endothermic effect on the DTA curve at 80 and 290°C. The formation and release of zinc bromide (exp. 226.8, theor. 225.4 mg $mmol^{-1}$) occurs above 500°C. The following reaction is proposed for the thermal decomposition:

$$(CH_3CH_2CHBrCOO)_2Zn\cdot tbr \rightarrow tbr+2CH_3CH_2CHO+2CO+ZnBr_2$$

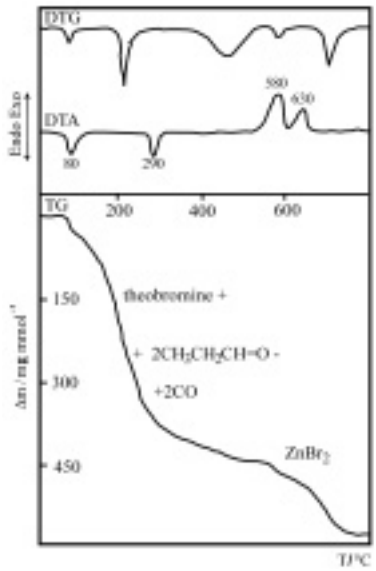

Fig. 1 TG, DTG and DTA curves of $(2\text{-Brbut})_2Zn\cdot tbr$

$(2\text{-Brbut})_2Zn\cdot tph$ (II)

This complex is stable up to 60°C (Fig. 2). The release of theophylline (exp. 181.8, theor. 180.17 mg $mmol^{-1}$) occurs above this temperature with an endothermic

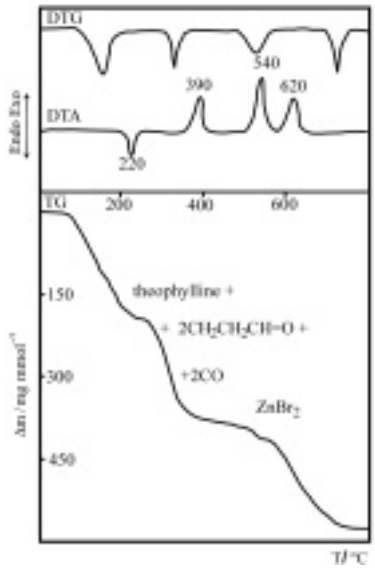

Fig. 2 TG, DTG and DTA curves of $(2\text{-Brbut})_2Zn\cdot tph$

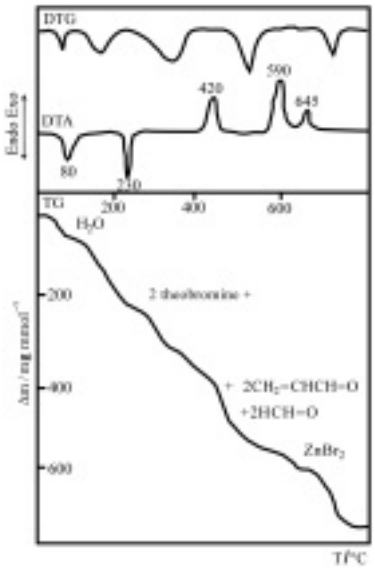

Fig. 3 TG, DTG and DTA curves of $(4\text{-Brbut})_2Zn\cdot tbr_2\cdot H_2O$

effect in the DTA curve at 220°C. The next step of the thermal decomposition is the release of two molecules of propylaldehyde and two molecules of carbon monooxide (exp. 172.5, theor. 173.1 mg $mmol^{-1}$) with an exothermic effect at temperature range 350–400 with a maximum at 390°C. At higher temperatures zinc bromide is formed and released (exp. 222.5, theor. 225.4 mg $mmol^{-1}$). The following reaction is proposed for the thermal decomposition:

$$(CH_3CH_2CHBrCOO)_2Zn\cdot tph \rightarrow tph+2CH_3CH_2CHO+2CO+ZnBr_2$$

$(4\text{-Brbut})_2Zn\cdot tbr_2\cdot H_2O$ (III)

This compound is stable up to 70°C (Fig. 3). Above this temperature one molecule of water is released (exp. 18.6, theor. 18.02 mg $mmol^{-1}$) with an endothermic effect in the DTA curve at 80°C. It is followed by the release of two molecules of theobromine, two molecules of acrylaldehyde and two molecules of formaldehyde (exp. 531.5, theor. 533.44 mg $mmol^{-1}$). It is demonstrated on the DTA curve at 230°C by an endothermic effect and in temperature range 410–440 by an exothermic effect with a maximum at 420°C. The last product of thermal decomposition zinc bromide (exp. 226.7, theor. 225.4 mg $mmol^{-1}$) is formed and released above this temperature. The following reaction is proposed for the decomposition process:

$$(BrCH_2CH_2CH_2COO)_2Zn\cdot tbr_2\cdot H_2O \rightarrow H_2O+2tbr+2CH_2{=}CHCHO+2CH_2O+ZnBr_2$$

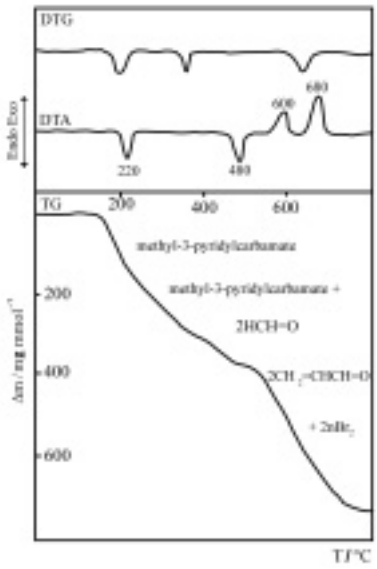

Fig. 4 TG, DTG and DTA curves of $(4\text{-Brbut})_2Zn\cdot mpc_2$

$(4\text{-Brbut})_2Zn{\cdot}mpc_2$ (IV)

This complex is stable up to 140°C (Fig. 4). Methyl-3-pyridyl carbamate is released above this temperature with an endothermic peak at 220°C (exp. 307.7, theor. 304.3 mg $mmol^{-1}$). Methyl-3-pyridyl carbamate was detected by mass spectrometry (*m/z*=152) as is demonstrated in Fig. 5. Above this temperature two molecules of formaldehyde are obtained (exp. 61.5, theor. 60.0 mg $mmol^{-1}$). The final step is the release of two molecules of acrylaldehyde and $ZnBr_2$ (exp. 335.7, theor. 337.4 mg $mmol^{-1}$). The following reaction is proposed for the thermal decomposition:

$$(BrCH_2CH_2CH_2COO)_2Zn{\cdot}mpc_2 \rightarrow 2mpc+2CH_2O+2CH_2{=}CHCHO+ZnBr_2$$

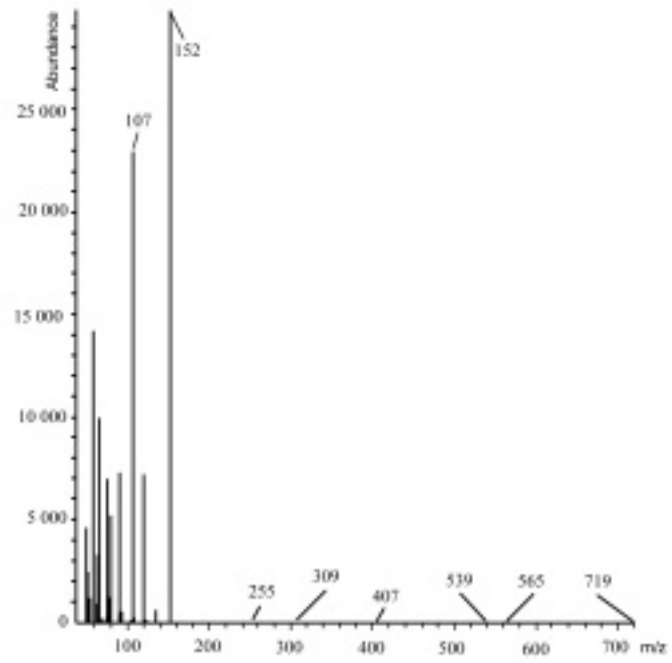

Fig. 5 Mass spectrum of $(4\text{-Brbut})_2Zn{\cdot}mpc_2$ heated to 220°C

Conclusions

The thermal behaviour of the synthetized compounds depends on the character of organic ligand and on the position of the bromine atom. Thermal decomposition of the hydrated compound begins with the release of a water molecule above 70°C. After dehydration the organic ligands are released. This is followed by pyrolysis of the carboxylate anion. In the case of 2-bromobutyrates the volatile products are $CH_3CH_2CH{=}O$, CO, $ZnBr_2$ and in the case of 4-bromobutyrates they are

CH_2=CHCH=O, CH_2O, $ZnBr_2$. The most stable of our new synthetized compounds are those with theophylline and methyl-3-pyridyl carbamate:

$$(2\text{-Brbut})_2Zn\cdot tph = (4\text{-Brbut})_2Zn\cdot mpc_2 > (4\text{-Brbut})_2Zn\cdot tbr_2\cdot H_2O = (2\text{-Brbut})_2Zn\cdot tbr$$

(II) (IV) (III) (I)

DTA: 220 endo = 220 endo > 80 endo = 80 endo/°C

The mechanism and products of thermal decomposition of the newly synthetized zinc(II) bromobutyrates (I, II, III, IV) correspond with the thermal decomposition of previously studied zinc(II) complexes [12, 15]. The only differences were in the initial temperature of the thermal decomposition depending on the type of organic ligand in complex compound.

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