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THERMAL BEHAVIOUR OF NEW ZINC(II) BROMOBUTYRATE COMPLEX COMPOUNDS

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Abstract

New zinc bromobutyrate complexes of general formula $ZnX_2\cdot 1{-}2L\cdot nH_2O$ (X= $CH_2Br(CH_2)_2COO^-$; $CH_3CH_2CHBrCOO^-$) containing one or two molecules of caffeine, nicotinamide and phenazone as ligands (L) were prepared.

The compounds were characterized by MS-, IR- spectroscopy, chemical and thermal analysis. The thermal decomposition of hydrated compounds starts by the release of water molecules. In anhydrous compounds the loss of organic ligands takes place followed by the decomposition of the bromobutyrate anion at higher temperatures. Zinc bromide was found among the final products of thermal decomposition. Water, carbon monoxide, propylaldehyde, vinylaldehyde and formaldehyde were detected in the gaseous products of the thermally decomposed samples on heating up to 700°C.

Keywords: bromobutyrate, caffeine, nicotinamide, phenazone, thermal behaviour, zinc complex compounds

Introduction

Metals are known to display antimicrobial activity. Toxicity of metals increases with their atomic mass [1] and has to be related to the electronegativity of metallic ions and the stability of metal chelates [2].

Zinc represents an essential trace element functioning in biochemical reactions. Therefore zinc(II) compounds have very important pharmaceutical effects. An antimicrobial effect was observed for zinc(II) with indan-1,3-dion-2-imin-N-CH_2COOH [3] and zinc(II) 8-hydroxyquinolinate [4] on Escherichia coli, Proteus mirabilis, Staphylococcus aureus and Streptococcus falcalis.

Zinc(II) carboxylates with O,N,S-donor ligands belong to the coordination compounds that are interesting from the structural viewpoint and biological activity. So far, the spectral and thermal properties of coordination complexes having the structure of Zn(II) formate, acetate, halogenoacetate, propionate, halogenopropionate and butyrate were studied [5–7].

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The aim of this paper is to determine the thermal stability and to compare the thermal behaviour of newly synthetized zinc bromobutyrate complex derivatives.

Experimental

Synthesis of the compounds

In the synthesis of zinc bromobutyrate complex compounds the following chemicals of p.a. grade were used: $CH_3CH_2CHBrCOOH$, $CH_2BrCH_2CH_2COOH$, $ZnCl_2$, K_2CO_3, caffeine, nicotinamide and phenazone.

Complexes Zn(2-Brbut)$_2$·caf·2H_2O (**1**), Zn(2-Brbut)$_2$·nam·H_2O (**2**), Zn(2-Brbut)$_2$·2phen (**3**), Zn(4-Brbut)$_2$·caf·H_2O (**4**), Zn(4-Brbut)$_2$·2nam (**5**), and Zn(4-Brbut)$_2$·phen·H_2O (**6**) were synthetized in water solution by the reaction of the respective zinc bromobutyrate with alkaloid compounds as ligands in the stoichiometric ratios at the temperature 50–70°C. Zinc 2-bromobutyrate and zinc 4-bromobutyrate were received from the reaction of the corresponding bromobutyric acid and zinc carbonate, freshly prepared by mixing solutions of $ZnCl_2$ and K_2CO_3.

Instrumentation

The elemental analysis of the prepared compounds was carried out by means of CHN Analyser Hewlett Packard (Model 185). The IR spectra of complex compounds as well as of the solid decomposition intermediates were recorded on Specord IR M-80 (Zeiss Jena) using KBr pellets, in the range 4000–200 cm^{-1}. The gaseous products were identified by means of IR spectroscopy and methods of qualitative chemical analysis. Zinc content was determined complexometrically.

Thermogravimetric measurements (TG) were performed in air with the Derivatograph MOM OD 102 (Hungary), (sample mass 100 mg, sensitivity of TG 100 mg, sensitivity of DTG 1/10, DTA 1/10, heating rate 6°C min^{-1}, a ceramic pan). For comparison also the TG in nitrogen atmosphere was carried out using Perkin Elmer TGA 7 instrument at a heating rate 10°C min^{-1} and sample mass of approximately 10 mg in platinum pan.

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

Mass spectrometer MAT 711 was used for the characterization of volatile thermal decomposition products of the complex compounds under study.

Results and discussion

Characteristics of the synthetized compounds

The bromobutyrate complexes are white, yellow and pink in colour and stable on light at 70°C in air. The results of CHN analysis as well as of zinc content agree well with the theoretical values corresponding to the chemical composition of the above mentioned compounds.

The characteristic absorption bands of IR spectra used for the identification of the synthetized compounds are presented in Table 1. The observed absorption bands were adjusted in accordance with the literature [8, 9].

Relatively small change in the position of the absorption bands corresponding to the symmetric vibration of COO^- group ν_{sCOO^-} ($1460\rightarrow1450$ cm^{-1}) was observed for all studied bromobutyrate compounds containing organic ligands. In case of the prepared zinc bromobutyrate complexes the symmetric vibration ν_{sCOO^-} was found at 1460 cm^{-1}, i.e. higher than in zinc bromobutyrate without the organic ligand (1430 cm^{-1}). This tendency is quite the opposite of the case of halogenless zinc butyrate complexes, where a shift from 1480 cm^{-1} (zinc butyrate) to much lower values ~1360 cm^{-1} was observed for zinc butyrate complexes containing organic ligands [10].

Asymmetric vibration ν_{asCOO^-} in 2-bromocompounds with caffeine and nicotinamide (**1**, **2**) is smaller than in the respective 4-bromoderivatives (**4**, **5**). The 2-bromocompound with phenazone (**3**) shows on the other hand higher value of ν_{asCOO^-} by about 40 cm^{-1} than 4-bromocompound (**6**). These shifts are obviously affected by the way in which zinc is bonded towards the carboxylate anion. The influence of the particular neighbouring zinc ligands as well as of the bromine position is demonstrated by the changing values of stretching C-Br bond vibrations in the range 660–700 cm^{-1} (Table 1).

Thermal behaviour of the synthetized compounds

In the following paragraphs the thermal stabilities and behaviour of compounds tested during heating in air and nitrogen are described on the basis of the thermal analysis and MS results.

$Zn(2\text{-}Brbut)_2\cdot caf\cdot 2H_2O$

As it follows from Fig. 1, this compound is stable in air up to 60°C. Above this temperature the sample loses 2 mol H_2O as demonstrated by the TG curve and the DTA endothermal effect at 70°C (Fig. 1). In the temperature range 250–550°C the thermal decomposition of anhydrous complex takes place. Following scheme of thermal decomposition of anhydrous compound is supposed:

$$Zn(CH_3CH_2CHBrCOO)_2\cdot caf \rightarrow caf + 2CH_3CH_2CHO + 2CO + ZnBr_2$$

As indicated by the MS spectra caffeine is librated from the complex (*m/z*=194, 109, 82, 67, 55) similarly to previously studied $Zn(but)_2\cdot 2caf$ compound [8]. $ZnBr_2$ was detected by MS (*m/z*=222, 224, 226) as it was the case already in $Zn(Bracet)_2\cdot nam$ [6].

$Zn(2\text{-}Brbut)_2\cdot nam\cdot H_2O$

As it is obvious from Fig. 2 the compound is stable in air up to 70°C. When heated above this temperature, the release of water takes place as indicated on

Table 1 Characteristic absorption bands (ν/cm^{-1}) in infrared spectra of zinc(II) bromobutyrate complexes

Assignment	Compounds					
	1.	2.	3.	4.	5.	6.
ν_{asCOO^-}	1620–1580 w	1620–1580 s	1660–1600 w	1640 m	1630–1550 m	1620 s
ν_{asCOO^-}	1460–1420 m	1460–1380 m	1460–1400 w	1460 w	1450–1410 s	1450–1400 m
νO–H(H_2O)	3580–3400 m	3400 m		3510 m		3600–3450 m
δO–H(H_2O)	1630 s	1650 s		1650 s		1610 s
νN–H(–NH_2)	3390 m				3400 m	
νC=C(=C=O_{nam})		1660 vs			1640 m	
νC–H(–CH_3)	2990 m		2970 vs	2980 m		
δC–H(–CH_3)	1320 w		1370 m	1380 w		
νC=C(=C=O_{caf})	1650 vs			1680–1600 vs		
νC=C(=C=O_{phen})			1620 w			1650 vs
νC=C_{arom}	1590–1410 m			1580–1400 w		
νC–H_{arom}		3050 m	3070 vs		3060 m	3080 m
γC–H_{arom}		700–650 w	800–590 s		700–600 m	810–580 s
νC–C_{arom}		1420–1400 m	1460 s		1440–1400 s	1500 m
νC–Br	680 m	700 w	670 s	680–620 m	670 m	680 m

vs – very strong; s – strong; m – medium; w – weak

1. $(CH_3CH_2CHBrCOO)_2Zn\cdot caf\cdot 2H_2O$; 2. $(CH_3CH_2CHBrCOO)_2Zn\cdot nam\cdot H_2O$; 3. $(CH_3CH_2CHBrCOO)_2Zn\cdot 2phen$; 4. $(Br(CH_2)_3COO)_2Zn\cdot caf\cdot H_2O$; 5. $(Br(CH_2)_3COO)_2Zn\cdot 2nam$; 6. $(Br(CH_2)_3COO)_2Zn\cdot phen\cdot H_2O$

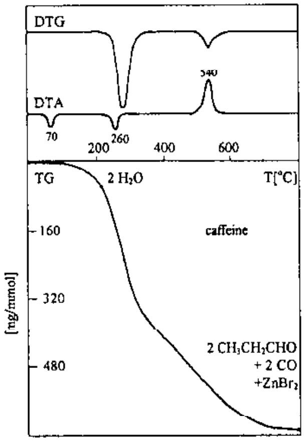

Fig. 1 TG/DTG and DTA curve of $Zn(2\text{-}Brbut)_2{\cdot}caf{\cdot}2H_2O$

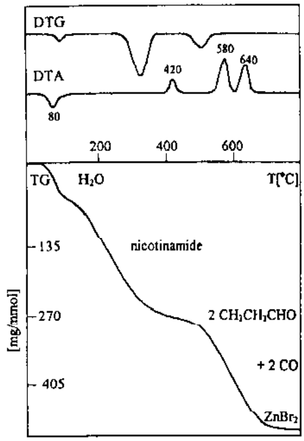

Fig. 2 TG/DTG and DTA curve of $Zn(2\text{-}Brbut)_2{\cdot}nam{\cdot}H_2O$

TG/DTG and DTA curve at 80°C. The total mass loss corresponds to 1 molecule H_2O. The thermal decomposition of the anhydrous product takes place in two steps in the temperature range 150–650°C. The observed MS spectrum of the gaseous decomposition products at 350°C is in a good agreement with our previous results [6] and can be schematically presented:

$$Zn(CH_3CH_2CHBrCOO)_2{\cdot}nam{\cdot}H_2O \rightarrow H_2O+nam+2CH_3CH_2CHO+2CO+ZnBr_2$$

Zn(2-Brbut)$_2$·2phen

The compound was prepared in an anhydrous state. Its thermal behaviour is illustrated in Fig. 3. In the temperature range between 20–350°C no enthalpy change was observed on DTA curve. It is obvious from the TG curve that the compound is stable up to the temperature 100°C. With the increasing temperature, both molecules of phenazone are gradually liberated in two steps up to 370°C. Even at higher temperature, up to 650°C, two molecules of CH_3CH_2CHO, 2CO and $ZnBr_2$ are released. On the DTA curve we can detect two exotherms in this temperature region, namely at

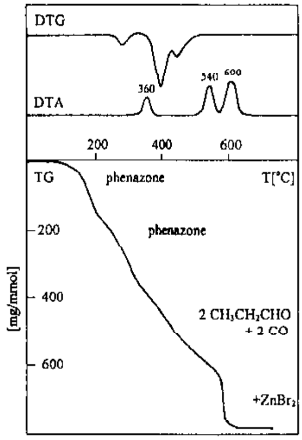

Fig. 3 TG/DTG and DTA curve of Zn(2-Brbut)$_2$·2phen

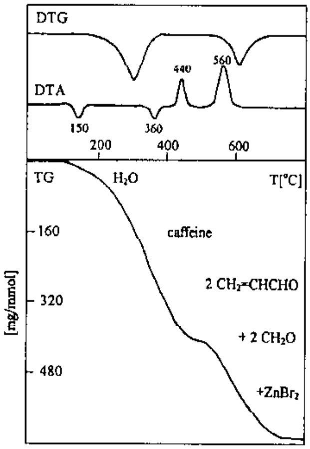

Fig. 4 TG/DTG and DTA curve of Zn(4-Brbut)$_2$·caf·H_2O

540 and 600°C. The thermal decomposition takes place according to the following scheme:

$$\mathrm{Zn(CH_3CH_2CHBrCOO)_2\cdot 2phen \rightarrow 2phen+2CH_3CH_2CHO+2CO+ZnBr_2}$$

$\mathrm{Zn(4\text{-}Brbut)_2\cdot caf\cdot H_2O}$

As it follows from Fig. 4 the sample is thermally stable up to 130°C. When heated above this temperature the release of water takes place. The thermal decomposition of the anhydrous salt, starts at 160°C. The release of caffeine was observed by MS, which is also indicated in Fig. 4 as the endothermal process by DTA, peak at 360°C. The decomposition of the bromobutyrate anion results in the formation of two molecules of vinylaldehyde, two molecules of formaldehyde and $ZnBr_2$. Following reaction scheme is proposed for the decomposition process:

$$\mathrm{Zn(CH_2BrCH_2CH_2COO)_2\cdot caf\cdot H_2O \rightarrow H_2O+caf+2CH_2{=}CHCHO+2CH_2O+ZnBr_2}$$

$\mathrm{Zn(4\text{-}Brbut)_2\cdot 2nam}$

The TG/DTG and DTA curves are demonstrated in Fig. 5. The thermal decomposition starts above 200°C lasting up to 600°C. As observed on DTA curve the beginning of the process is accompanied by the endothermal effect peaked at 220°C. In this temperature range nicotinamide is released. The decomposition of the bromobutyrate anion takes place subsequently. During the decomposition vinylaldehyde, formaldehyde and $ZnBr_2$ are formed. The following reaction scheme is proposed for the decomposition process:

$$\mathrm{Zn(CH_2BrCH_2CH_2COO)_2\cdot 2nam \rightarrow 2nam+2CH_2{=}CHCHO+2CH_2O+ZnBr_2}$$

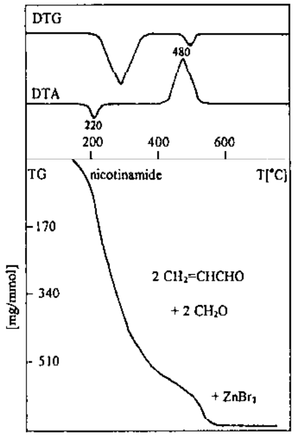

Fig. 5 TG/DTG and DTA curve of $\mathrm{Zn(4\text{-}Brbut)_2\cdot 2nam}$

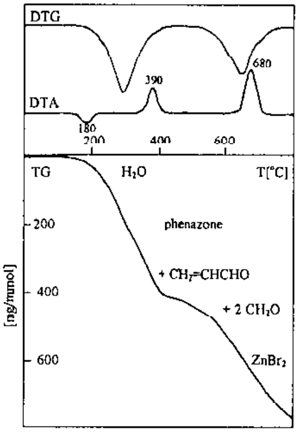

Fig. 6 TG/DTG and DTA curve of $Zn(4\text{-}Brbut)_2$·phen·H_2O

$Zn(4\text{-}Brbut)_2$·phen·H_2O

As it follows from Fig. 6 the sample is thermally stable up to 160°C. The dehydration of the compound is finished at 220°C. The thermal decomposition of the anhydrous product starts at 220°C lasting up to 690°C as indicated by the TG/DTG curves. In this temperature range phenazone is released. The decomposition of the halogenobutyrate anion takes place subsequently. During the decomposition vinylaldehyde, formaldehyde and $ZnBr_2$ are formed. The thermal decomposition takes place according to the following scheme:

$$Zn(CH_2BrCH_2CH_2COO)_2\cdot phen\cdot H_2O \rightarrow H_2O+phen+CH_2{=}CHCHO+2CH_2O+ZnBr_2$$

Conclusions

By means of thermoanalytical, IR- and MS- spectroscopic measurements, the following information about the thermal behaviour of the zinc halogenobutyrate complex compounds have been obtained:

- The thermal decomposition of hydrated compounds begins as an endothermic process by the release of water, bonded as crystal water, in the temperature range 70–180°C.
- On the other hand, the anhydrous compounds undergo a release of the respective organic ligands as the first step of decomposition. The thermal stability of the anhydrous complex compounds increases in this order:

	$Zn(2\text{-}Brbut)_2$·caf <	$Zn(2\text{-}Brbut)_2$·2phen <	$Zn(2\text{-}Brbut)_2$·nam
DTA, °C:	260 endo	360 exo	420 exo

	$Zn(4\text{-}Brbut)_2 \cdot 2\,nam$ <	$Zn(4\text{-}Brbut)_2 \cdot caf$ <	$Zn(4\text{-}Brbut)_2 \cdot phen$
DTA, °C:	220 endo	360 endo	390 exo

Zinc 2-bromobutyrates with caffeine and phenazone are less stable than the respective 4-bromobutyrate complexes, while the $Zn(2\text{-}Brbut)_2 \cdot nam$ was found to be the most stable derivative of all studied complexes. Its decomposition proceeded even 200°C higher than of $Zn(4\text{-}Brbut)_2 \cdot 2nam$. Free nicotinamide melts at decomposition around 130°C. It is obvious that the presence and the position of the halogenatom in the zinc complex compounds influence the mechanism of their thermal behaviour. But also the character of the respective ligand and the number of its attached molecules influence the thermal properties of the studied complexes.

- At even higher temperatures the decomposition of halogenobutyrate anion takes place. CH_3CH_2CHO, CO and $ZnBr_2$ were detected in the gaseous products of 2-bromobutyrates while 4-bromobutyrates released CH_2=CHCHO, CH_2O and $ZnBr_2$ on heating up to 680°C. Somewhat similar thermal behaviour was observed in case of chloroacetate complex compounds when $ClCH_2CHO$, CO, CO_2, CH_2O and $ZnCl_2$ were found among the gaseous products of their thermal decomposition [10].

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References

1 A. E. S. McCallan and F. Wilcoxon, Contrib. Boyce Thompson Inst., 6 (1934) 479.
2 E. Somers, Ann. Appl. Biol., 49 (1961) 246.
3 K. Nikijama, T. Yasuda and H. Nakazawa. J. Chromatogr., 502 (1990) 379.
4 R. J. Fenn and M. T. Alexander, J. Liq. Chromatogr., 11 (1988) 343.
5 K. Györyová, V. Balek, B. H. Behrens, A. Matuschek and A. Kettrup, J. Thermal Anal., 48 (1997) 1263.
6 V. Zeleňák and K. Györyová, J. Císařová, Main Group Metall Chem., 18 (1995) 211.
7 V. Zeleňák, K. Györyová and J. Simon, J. Thermal Anal., 46 (1996) 573.
8 IRSCOT – Infrared Structural Correlation Tables and Data Cards, London NWH 1969.
9 L. Y. Bellamy, The Infrared Spectra of Complex Molecules, London 1975.
10 K. Györyová et al., Proceedings of 14th Conference on Coordination Chemistry, Smolenice 1993, p. 485.