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Thermal properties of zinc butyrate complex compounds. Part 1: Urea and thiourea ligands [☆]

K. Györyová [a,*], V. Balek [b], J. Kovářová [c]

[a] Department of Inorganic Chemistry, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovak Republic
[b] Nuclear Research Institute, 250 68 Prague-Řež, Czech Republic
[c] Institute of Macromolecular Chemistry, AV ČR 162 06 Prague, Czech Republic

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Abstract

The new zinc(II) complexes of general formula $Zn(CH_3CH_2CH_2COO)_2 \cdot nL$ (where L = thiourea, urea; $n = 1$ or 2) were prepared and identified. The thermal properties of this compounds were investigated by thermal analysis (TG, DTG, DTA, DSC, DDSC).

The gaseous products of thermal decomposition were detected by IR spectroscopy and mass spectroscopy. The final product of thermal decomposition was determined by X-ray patterns.

Keywords: Thermal properties; Thiourea; Urea; Zinc butyrate

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1. Introduction

It is known that zinc is important in living organisms for the activity of metalloenzymes. The presence of zinc(II) and copper(II) carboxylates with various organic ligands is considered important in biological systems. Melnik et al. [1–3] studied the copper(II) carboxylates.

We have already investigated the thermal and spectral properties and biological activity of zinc formate and zinc acetate [4–7]. In the present paper thermochemical properties of other biologically active zinc compounds—newly synthesized zinc butyrates with urea and thiourea ligands—are described.

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[*] Corresponding author.

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2. Experimental

2.1. Chemicals and synthesis

In the synthesis of zinc butyrate the following chemicals (p.a. grade) were used: $ZnCl_2$, $(NH_4)_2CO_3$, thiourea, urea (Lachema Brno), butyric acid (Aldrich). The $ZnCO_3$ was prepared by the reaction of $ZnCl_2$ and $(NH_4)_2CO_3$ in solution.

The zinc butyrate was formed by the reaction of aqueous suspensions of zinc carbonate and butyric acid in the stoichiometric ratio according to the scheme:

$$ZnCO_3 + 2CH_3CH_2CH_2COOH \rightarrow Zn(CH_3CH_2CH_2COO)_2 + H_2CO_3$$

White crystalline needles of zinc butyrate were obtained as the reaction product. Subsequently an aqueous solution of the zinc butyrate was mixed with an equimolar amount of aqueous solution of organic ligand, according to the scheme:

$$Zn(CH_3CH_2CH_2COO)_2 + nL \rightarrow Zn(CH_3CH_2CH_2COO)_2 \cdot nL$$

where $n = 1, 2$

After filtration and crystallization white crystals or powder products were obtained. In this way the following compounds were synthesized: $Zn(but)_2 \cdot 2H_2O$, $Zn(but)_2 \cdot tu$, $Zn(but)_2 \cdot 2tu$ and $Zn(but)_2 \cdot 2u$, where but = butyrate, tu = thiourea and u = urea.

2.2. Instrumentation

The prepared substances were identified by elemental analysis using an Hewlett-Packard model 185 CHN Analyser. Zinc content was determined complexometrically using eriochrome black as indicator. The presence of functional groups was identified in solid samples by the IR spectra (using KBr disc 3 mg/400 mg KBr). The gaseous intermediate products of thermal decomposition were identified by Specord IR M-80, Zeiss Jena, in the range 4000–200 cm^{-1}.

The TG, DTG and DTA measurements were carried out using a Derivatograph (MOM OD 102, Hungary) under dynamic conditions in an argon atmosphere; heating rate 9 K min^{-1}, Pt crucibles, 100 mg sample, sensitivity of derivatographic curves: DTA: 1/10, DTG: 1/10, TG: 100 mg.

The enthalpy changes were studied in air under dynamic conditions by use of a Netzsch STA 409 thermoanalyser.

The X-ray patterns were carried out using the Micrometa (Chirana, ČSFR).

The mass spectroscopy was carried out on a Finnigan MAT 5988 spectrometer at various temperatures.

3. Results and discussion

The investigated compounds are stable at 293 K in air and light. Their qualitative solubilities in various solvents is given for information in Table 1. The chemical

Table 1
Qualitative solubility characteristics of zinc butyrates in various solvents

Compound	Solvent[a]							
	H_2O	CH_3OH	C_2H_5OH	CH_3COCH_3	$CHCl_3$	CCl_4	$(C_2H_5)_2O$	C_6H_6
$Zn(but)_2 \cdot 2H_2O$	sol	sol	sol heat	insol	insol	insol	sol	insol
$Zn(but)_2 \cdot tu$	sol	sol	sol	sol	sol	insol	insol	sol
$Zn(but)_2 \cdot 2tu$	sol heat	sol heat	sol heat	sol heat	insol	insol	sol heat	sol heat
$Zn(but)_2 \cdot 2u$	sol	sol heat	sol	sol	insol	insol	sol	sol

[a] Abbreviations: sol = soluble at 293 K; insol = insoluble even when heated to 353 K; sol heat = soluble on heating to 353 K.

compositions of these compounds, confirmed by elemental analysis, were in a good agreement with the theoretical values [8].

3.1. Thermal properties of the prepared compounds

$Zn(but)_2 \cdot 2H_2O$—(see Fig. 1)

The thermal decomposition of this compound starts at 333 K accompanied by the release of two molecules of water of crystallization in an endothermal process with the maximum at 353 K (Fig. 1a). On further heating an endothermic process with maximum at 593 K takes place, the alkylketone and carbon dioxide being released. These gaseous products were identified by IR spectroscopy. The characteristic absorption bands for alkylketone (ν_{C-H} 2976; δ_{C-H} 1448, 1368; ν_{C-C} 912; $\nu_{C=O}$ 1744 cm^{-1}) and carbon dioxide (ν_{asCO_2} 2328; δ_{CO_2} 676 cm^{-1}) are shown in Fig. 1b. The final product of thermal decomposition, ZnO, was identified by IR spectroscopy (ν_{ZnO}: 456 cm^{-1}) [9] and X-ray measurement (Fig. 1c).

$Zn(but)_2 \cdot tu$—(see Fig. 2)

The zinc butyrate containing thiourea ligand melts at 403 K. As shown by the TG–DTA curve on Fig. 2a, the thermal decomposition starts at 413 K. During the endothermic process the hydrogen isothiocyanate and alkylketone are released. The second step of the reaction, an exothermic process with the maximum at 853 K is accompanied by the release of CO_2 and NH_3. The decomposition processes are finished at 893 K. The final product of thermal decomposition is ZnO.

It was of interest to investigate the thermal behaviour of thiourea as such and to compare it with the behaviour of thiourea as the ligand in the complex compound. The decomposition of the organic ligand thiourea results in hydrogen isothiocyanate (HNCS) and ammonia (NH_3). The gaseous products were identified by IR spectroscopy. The characteristic absorption bands for isothiocyanate (ν_{NCS} 2181–2086 cm^{-1}) and ammonia (ν_{N-H} 3400–3200; δ_{N-H} 1624–1550; ν_{N-H} 1200–700 cm^{-1}) are shown in Fig. 2b. Thus the gaseous product of the thiourea decomposition are the same in the

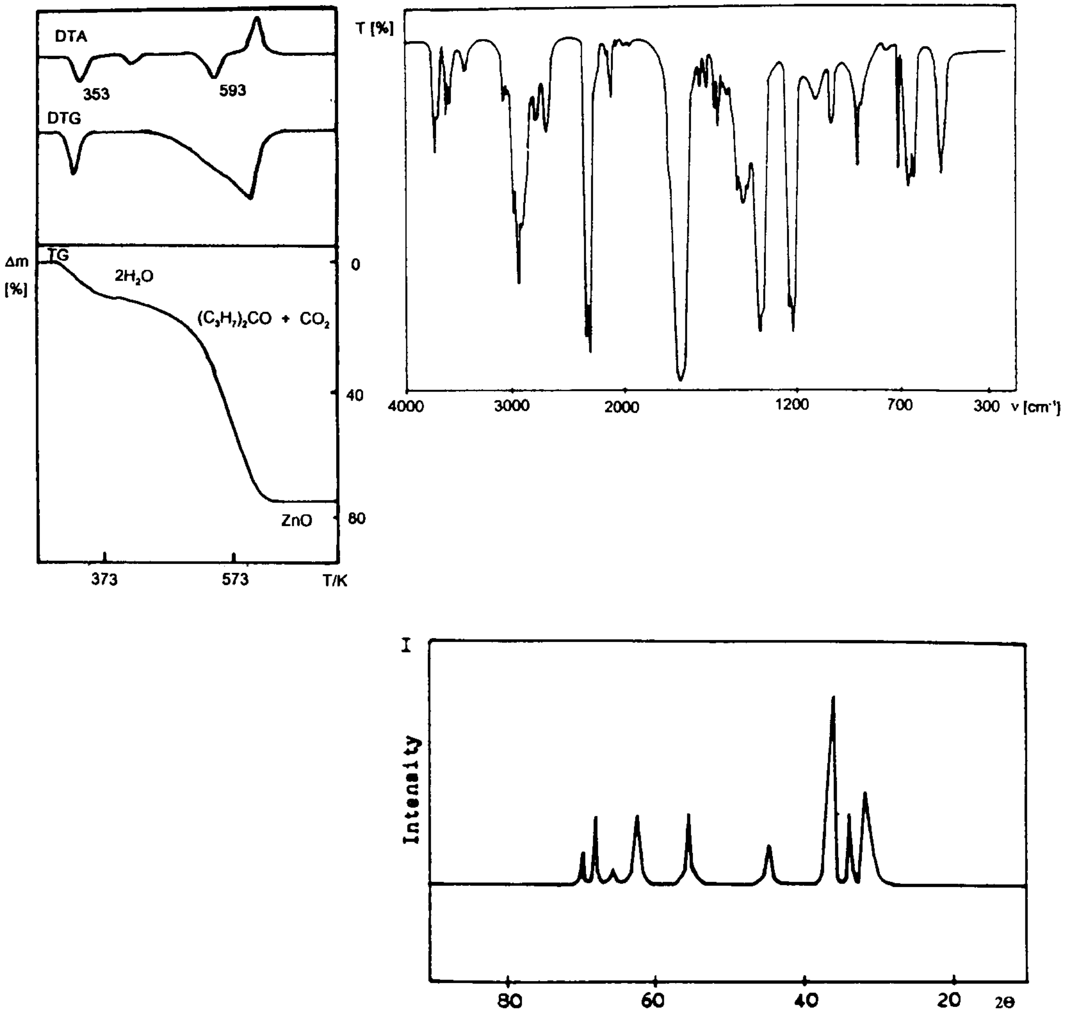

Fig. 1. (a) TG–DTG and DTA curves of $Zn(but)_2 \cdot 2H_2O$; (b) IR absorption spectra of the gaseous product of $Zn(but)_2 \cdot 2H_2O$ heated at 593 K; (c) X-ray pattern of $Zn(but)_2 \cdot 2H_2O$ heated at 673 K.

case of free compounds and the ligand. In the case of free thiourea the temperature interval of the decomposition is 443–863 K.

$Zn(but)_2 \cdot 2tu$—(see Fig. 3)

The thermal decomposition starts at 423 K as indicated on the TG and DTA curves. Release of alkylketone and HNCS accompanies the endothermic process with maxima at 473 K and 653 K. In the subsequent exothermic process with a maximum at 903 K, 2 mol of NH_3 and CO_2 are released. The thermal decomposition is finished at 933 K, the final product being ZnO.

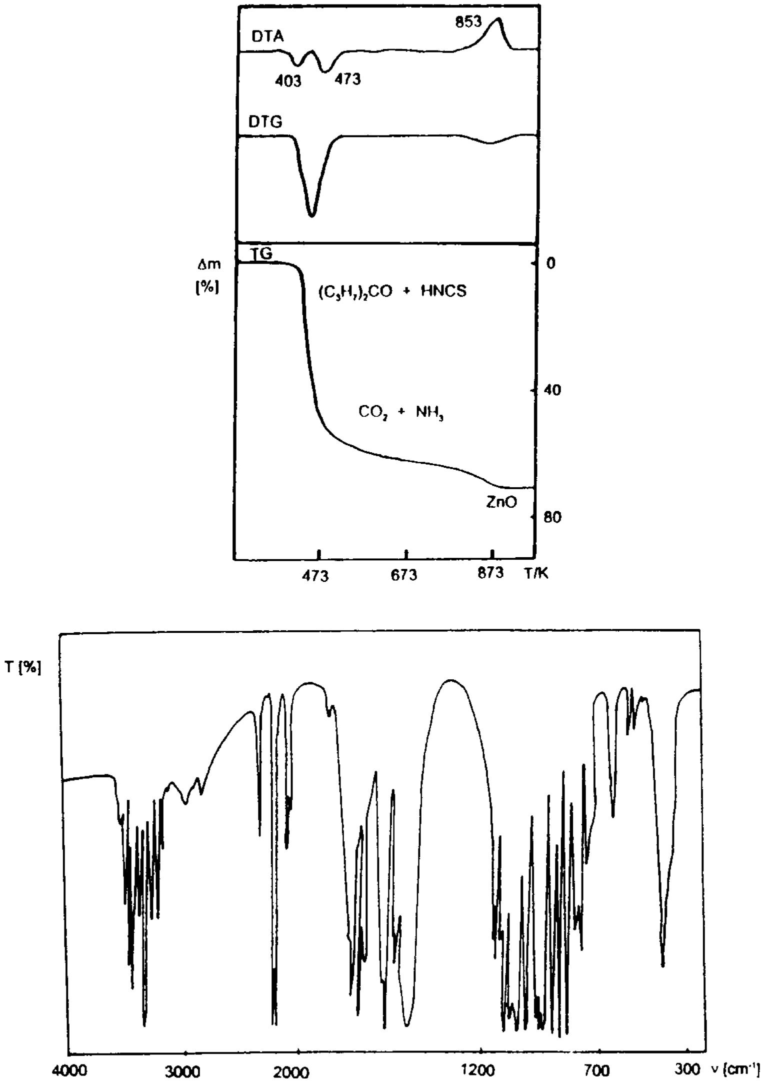

Fig. 2. (a) TG–DTG and DTA curves of $Zn(but)_2 \cdot tu$; (b) IR spectra of the gaseous product of $Zn(but)_2 \cdot tu$ heated at 603 K.

$Zn(but)_2 \cdot 2u$—(see Fig. 4)

The zinc butyrate with two urea molecules melts at 383 K and the endothermic process of decomposition is observed at 493 K, alkylketone and CO_2 being released (Fig. 4a). At this temperature also the decomposition of urea starts, resulting in HNCO and NH_3. This is in a good agreement with observations by Wynne [10]. ZnO is the final product of the thermal decomposition. The enthalpy changes during heating can be seen on the DSC–DDSC curves (Fig. 4b).

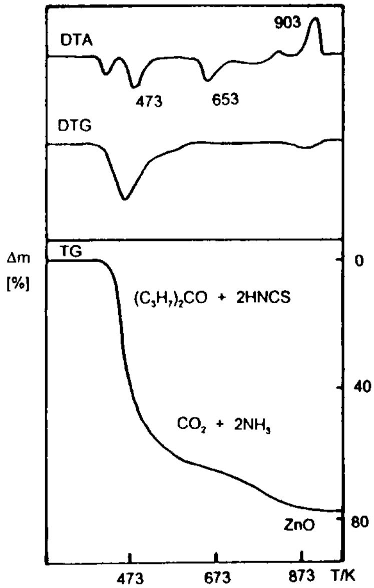

Fig. 3. TG–DTG and DTA curves of $Zn(but)_2 \cdot 2tu$.

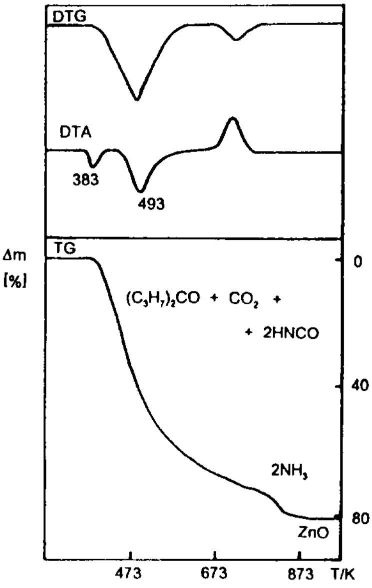

Fig. 4. (a) TG–DTG and DTA curves of $Zn(but)_2 \cdot 2u$; (b) DSC–DDSC of $Zn(but)_2 \cdot 2u$.

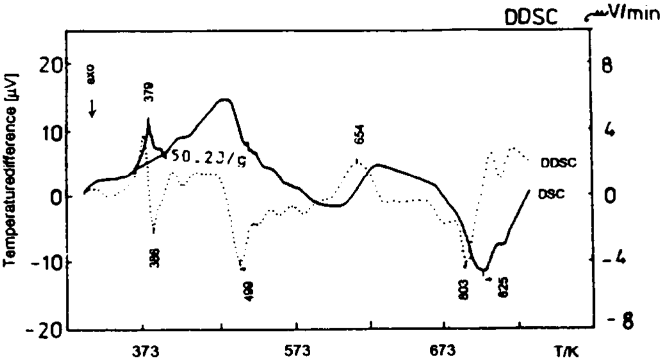

Fig. 4. (*Continued*)

4. Conclusion

The solubilities in various polar and non-polar solvents and the thermal behaviour of new zinc butyrate solid complex compounds with urea and thiourea have been described.

The thermal decomposition of the studied hydrate complex compound begins at 333 K with release of water.

The thermal decomposition temperatures of anhydrous compounds increase in this order:

$$\begin{array}{cccc} \mathrm{Zn(but)_2\cdot 2u} < & \mathrm{Zn(but)_2\cdot 2tu} < & \mathrm{Zn(but)_2\cdot tu} < & \mathrm{Zn(but)_2} \\ T/\mathrm{K} = 393 & 403 & 413 & 423 \end{array}$$

(T is the initial temperature of thermal decomposition of the anhydrous compounds).

The fact that organic ligands are released before the decomposition of zinc butyrate, corresponds with data published earlier for zinc formates, acetates and propionates [4, 5]. During the thermal decomposition of zinc formate compounds containing urea and thiourea, carbon monoxide and water were released [5]. In the case of zinc acetate complex compounds with urea and thiourea, carbon monoxide, carbon dioxide, acetaldehyde and dimethylketone were detected in our study [4]. In the present paper we have demonstrated that during the thermal decomposition of zinc butyrates, HNCS, HNCO, NH_3, CO_2 and alkylketone are released. These results are in an accordance with observations by Wynne [10].

In all compounds ZnO was confirmed by X-ray diffraction patterns and IR spectra of the final product.

In the next communication the thermal behaviour of zinc butyrate complex compounds containing other ligands, e.g. nicotinamide, caffeine etc., will be described.

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