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THERMAL STABILITY OF NEW ZINC ACETATE-BASED COMPLEX COMPOUNDS

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New zinc acetate based complex compounds (of general formula $Zn(CH_3COO)_2 \cdot 1\text{–}2L \cdot nH_2O$) containing one or two molecules of urea, thiourea, coffeine and phenazone were prepared namely: $Zn(CH_3COO)_2 \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2u \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot tu \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot 2tu$, $Zn(CH_3COO)_2 \cdot cof \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2cof \cdot 3.5H_2O$, $Zn(CH_3COO)_2 \cdot 2phen \cdot 1.5H_2O$.

The compounds were characterized by IR spectroscopy, chemical analysis and thermal analysis. Thermal analysis showed that no changes in crystallographic modifications of the compounds take place during (heating in nitrogen before) the thermal decompositions. The temperature interval of the stability of the prepared compounds were determined. It was found that the thermal decomposition of hydrated compounds starts by the release of water molecules. During the thermal decomposition of anhydrous compounds in nitrogen the release of organic ligands take place followed by the decomposition of the acetate anion. Zinc oxide and metallic zinc were found as final products of the thermal decomposition of the zinc acetate based complex compounds studied. Carbon dioxide and acetone were detected in the gaseous products of the decomposition of the compounds if ZnO is formed. Carbon monoxide and acetaldehyde were detected in the gaseous products of the decomposition, if metallic Zn is formed. It is supposed that ZnO and Zn resulting from Zn acetate complex compounds here studied, possess different degree of structural disorder. Annealing takes place by further heating above 600°C.

Keywords: complexes, IR, thermal stability, zinc acetate-based complex compounds

Introduction

Zinc carboxylates with N-donor ligands have potential antifungal effects. Zinc acetate based complex compounds may be used as potential drugs for controlling zinc concentration in living organisms [1, 2].

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At the Department of Inorganic Chemistry of Šafarik University Košice a number of new zinc acetate based complex compounds containing coffeine, phenazone, urea and thiourea as ligands were synthetized.

For the practical use of these compounds it was of interest to investigate their thermal behaviours, namely to determine their thermal stability and to ascertain whether phase modification changes in the solid samples before the thermal decomposition take place. These changes may influence the solubility and biological activity of the compounds.

The aim of this paper is to determine the thermal stability and to describe the thermal behaviours of newly synthetized zinc acetate complex compounds.

Experimental

Synthesis of the compounds

In the synthesis of zinc acetate based compounds the following chemicals of p.a. grade were used: $ZnCl_2$, K_2CO_3, CH_3COOH 98% (Lachema Neratovice); urea, thiourea (Lachema Brno); coffeine, phenazone (Farmakon Hlohovec).

Compounds $Zn(CH_3COO)_2 \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2u \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot tu \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot 2tu$, $Zn(CH_3COO)_2 \cdot cof \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2cof \cdot 3.5H_2O$, $Zn(CH_3COO)_2 \cdot 2phen \cdot 1.5H_2O$ were synthetized by the reactions in water solutions at the temperature 40°–80°C using zinc acetate and respective organic compounds used as ligands in the stoichiometric ratios.

Zinc acetate was prepared from the acetic acid and zinc carbonate freshly synthetized for every compound (by mixing solution of $ZnCl_2$ and K_2CO_3).

Instrumentation

The elemental analysis of the prepared compounds was carried out by means of CHN Analyser Hewlet Packard (Model 185). The IR spectra were measured by means of Specord IR M-80 (Zeiss Jena) using KBr pellets, in the region 4000–200 cm^{-1}.

Thermal analysis was carried out by means of Derivatograph OD 102 (MOM Budapest, Hungary) in Pt crucibles, sample weight 0.1 g; gas atmosphere N_2; heating rate 10 $deg \cdot min^{-1}$.

The zinc amount in the synthetized compounds was determined by complexometric titration using EDTA as agent and eriochrom black as indicator.

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

Results and discussion

Characteristics of the synthetized compounds

The compounds are white in colour and stable on light at 20°C in air. The results of the CHN elemental analysis are summarized in Table 1. The results of CHN analysis as well as zinc content agree well with the theoretical content corresponding to the above chemical composition of the compounds.

The IR spectra of the synthetized compounds are summarized in Table 2. In the Table 2 the characteristic absorption bands are used for identification of the synthetized compounds. The absorption bands observed were identified in accordance with the literature data [3, 4].

Moreover, the IR spectra were used for the investigation of the character of chemical bonding in the synthetized compounds. The influence of the presence of organic ligands on the zinc acetate was estimated by the following comparison of the IR bands positions:

– No change in the position of absorption bands corresponding to the symmetric vibration of COO^- group $\nu_{s\,COO^-}$ (1400 cm^{-1}) was observed for zinc acetate and all the compounds containing organic ligands.

– However in the position of the acetate asymmetric vibration of COO^- group $\nu_{as\,COO^-}$ a shift by 10–14 cm^{-1} towards higher wavelengths was observed only with urea and thiourea, whereas no shift was observed with coffeine and phenazone ligands. Consequently, an interaction between the urea and thiourea and COO^- anion of the zinc acetate can be supposed.

Nevertheless in the case zinc acetate compound containing phenazone a shift in the absorption band of $\nu_{C=O}$ by 40 cm^{-1} towards higher wavelength was observed, as compared with the absorption band of the phenazone compound. Consequently, a deformation of the C=O bond in phenazone can be supposed if being the ligand to zinc acetate.

Thermal behaviour of the synthetized compounds

In the following paragraphs the thermal stabilities and behaviours of compound tested during heating in nitrogen (heating rate 10 deg·min^{-1}) are described on the bases of the thermal analysis and MS results.

$Zn(acetate)_2 \cdot 2.5H_2O$

At it is obvious from the TG/DTG and DTA curves in Fig. 1, the compound is stable in nitrogen up to 70°C. When heated above this temperature, the relase of water takes place starting at 70°C, which is demonstrated by the loss of mass and

Table 1 Chemical analysis

	Compounds	C / %		H / %		N / %		Zn / %	
		Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
1.	$Zn(CH_3COO)_2 \cdot 2.5H_2O$	20.95	21.02	4.70	4.82	—	—	27.47	28.63
2.	$Zn(CH_3COO)_2 \cdot 2u \cdot 0.5H_2O$	23.05	22.96	4.86	4.78	17.93	17.86	19.87	20.84
3.	$Zn(CH_3COO)_2 \cdot tu \cdot 0.5H_2O$	22.10	22.33	4.01	4.09	10.50	10.43	23.43	24.35
4.	$Zn(CH_3COO)_2 \cdot 2tu$	21.41	21.45	4.17	4.17	16.80	16.68	19.18	19.48
5.	$Zn(CH_3COO)_2 \cdot cof \cdot 2.5H_2O$	34.12	34.08	4.90	4.97	13.30	13.25	15.07	15.47
6.	$Zn(CH_3COO)_2 \cdot 2cof \cdot 3.5H_2O$	37.80	37.84	5.28	5.20	17.85	17.65	9.94	10.31
7.	$Zn(CH_3COO)_2 \cdot 2fen \cdot 1.5H_2O$	53.61	53.17	5.57	5.62	9.57	9.54	9.99	11.14

the double DTG effect. The total weight loss which takes place in the temperature range up to 70°–150°C corresponds to 2.5 molecules H_2O, (the first step corresponding to 1.5 mol H_2O and second to 1 mol H_2O). The thermal decomposition of the anhydrous product takes place in one step in the temperature range 150°–320°C. As it was observed by the MS spectrum of the gaseous decomposition products at the temperature of 250°C, molecule of acetone and one molecule of CO_2 are released from the sample as the results of thermal decomposition. This

Table 2 Characteristic absorption bands (ν/cm^{-1}) in infrared spectra

Assignment	Compounds						
	1.	2.	3.	4.	5.	6.	7.
ν_{asCOO^-}	1570 vs	1580 vs	1584 vs	1584 vs	1570 vs	1570 vs	1570 vs
ν_{sCOO^-}	1400 vs	1400 vs	1400 vs	1400 vs	1400 vs	1400 s	1400 s
δ_{COO^-}	696 s	700 s	712 s	750, 720 s	692 s	692 s	700 s
$\nu_{O-H\ (H_2O)}$	3500 w	3500 w	3530 w		3500 w	3550 w	3500 m
$\delta_{O-H\ (H_2O)}$	1600 s	1605 s	1600 s		1604 s	1600 s	1600 s
$\nu_{N-H\ (-NH_2)}$		3460 w	3376 w	3380 m			
$\delta_{N-H\ (-NH_2)}$		1624 s	1624 s	1624 s			
$\nu_{C=O\ (=C=O)}$		1670 s					
$\nu_{C=S\ (=C=S)}$			1400, 1336 1136 s	1404, 1336 1136 s			
$\nu_{C-H\ (-CH_3)}$	2940 w	2950 w	2900 w	2900 w	2950 w	2950 w	2900 w
$\delta_{C-H\ (-CH_3)}$	1375 s	1360 s	1356 m	1352 m	1370 s	1372 m	1350 m
$\nu_{C=O\ (=C=O_{cof})}$					1700 s 1688 s	1710 s 1680 s	
$\nu_{C-H\ (purin_{cof})}$					3070 w	3068 w	
$\delta_{C-H\ (purin_{cof})}$					1024 s	1024 s	
$\nu_{C=O\ (=C=O_{phen})}$							1700 s
$\nu_{N-H\ (pyrazol_{phen})}$							3400 w
$\nu_{C-H\ (-C_6H_{5phen})}$							3150 w
$\delta_{C-H\ (-C_6H_{5phen})}$							1450 s
$\gamma_{C-H\ (-C_6H_{5phen})}$							850 m 650 m

vs – very strong, m – medium, s – strong

1. $Zn(CH_3COO)_2{\cdot}2.5H_2O$,
2. $Zn(CH_3COO)_2{\cdot}2u{\cdot}0.5H_2O$,
3. $Zn(CH_3COO)_2{\cdot}tu{\cdot}0.5H_2O$,
4. $Zn(CH_3COO)_2{\cdot}2tu$,
5. $Zn(CH_3COO)_2{\cdot}cof{\cdot}2.5H_2O$,
6. $Zn(CH_3COO)_2{\cdot}2cof{\cdot}3.5H_2O$
7. $Zn(CH_3COO)_2{\cdot}2phen{\cdot}1.5H_2O$.

is in a good agreement with the result by Bernard and Panevcik [5, 6] that after the dehydration acetanhydride is formed which decomposes in the presence of ZnO giving acetone and CO_2. The final product of the thermal decomposition is ZnO of a poor crystallinity (as shown by the X-ray diffraction patterns).

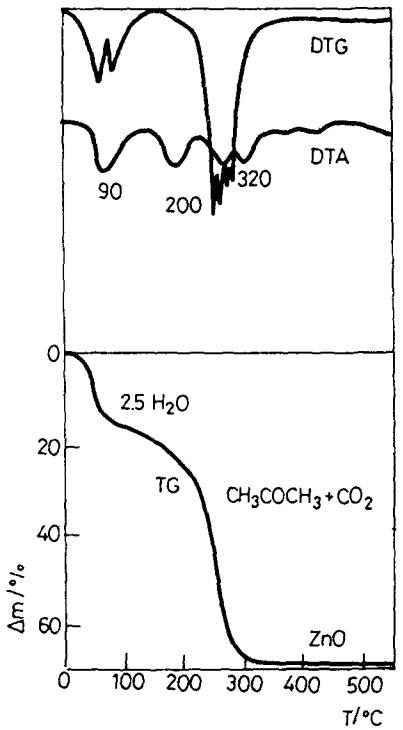

Fig. 1 Thermal decomposition of $Zn(CH_3COO)_2 \cdot 2.5H_2O$

Following scheme has been suggested for the thermal decomposition of $Zn(CH_3COO)_2 \cdot 2.5H_2O$:

$$Zn(CH_3COO)_2 \cdot 2.5H_2O \rightarrow 2.5H_2O + CH_3COCH_3 + CO_2 + ZnO$$

Zn(acetate)$_2$·2urea·0.5H_2O

As it follows from Fig. 2, this compound is stable in nitrogen up to 50°C. No phase change is indicated by DTA in the temperature range 20°–60°C. Above this temperature range the sample losses 0.5 mol H_2O as demonstrated by the TG curve and the DTA endothermal effect (Fig. 2). At the temperatures 130°C the anhydrous complex compound is stable. Its thermal decomposition takes place in the temperature range 140°–500°C, as indicated by the DTG curve and DTA en-

dothermal effects. Following scheme of thermal decomposition of anhydrous compound is supposed:

$$Zn(CH_3COO)_2 \cdot 2NH_2CONH_2 \rightarrow 2NH_2CONH_2 + H_2O + 2CO + CH_3CHO + Zn$$

As indicated by the MS spectra urea is liberated from the complex compound as whole molecule. Metallic zinc results as final decomposition product. Its high defect stage is believed to change into a more disperse consolidated structure above 560°C, as indicated by the slight exothermal effect on the DTA. This statement will be confirmed by means of Emanation thermal analysis [7, 8] which is suitable to the study of the changes in the defect stage of solids.

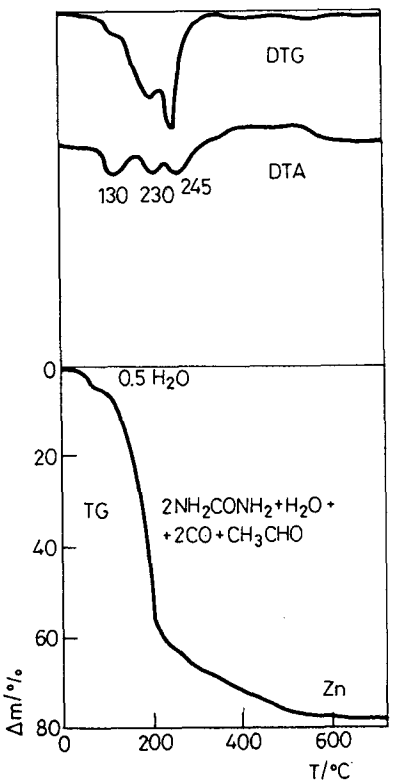

Fig. 2 Thermal decomposition of $Zn(CH_3COO)_2 \cdot 2u \cdot 0.5H_2O$

Zn(acetate)$_2$·thiourea·0.5H$_2$O

The TG/DTG and DTA curves are demonstrated in Fig. 3. It is obvious that the compound is stable up to the temperature of 75°C; in the temperature range be-

tween 20° and 75°C no phase change connected with enthalpy effect was observed. The release of $0.5H_2O$ takes place in the temperature range from 75° to 180°C. The anhydrous complex compound is stable up to 190°C. By heating above this temperature the thermal decomposition according to the following scheme takes place:

$$Zn(CH_3COO)_2 \cdot NH_2CSNH_2 \rightarrow NH_2CSNH_2 + H_2O + 2CO + CH_3CHO + Zn$$

As observed by the MS the molecule of thiourea is released first, followed by the decomposition of the acetate anion, acetaldehyde, H_2O and CO being found in the gaseous phase. The decomposition process is finished at 510°C, metallic zinc resulting as the final decomposition product. It is believed that the highly disordered stage of the decomposition product changes by heating above 600°C into a sintered product which is indicated by the DTA exothermal effect. The additional investigation by means of ETA will be carried out with the aim to confirm this statement.

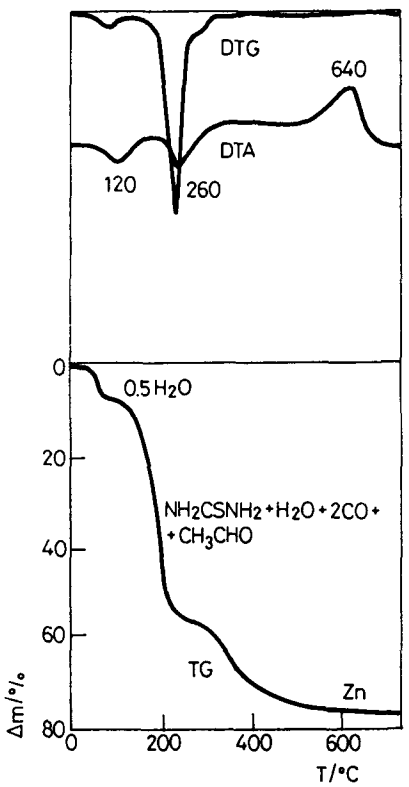

Fig. 3 Thermal decomposition of $Zn(CH_3COO)_2 \cdot tu \cdot 0.5H_2O$

Zn(acetate)$_2$·2thiourea

This compound was prepared anhydrous. The thermal decomposition start at 140°C, as indicated by the curves of TG/DTG in Fig. 4. The decomposition process is endothermic and is demonstrated on the DTG curve by a double peak, indicating two steps of the decomposition. As confirmed by MS in the first step the release of thiourea molecules takes place.

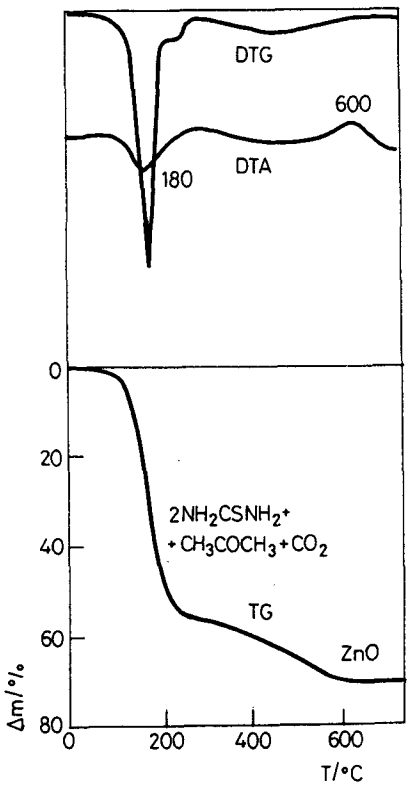

Fig. 4 Thermal decomposition of $Zn(CH_3COO)_2$·2tu

Consequently the acetate anion is decomposed, acetone and CO_2 being released. Following reaction scheme is supposed:

$$Zn(CH_3COO)_2 \cdot 2NH_2CSNH_2 \rightarrow 2NH_2CSNH_2 + CH_3COCH_3 + CO_2 + ZnO$$

ZnO in highly disperse stage was found as the final decomposition product, which sinters above 600°C (as indicated by the DTA exothermic peak). This statement will be confirmed by the independent ETA measurement [7].

$Zn(acetate)_2 \cdot coffeine \cdot 2.5H_2O$

As it follows from Fig. 5, the sample is thermally stable up to 65°C, no phase change connected with enthalpy changes was indicated up to this temperature.

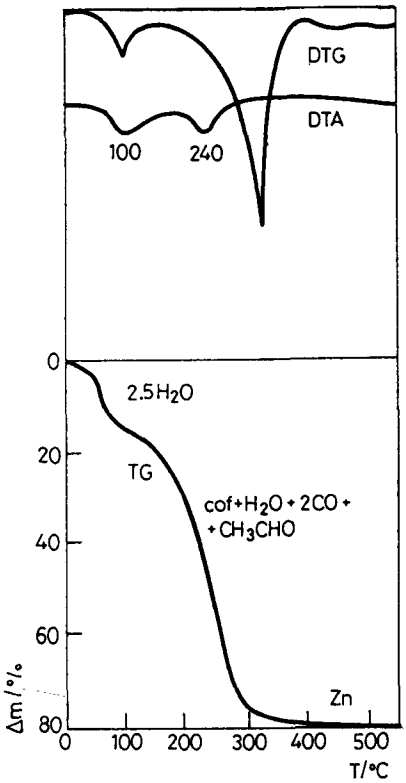

Fig. 5 Thermal decomposition of $Zn(CH_3COO)_2 \cdot cof \cdot 2.5H_2O$

The dehydration of the compound starts at 65° and is finished at 130°C, 2.5 mol H_2O being released in one step. The thermal decomposition of the anhydrous product starts at 210° lasting up to 420°C as indicated by the TG/DTG curves. As observed on the DTA curve in Fig. 5 only the beginning of the process is accompanied by the endothermal effect peaked at 240°C. In this temperature range coffeine is released, the decomposition of the acetate anion takes place subsequently. During the decomposition acetaldehyde and CO are formed. Metallic zinc results as the final decomposition product. The following reaction scheme is proposed for the decomposition process:

$$Zn(CH_3COO)_2 \cdot cof \rightarrow cof + H_2O + 2CO + CH_3CHO + Zn$$

$Zn(acetate)_2 \cdot 2coffeine \cdot 3.5H_2O$

As it follows from Fig. 6 the sample is thermally stable up to 60°C. When heated above this temperature the release of 3.5 molecules of water takes place in one step. The thermal decomposition of the anhydrous salts, start at 190° and last up to 390°C. Following reaction scheme is proposed for the decomposition process:

$$Zn(CH_3COO)_2 \cdot 2cof \rightarrow 2cof + CH_3COCH_3 + CO_2 + ZnO$$

The release of coffeine was observed by MS in the first period of decomposition, which is indicated in Fig. 6 as the endothermal process by the DTA, peak at 230°C. The decomposition of the acetate anion results in the formation of acetone and CO_2. ZnO is formed as the final decomposition product.

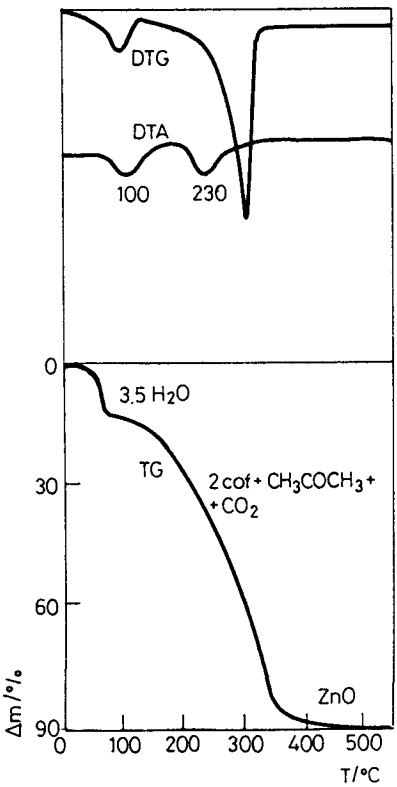

Fig. 6 Thermal decomposition of $Zn(CH_3COO)_2 \cdot 2cof \cdot 3.5H_2O$

$Zn(acetate)_2 \cdot phenazone \cdot 1.5H_2O$

As it follows from the TG/DTG curves in Fig. 7, this compound is stable up to 60°C in nitrogen. No phase changes of the compound were indicated by thermal analysis in the temperature range from 20° to 60°C. The dehydration begins at 60° lasting to 200°C. At the temperatures of 220° to 510°C the thermal decomposition takes place according to the following scheme:

$$Zn(CH_3COO)_2 \cdot 2phen \rightarrow 2phen + H_2O + 2CO + CH_3CHO + Zn$$

The molecule of phenazone was found by MS as the decomposition product in the gaseous phase at the temperature of 250°C. The decomposition of the acetate anion results in the acetaldehyde, H_2O and CO. Metallic zinc was found as the final decomposition product at 600°C. The DTA endothermic effect is believed to indicate the thermal annealing of the highly disperse product of thermal decomposition.

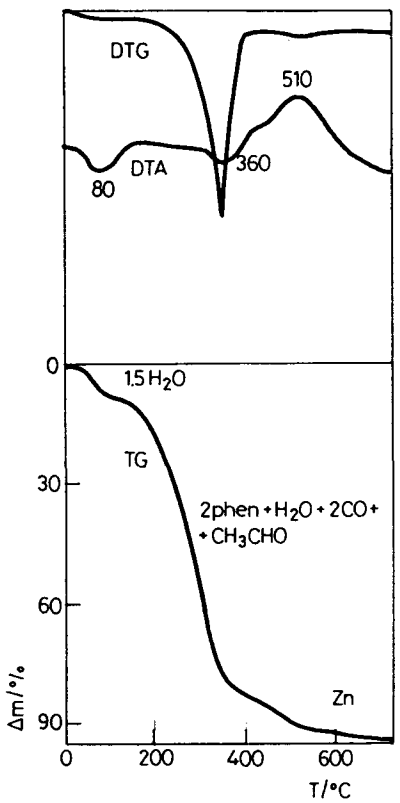

Fig. 7 Thermal decomposition of $Zn(CH_3COO)_2 \cdot 2phen \cdot 1.5H_2O$

However, this should be confirmed by the independent measurements of surface area by ETA, etc.

Conclusion

By means of thermoanalytical, IR spectroscopic and mass spectrometric measurements, the following information about the thermal behaviours of the Zn acetate based complex compounds have been obtained:

No crystallographic modifications take place in the solids before the thermal decomposition.

The thermal decomposition of all studied hydrated compounds begins by the release of water, bonded as crystal water. The thermal stability of the anhydrous complex compounds decrease as follows:

$$\text{Zn acet}_2\cdot\text{2phen} > \text{Zn acet}_2\cdot\text{tu} > \text{Zn acet}_2\cdot\text{cof} > \text{Zn acet}_2\cdot\text{2u} \approx \text{Zn acet}_2\cdot\text{2cof} > \text{Zn acet}_2\cdot\text{2tu}$$

During the thermal decomposition of the anhydrous compounds containing different ligands the release of the organic ligands take place at the first step of the decomposition, followed by the thermal decomposition of acetate anion. By comparison of the thermal stability of Zn acetate – based compounds containing various organic ligands and the thermal stability of the respective organic compounds used as ligands, the following information was obtained:

– In the case of coffeine and phenazone the temperatures of the release of organic ligands from the complex compounds are higher than the decomposition temperatures of the organic ligands themself.

– The complex compound containing thiourea (Zn acetate$_2$·2tu) decomposes at the temperature by 40°C lower than thiourea itself.

– The compounds Zn acetate$_2$·tu and Zn acet$_2$·2u are decomposed at the same temperatures as the respective organic compounds which contain.

It was found for coffeine and thiourea ligands that the presence of ligands in the complex compounds influence the mechanism of the thermal decomposition of acetate anion:

– If only one molecule of the ligand is present in the complex compound, Zn results as final decomposition product and CO and acetaldehyde are formed as gaseous decomposition products of the acetate anion. If two molecules of the ligands are present in the complex compound, ZnO results as the final decomposition product and CO_2 and acetone are formed during the decomposition of the acetate anion.

Metallic zinc and zinc oxide are final decomposition products of all studied zinc acetate – based complex compounds. Carbon dioxide and acetone were detected in the gaseous products of the decomposition of the compounds if ZnO is formed. Carbon monoxide and acetaldehyde were detected in the gaseous products of the decomposition, if metallic Zn is formed. It is supposed that ZnO and Zn resulting as final decomposition products possess different degrees of structural disorder. The latter is annealed by heating above 600°C.

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Zusammenfassung — Neue Komplexverbindungen (der allgemeinen Formel $Zn(CH_2COO)_2 \cdot 1\text{-}2 \cdot LnH_2O$) auf Zinkacetatbasis mit einem Gehalt von einem oder zwei Molekülen Harnstoff(u), Thioharnstoff(tu), Koffein(cof) und Phenazon(phen) wurden hergestellt: $Zn(CH_3COO)_2 \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2u \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot tu \cdot 0.5H_2O$, $Zn(CH_3COO)_2 \cdot 2tu$, $Zn(CH_3COO)_2 \cdot cof \cdot 2.5H_2O$, $Zn(CH_3COO)_2 \cdot 2cof \cdot 3.5H_2O$, $Zn(CH_3COO)_2 \cdot phen \cdot 1.5H_2O$.
Die Verbindungen wurden mittels IR-Spektroskopie, Elementaranalyse und Thermoanalyse beschrieben. Die Thermoanalyse zeigt, daß während (des Erhitzens in Stickstoff vor) der thermischen Zersetzung keine Änderungen der kristallographischen Modifikationen der Verbindungen erfolgen. Für die hergestellten Verbindungen wurde der stabile Temperaturbereich ermittelt. Es wurde festgestellt, daß die thermische Zersetzung der hydratierten Verbindungen mit der Abgabe von Wassermolekülen beginnt. Beim thermischen Zerfall wasserfreier Verbindungen in Stickstoff findet die Abgabe von organischen Liganden statt, gefolgt von der Zersetzung des Acetat-Anions. Als Endprodukte der thermischen Zersetzung der untersuchten Komplexverbindungen auf Zinkacetatbasis erhält man Zinkoxid und metallisches Zink. Wird ZnO gebildet, findet man unter den gasförmigen Produkten der thermischen Zersetzung Kohlendioxid und Aceton. Wird metallisches Zn gebildet, findet man unter den gasförmigen Produkten der thermischen Zersetzung Kohlenmonoxid und Acetaldehyd. Es wird angenommen, daß das aus den untersuchten Zinkacetatkomplexverbindungen entstehende ZnO und Zn einen verschiedenen Grad struktureller Fehlordnung besitzt. Bei weiterem Erhitzen oberhalb 600°C erfolgt Tempern.