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PREPARATION, IDENTIFICATION AND THERMAL PROPERTIES OF $(CH_3CH_2COO)_2Zn \cdot 2L \cdot H_2O$ (*L*=THIOUREA, NICOTINAMIDE, CAFFEINE OR THEOBROMINE)

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Abstract

Zinc carboxylates complexed with N-donor ligands have potential antifungal effects. The preparation, identification and especially the thermal properties of four hitherto non-characterized compounds of this group of general formula $(CH_3CH_2COO)_2Zn \cdot 2L \cdot H_2O$ are described in this paper. The experimental results are confronted with present knowledge on analogous compounds.

Keywords: donor ligands, preparation, thermal properties, zinc propionate

Introduction

Zinc carboxylates complexed with N-donor ligands (*L*) are a group of compounds exhibiting potential antifungal (fungicidal) effects. While the zinc carboxylates themselves have been described in the literature from the viewpoints of their preparation, properties and (in some cases) structure [1–4], similar information on complexes of zinc carboxylates containing N-donor ligands is lacking or only sporadic [5, 6]. In this context this study is aimed at the preparation, identification and thermal properties of a series of compounds of formula $(CH_3CH_2COO)_2Zn \cdot 2L \cdot H_2O$, where *L* is thiourea, nicotinamide, caffeine or theobromine.

Experimental

The investigated series of substances comprised the compounds with the following formulae:

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$(CH_3CH_2COO)_2Zn{\cdot}2TU{\cdot}H_2O$ $(CH_3CH_2COO)_2Zn{\cdot}2COF{\cdot}H_2O$

$(CH_3CH_2COO)_2Zn{\cdot}2NAD{\cdot}H_2O$ $(CH_3CH_2COO)_2Zn{\cdot}2TBR{\cdot}H_2O$

(*TU*=thiourea, *NAD*=nicotinamide, *COF*=caffeine, *TBR*=theobromine.)
The preparation of these substances necessitates the use of pure zinc propionate, which can be prepared in anhydrous or crystalline form depending on the method of isolation from solution. However, both forms are appropriate for further syntheses.

The preparation of the investigated compounds was based on the interaction of an aqueous solution of zinc propionate with the corresponding stoichiometric amount of the N-donor ligand in the solid state. All the ligands used are soluble in an aqueous solution of zinc propionate. After mild heating, which may reach even 80°C in the case of theobromine, and partial evaporation of the solvent, the products freely crystallize. A longer crystallization affords well-defined and very pure products. The yield amounts to 40–60% and the products are white crystalline substances. The preparation may be expressed by the following equation:

$$(CH_3CH_2COO)_2Zn + 2L + H_2O \rightarrow (CH_3CH_2COO)_2Zn{\cdot}2L{\cdot}H_2O$$

Analytical identification

The compositions of the investigated compounds were determined by CHN analyses. Zinc was determined complexometrically. The results of analyses are given in Table 1.

Infrared spectra

The infrared spectra of the investigated compounds were measured in the region 4000–400 cm^{-1} on a SPECORD M-80 spectrometer by using the KBr technique. The measured spectra were compared with the spectra of the N-donor ligands as such and the spectrum of zinc propionate. The characteristic wavenumbers for the individual compounds are given in Table 2.

Thermal measurements

The thermal decompositions of the investigated compounds were followed on an OD-102 derivatograph under the following experimental conditions: Sample 100 mg, TG-100, ceramic crucible, heating rate 6 $deg{\cdot}min^{-1}$, static air atmosphere. The courses of thermal decomposition of the investigated compounds are presented in Figs 1–4 and Table 3.

Table 1 Results of analyses

Compound	C		H		N		Zn	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$(CH_3CH_2COO)_2 \cdot Zn \cdot 2TU \cdot H_2O$	26.3	25.17	5.09	5.28	15.98	15.98	16.6	17.1
$(CH_3CH_2COO)_2 \cdot Zn \cdot 2NAD \cdot H_2O$	47.24	47.45	4.91	4.86	12.38	12.29	14.7	14.3
$(CH_3CH_2COO)_2 \cdot Zn \cdot 2COF \cdot H_2O$	42.80	42.77	5.30	5.22	19.64	18.14	10.1	10.9
$(CH_3CH_2COO)_2 \cdot Zn \cdot 2TBR \cdot H_2O$	40.69	40.72	4.47	4.78	18.59	19.00	10.4	11.0

TU=thiourea, *NAD*=nicotinamide, *COF*=caffeine, *TBR*=theobromine

Table 2 Infrared spectra

Compound	ν(NH)s, as	ν(CH)s, as	ν(=CH)	ν(CH)	ν(C=N)	ν(C=O)	ν(C=C)	ν(N–H) | (C=S)	δ(NH)	ν(Zn–O)
I.	3416 m	–	–	2984 m	–	1628 vs	–	1552 s	–	
	3432 w	–	–	3000 m	–	1608 s	–	1532 m		496 m
II.				2984 m		1704 vs				
	3360 w	3184* m	–	3000 m	1664* m	1664 m	1600* m	–	1452* m	516 m
III.	–	–	–	2976 m	1660 vs	1660 vs	1580 m	–	–	480 m
IV.				2824 m						
	3432 m	3280 m	3032 m	2864 m	–	1684 vs	–	–	–	456 m

I – $(C_2H_5COO)_2 \cdot Zn \cdot 2TU \cdot H_2O$; II – $(C_2H_5COO)_2 \cdot Zn \cdot 2NAD \cdot H_2O$; III – $(C_2H_5COO)_2 \cdot Zn \cdot 2COF \cdot H_2O$; IV – $(C_2H_5COO)_2 \cdot Zn \cdot 2TBR \cdot H_2O$;
* vibrations of pyridine; vs – very strong; s – strong; m – medium: w – weak

X-ray powder diffraction

X-ray powder diffraction examinations on the final decomposition products were made on a MIKROMETA II instrument by using CuK_α radiation. The records were compared with ASTM tables.

Results and discussion

The preparations of the investigated compounds exhibit a number of common features and also particulars. In this connection, we must mention the different volume ratios in which the N-donor ligands react with a solution of zinc propionate, the properties of the N-donor ligand themselves, such as their solubility, and the temperature at which the reaction with zinc propionate in solution sets in. An extended crystallization allows the preparation of well-defined products, whereas preparation involving a rapid decrease in solvent does not lead to reproducible results.

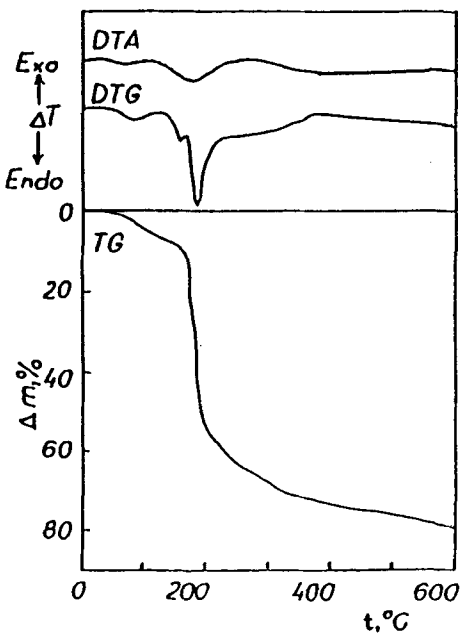

Fig. 1 Thermal curves of $(CH_3CH_2COO)_2Zn{\cdot}2TU{\cdot}H_2O$

Though the measured infrared spectra are complicated, the principal characteristic bands corresponding to the investigated compounds can be identified. The measured infrared spectra were compared with the spectra of the N-donor ligands and with that of zinc propionate. It follows from Table 2 that the char-

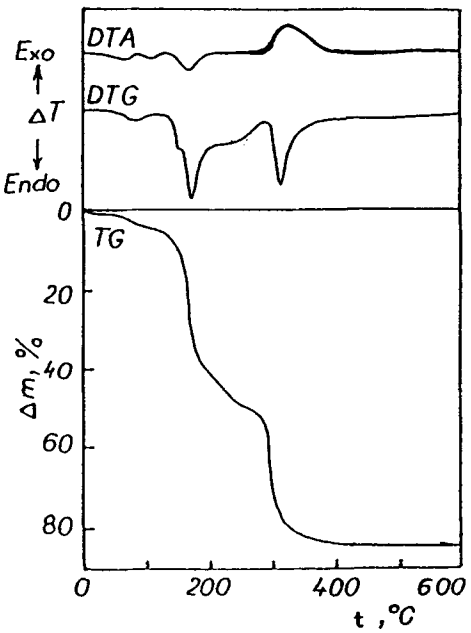

Fig. 2 Thermal curves of $(CH_3CH_2COO)_2Zn{\cdot}2NAD{\cdot}H_2O$

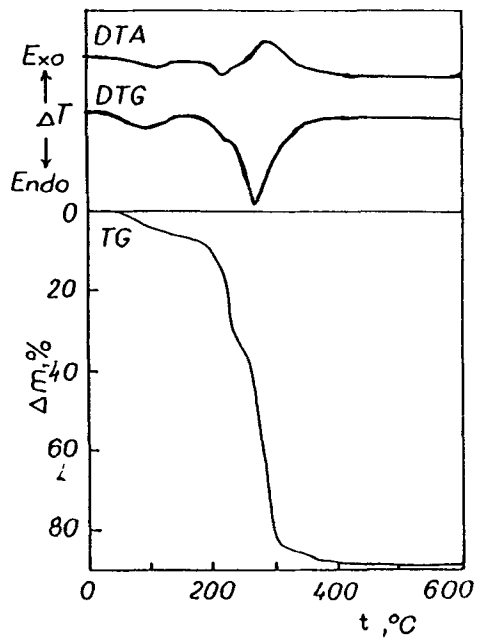

Fig. 3 Thermal curves of $(CH_3CH_2COO)_2Zn{\cdot}2COF{\cdot}H_2O$

Table 3 Data on thermal decomposition of the prepared compounds

Compound	T /°C	Mass loss/%		Composition of product
		obs.	calc.	
$(CH_3CH_2COO)_2Zn \cdot 2TU \cdot H_2O$	50–110 (endo)	4.5	4.7	$(CH_3CH_2COO)_2Zn \cdot 2TU$
	140–600 (endo, exo)	74.0	74.9	ZnO
$(CH_3CH_2COO)_2Zn \cdot 2NAD \cdot H_2O$	50–105 (endo)	4.0	3.8	$(CH_3CH_2COO)_2Zn \cdot 2NAD$
	120–225 (endo)	47.0	51.0	$(CH_3CH_2COO)_2Zn$
	235–350 (exo)	31.0	28.0	ZnO
$(CH_3CH_2COO)_2Zn \cdot 2COF \cdot H_2O$	50–110 (endo)	4.0	2.9	$(CH_3CH_2COO)_2Zn \cdot 2COF$
	160–400 (endo, exo)	81.0	86.0	ZnO
$(CH_3CH_2COO)_2Zn \cdot 2TBR \cdot H_2O$	50–110 (endo)	4.0	3.1	$(CH_3CH_2COO)_2Zn \cdot 2TBR$
	120–400 (endo, exo)	88.0	85.8	ZnO

TU=thiourea, *NAD*=nicotinamide, *COF*=caffeine, *TBR*=theobromine

acteristic bands confirm the presence not only of zinc propionate, but also of the corresponding N-donor ligand in the investigated compounds. However, study of the infrared spectra provides additional information on the compositions and characters of these compounds.

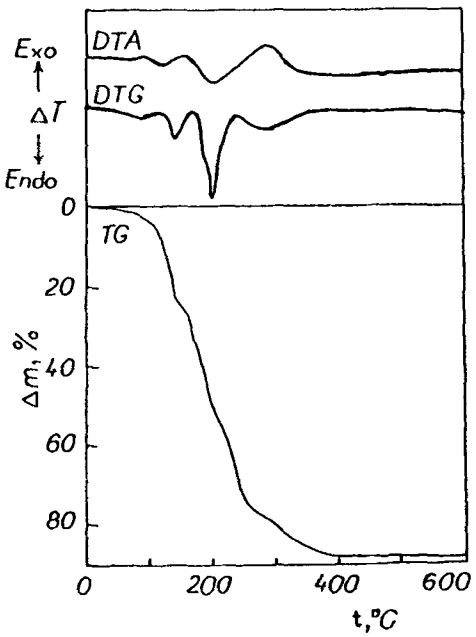

Fig. 4 Thermal curves of $(CH_3CH_2COO)_2Zn \cdot 2TBR \cdot H_2O$

Study of the thermal properties under dynamic conditions shows that, regardless of the nature of the N-donor ligand, the crystalline water is liberated in the first stage of decomposition, accompanied by a slight endothermic effect. The calculated amounts agrees well with the found amount of liberated water and this decomposition step is fairly differentiated from the following step on the temperature coordinate. The subsequent steps are accompanied by endoprocesses and lastly by an exoprocess, corresponding to liberation of the N-donor ligands and finally to the decomposition of zinc propionate, which gives rise to ZnO as the final product of decomposition. In the case of nicotinamide, its liberation can be distinguished from the subsequent decomposition, consistently with its calculated amount. The fact that the N-donor ligands are set free before the decomposition of zinc propionate is confirmed by published data [1, 7] concerning the thermal decomposition of different forms of zinc propionate. In this context, the critical intervals of the decomposition temperatures correlate fairly well with the data published in this paper (Table 3). For this reason, we may assume an analogous mechanism for the final stage of decomposition of

the investigated compounds. The final product of decomposition was identified as ZnO by the use of X-ray powder diffraction as well. Information obtained from ASTM tables shows a good correlation with the literature data on the final products of thermal decomposition of zinc propionate [7].

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Zusammenfassung — Komplexe aus Zinkkarboxylaten mit N-Donorliganden besitzen potentielle fungizide Effekte. Vorliegend werden Herstellung, Identifizierung und insbesondere die thermischen Eigenschaften von vier bislang nicht beschriebenen Verbindungen dieser Gruppe der allgemeinen Formel $(CH_3CH_2COO)_2Zn{\cdot}2L{\cdot}H_2O$ beschrieben. Den experimentellen Ergebnissen werden die vorhandenen Kenntnisse über analoge Verbindungen gegenübergestellt.