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THERMAL PROPERTIES OF ZINC(II) CHLOROACETATE AND ITS COMPLEXES WITH NICOTINAMIDE AND CAFFEINE

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Abstract

Thermal decompositions of zinc(II) chloroacetate and its complexes with nicotinamide and caffeine were studied by means of TG/DTG, DTA, IR and mass spectroscopy. Thermal analysis showed that presence of the halogen significantly influenced the thermal decomposition. Decompositions may be characterized as two step reactions (release of nicotinamide or caffeine followed by pyrolysis of the carboxylate anion). Zinc chloride, CO, CO_2, CH_2O, $ClCH_2CHO$ were found in gaseous products of the thermal decomposition.

Keywords: chloroacetate, complexes, thermal stability, zinc

Introduction

Whereas the thermal properties of zinc(II) carboxylates were described in literature [1–3] the thermal properties of zinc(II) carboxylates containing organic ligands have not been extensively studied so far. Therefore, in our earlier papers [4, 5] we have described the thermal decompositions of zinc(II) formates and acetates with urea, thiourea, caffeine and phenazone. The results have shown release of organic ligands at the first step of decomposition followed by thermal decomposition of carboxylate anion.

In the course of a study of thermal properties of zinc(II) halogencarboxylates we prepared and investigated zinc(II) chloroacetate with and without nicotinamide or caffeine.

The aim of this paper is to describe the thermal properties of the newly synthesized zinc chloroacetate complex compounds.

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Experimental

Preparation of the samples

The zinc(II) chloroacetate dihydrate was synthesized by treating of aqueous solution of chloroacetic acid with a slight excess of freshly prepared aqueous suspension of zinc carbonate.

The compounds of composition $Zn(ClCH_2COO)_2 \cdot 2L$ where L=nicotinamide (NAM) or caffeine (CAFF) were prepared as follows. Aqueous solution of caffeine or nicotinamide was successively added in stoichiometric ratio to the aqueous solution of zinc(II) chloroacetate dihydrate at 60°C under constant stirring. Solution was filtered off and left to stand. White products precipitated within several days. These were washed with water and dried over silica gel.

Instrumentation

The infrared spectra were recorded with a Specord IR M-80 spectrophotometer using the KBr pellet technique and nujol-mull suspension.

The thermal properties of the compounds were studied on Derivatograph OD 102 (MOM Budapest, Hungary) under dynamic conditions. Al_2O_3 was used as a standard material. Sample weight of 100 mg was used and the heating rate was 9°C min^{-1}. The measurements were carried out in air using ceramic crucibles.

The mass spectra used for characterization of volatile thermal decomposition products were measured on a MAT 731 mass spectrometer (Finnigan).

Results and discussion

The course of the reactions of zinc(II) chloroacetate with caffeine and nicotinamide is different.

Reaction of the zinc(II) chloroacetate dihydrate with nicotinamide results dichloro-bis(nicotinamide-N^1-acetato)zinc(II) [6], instead of assumed bis(nicotinamide)bis(chloroacetato)zinc(II), according to the equation:

$$Zn(ClCH_2COO)_2 \cdot 2H_2O + 2L \rightarrow [ZnCl_2(L^+CH_2COO^-)_2] + 2H_2O$$

where L=nicotinamide=$CONH_2C_5H_4N$.

In this reaction the chlorine is replaced by the nicotinamide and bound to the zinc atom. This was confirmed by the results of the structural analysis [6] as well as the IR spectrum (presence ν(Zn–Cl) band at 296 cm^{-1} and absence ν(C–Cl) and ν(Zn–N) bands). The IR spectra are summarized in Table 1. The absorption bands were identified in accordance with the literature data [8–11].

Table 1 The infrared characteristics (cm^{-1})

Assignment	Compound					
	1.		2.		3.	
ν(O–H)	3448	w	–		–	
ν_{as}(N–H)	–		3360	m	–	
ν_s(N–H)	–		3192	m	–	
ν_{as}(C–H)	3016	w	3064^{nam}	m	3112^{caff}	w
ν_s(C–H)	2960	w	2992^{ac}	w	3024^{ac}	w
					2960^{caff}	w
ν(C=O)	–		1700	vs	1696	vs
	–				1660	vs
$\delta(NH_2)$	–		band overlapped		–	
δ(HOH)	1640	vs	–		–	
$\nu_{as}(COO^-)$	1612	vs	1648	vs	1616	s
$\nu_s(COO^-)$	1416	vs	1372	vs	1408	s
ν(ring^{pyr})	–		1496	w	1548	m
	–		1464	w	1480	m
ν(C–N)	–		1312	w		
δ(C–H)			1200	m	1240	s
					1180	w
					1024	m
ν(C–C)	936	m	908^{ac}	m	936^{ac}	w
			840^{nam}	w	860^{caff}	w
ν(C–Cl)	780	s	–		792	s
γ(C–H)			760	m	760	m
					744	s
δ(COO)	688	s				
δ(NCO)	–		632	s	–	
ν(Zn–N)	–		–		328	w
ν(Zn–Cl)	–		296	ms	–	

Notes: nam–nicotinamide, caff–caffeine, ac–chloroacetate anion, pyr–pyridine,
1. $Zn(ClCH_2COO)_2{\cdot}2H_2O$, 2. $[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$, 3. $Zn(ClCH_2COO)_2{\cdot}2CAFF$

On the other hand reaction of zinc(II) chloroacetate with caffeine gives bis(caffeine)bis(chloroacetato)zinc(II), what can be seen from the presence of ν(C–Cl) 792 cm^{-1} and ν(Zn–N) 328 cm^{-1} bands in the infrared spectrum.

The $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations of $Zn(ClCH_2COO)_2{\cdot}2CAFF$ (1616 and 1408 cm^{-1}) are similar to that observed for $Zn(ClCH_2COO)_2{\cdot}2H_2O$ (1612 and 1416 cm^{-1}). The stretching vibrations of the COO^- group in $[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$ are shifted towards higher $\nu_{as}(COO^-)$

1648 cm^{-1} respectively lower $\nu_s(COO^-)$ 1372 cm^{-1} wavenumbers, what is brought about by the presence of zwitterion ($CONH_2C_5H_4N^+CH_2COO^-$) as ligand.

Thermal behaviour

$Zn(ClCH_2COO)_2 \cdot 2H_2O$

The compound is stable up to 70°C. The sample loses two molecules of water above this temperature as demonstrated by the TG curve and DTA endothermic effect at 110°C (Fig. 1). The thermal decomposition of the anhydrous product may be characterized as a two-step reaction in temperature range from 210 to 570°C. Mass spectrum measured at 300°C showed presence of zinc chloride (m/z=134, 136, 138), $ClCH_2CHO$ (m/z=77, 79) and the IR spectra of the gaseous products checked the presence of CO (2176, 2120 cm^{-1}), CO_2 (2368, 2336 cm^{-1}) and aldehyde (1744 cm^{-1}) as products of decomposition. The following reaction is proposed for the decomposition process:

$$Zn(ClCH_2COO)_2 \cdot 2H_2O \rightarrow$$
$$2H_2O + CO + 1/2CO_2 + 1/2CH_2O + ClCH_2CHO + 1/2ZnCl_2 + 1/2ZnO$$

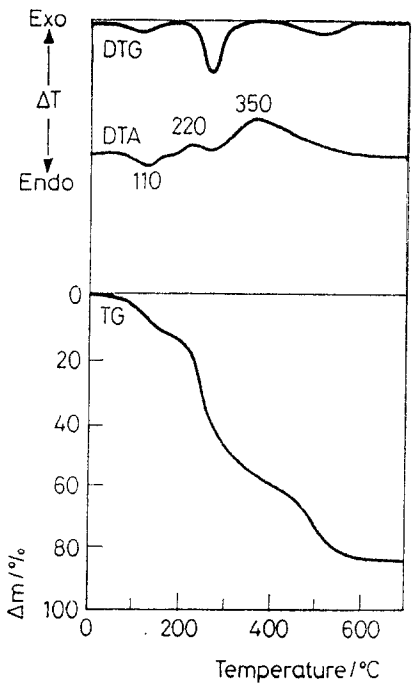

Fig. 1 Thermal decomposition of $Zn(ClCH_2COO)_2 \cdot 2H_2O$

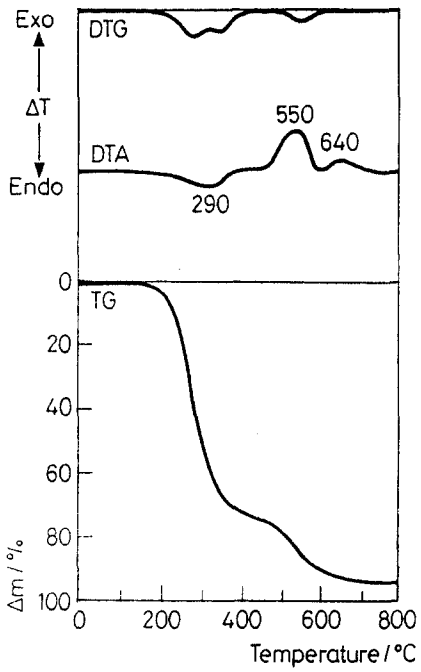

Fig. 2 Thermal decomposition of $Zn(ClCH_2COO)_2 \cdot 2CAFF$

$Zn(ClCH_2COO)_2 \cdot 2CAFF$

On Fig. 2 the sample is thermally stable up to 180 °C. The release and pyrolysis of caffeine takes place above this temperature ($m/z = 194$, 165, 109, 82, 67) – the first step of decomposition, followed by pyrolysis of the chloroacetate anion and release of $ZnCl_2$ ($m/z = 134$, 136, 138) being the second step of decomposition. The decomposition of the chloroacetate anion starts before total elimination of the caffeine and so it is not possible to isolate the Zn(II) chloroacetate after elimination of caffeine. As it is visible from the DTA curve in Fig. 2 the first step of decomposition is accompanied by an endothermic effect at 290°C and the second step by a double exothermic effect with peaks at 550 and 640°C. The final decomposition product corresponds with data given for ZnO [7]. The following reaction is proposed for the decomposition process:

$$Zn(ClCH_2COO)_2 \cdot 2CAFF \rightarrow$$
$$2CAFF + CO + 1/2CO_2 + 1/2CH_2O + ClCH_2CHO + 1/2ZnCl_2 + 1/2ZnO$$

$[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$

The thermoanalytical curves of $[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$ are in Fig. 3. The compound is stable up to 200°C. The decomposition may be char-

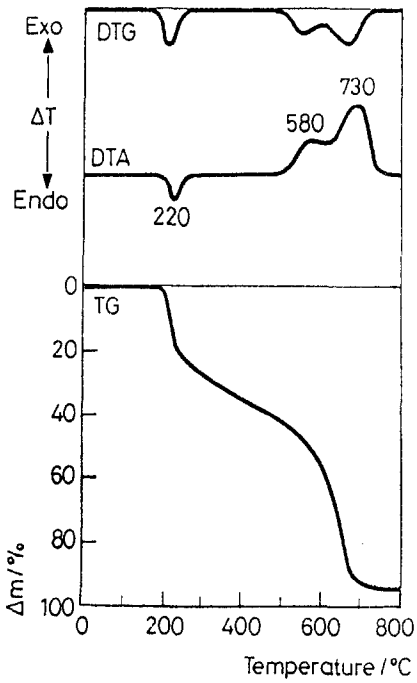

Fig. 3 Thermal decomposition of $[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$

acterized as a two step reaction. Release and pyrolysis of nicotinamide takes place in the first stage. This step of decomposition manifests itself on DTA curve as an endothermic process at 220°C. Release of nicotinamide was confirmed by mass spectrum measured at 220°C (m/z=122, 106, 78, 44). The second step of decomposition is characterized by pyrolysis of carboxylate anion and complete dehalogenation. The DTA curve shows two exothermic peaks in this stage. The mass spectrum measured at 400°C showed presence of $ZnCl_2$ in gaseous products of the decomposition (m/z=134, 136, 138). Thermal decomposition finishes at 700°C. The diffraction data of the solid residue is equally as in the cases of preceeding two compounds corresponding to the values given for ZnO [7].

Conclusion

Presence of halogene significantly influenced the course of the thermal decomposition. While acetone, water, carbon dioxide and ZnO were found as the products of the thermal decomposition of zinc(II) acetate dihydrate [2], zinc chloride, water, CO, CO_2, CH_2O, $ClCH_2CHO$, ZnO were found for $Zn(ClCH_2COO)_2 \cdot 2H_2O$.

The thermal decomposition of zinc(II) chloroacetate with caffeine and nicotinamide is characterized by release of the organic ligands at the first step of decomposition what is similar to decompositions of unsubstituted acetates [5].

Temperature of release of caffeine from $Zn(ClCH_2COO)_2 \cdot 2CAFF$ (180°C) is lower than the temperature observed for $Zn(CH_3COO)_2 \cdot 2CAFF \cdot 3.5H_2O$ (220°C) [5].

Although in the case of $[ZnCl_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$ the nicotinamide is not bound to zinc atom but acetate anion (forming zwitterion nicotinamide-N^1-acetato as ligand) [6], it is deliberated at the first step of decomposition likewise to organic ligands bound directly to the zinc atom [5].

Zinc chloride releases during the thermal decomposition of studied compounds. This release can be observed at the compound with nicotinamide where chlorine is bound to zinc atom but even at compounds where chlorine is bound to acetate anion. ZnO was found as solid residue of thermal decomposition in all the cases.

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