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THERMAL BEHAVIOUR OF ZINC(II) CARBOXYLATE COMPLEXES WITH METHYL-3-PYRIDYL CARBAMATE

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Abstract

Four new complex compounds were prepared by reaction of zinc carboxylate and methyl-3-pyridyl carbamate. The synthesized complex compounds of the general formula $(RCOO)_2ZnL_2$ ($RCOO^-$= $HCOO^-$ (form), CH_3COO^- (ac), $CH_3CH_2CH_2COO^-$ (but), $(CH_3)_2CHCOO^-$ (isobut), *L*= methyl-3-pyridyl carbamate (mpc)) were characterized by chemical analysis, IR spectroscopy and studied by methods of thermal analysis (TG/DTG, DTA). CH_2O, CO_2, $(CH_3)_2CO$, $(C_3H_7)_2CO$ were found as volatile products of thermal decomposition. ZnO was found as final product of thermal decomposition of the prepared complexes heated up to 700°C. Mass spectroscopy, X-ray powder diffraction method, IR spectra and chemical analysis were used for the determination of the thermal decomposition products.

Keywords: methyl-3-pyridyl carbamate, thermal and spectral properties, zinc(II) carboxylate complexes

Introduction

It is well documented that heterocyclic compounds play a significant role in many biological systems, e. g. N-donor compounds with six-membered ring being a component of several vitamins and drugs. Therefore such heterocyclic compounds incorporated in complexes as ligands have been investigated by many authors and their antimicrobial activities have been examined [1].

Metal complex compounds with nitrogen donor ligands have attracted an increasing interest in the last decade [2, 3]. Melnik *et al.* [4–6] studied from this point of view copper(II) carboxylates and magnesium(II) carboxylates. Mészáros-Szécsényi *et al*. studied Zn(II), Co(II), Mn(II) and Cu(II) complexes with pyrazole based ligands. The com-

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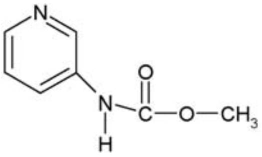
pounds were characterized by elemental analysis, FT-IR spectroscopy, thermal methods and molar conductivity measurements [7, 8]. Thermal and other properties were also characterized in 4,4'-bipyridinetrichloroacetato complexes of Mn(II), Ni(II) and Zn(II) [9]. The latest research at the field of thermal behaviour of Cu(II), Zn(II), Cd(II), Fe(III), Ni(II), Co(II) complexes of 6-(2-pyridylazo)-3-acetamidophenol was done by Mohamed *et al*. [10]. They found out that thermal decomposition of these compounds is a few step process and metal oxide remained as a solid product. In order to understand the drug-metal interactions, we have studied spectral and thermal properties of Zn(II) complexes with methyl-3-pyridyl carbamate, known as an important component of biological systems.

This work is a continuation of our previously reported studies [11–13] on the spectral and thermal properties of zinc(II) carboxylates with N-donor ligands such as caffeine, nicotinamide, papaverine, theophylline and theobromine.

Experimental

Synthesis of the compounds

The following A. R. grade chemicals were used for the preparation of the compounds under study: $ZnCO_3$ (Lachema Neratovice), HCOOH 86%, CH_3COOH 98%, $CH_3CH_2CH_2COOH$ 78%, $(CH_3)_2CHCOOH$ 78% (Aldrich), methyl-3-pyridyl carbamate, methanol (Merck).



methyl-3-pyridyl carbamate (mpc)

Scheme 1

F. W.=152.2 *m.p.*=121–123°C

The synthesis may be expressed by the following equation:

$$2RCOOH+ZnCO_3 \rightarrow (RCOO)_2Zn+H_2O+CO_2\uparrow$$

$$(RCOO)_2Zn+2mpc \rightarrow (RCOO)_2Zn\cdot mpc_2$$

Preparation of $Zn(form)_2\cdot mpc_2$ (**I**)

The methanolic suspension of 0.625 g $ZnCO_3$ (0.005 mol) and 45 cm^3 86% formic acid (0.01 mol) was gradually dissolved under continual stirring. Then 1.525 g methyl-3-pyridyl carbamate (0.01 mol) dissolved in hot methanol was added and the reaction mixture was refluxed for 4 h. In a few days $Zn(form)_2\cdot mpc_2$ was formed. The crystallized product was filtered off. The yield of the reaction is 74%.

Preparation of $Zn(ac)_2 \cdot mpc_2$ (**II**)

0.75 cm^3 98% acetic acid (0.01 mol) was added to methanolic suspension of 0.625 g $ZnCO_3$ and refluxed with 1.525 g methyl-3-pyridyl carbamate (0.01 mol) for 4 h. $Zn(ac)_2 \cdot mpc_2$ precipitated within several days and was filtered off. The yield of the reaction is 80%.

Preparation of $Zn(but)_2 \cdot mpc_2$ (**III**)

The methanolic suspension of 0.625 g $ZnCO_3$ (0.005 mol) and 1.2 cm^3 78% butyric acid (0.01 mol) was left to react under continual stirring until it dissolved. 1.525 g methyl-3-pyridyl carbamate (0.01 mol) was added to the reaction mixture and refluxed for 4 h. The white product $Zn(but)_2 \cdot mpc_2$, formed within a few days, was filtered off. The yield of the reaction is 86%.

Preparation of $Zn(isobut)_2 \cdot mpc_2$ (**IV**)

1.2 cm^3 78% isobutyric acid (0.01 mol) was treated along with 0.625 g $ZnCO_3$ (0.005 mol) in hot methanol under continual stirring while it was dissolved and 1.525 g methyl-3-pyridyl carbamate (0.01 mol) was added. The reaction mixture was refluxed in methanol for 4 h. In several days white product of $Zn(isobut)_2 \cdot mpc_2$ precipitated, and was filtered off. The yield of the reaction is 82%.

Instrumentation

The content of C, H, N was determined by CHN analyser Perkin Elmer 2400 and the content of zinc complexometrically using Complexone III as an agent and Eriochrome black T as an indicator.

Infrared spectra were recorded with EXCALIBUR FTS 3000 MX FTIR spectrophotometer in the region 4000–400 cm^{-1} using the diffusive reflection method.

The thermal behaviour (TG/DTG, DTA) was studied in air atmosphere in Pt crucibles (heating rate 9°C min^{-1}, 100 mg sample, heated up to 700°C) under dynamic conditions on Derivatograph OD 102 MOM (Hungary) and Perkin Elmer DSC 7 and TGA 7.

Gaseous products of the thermal decomposition were collected and determined by IR spectra, methods of qualitative chemical analysis and by mass spectrometer MS 5988 (Finnigan). Solid final products of thermal decomposition were identified by X-ray powder diffraction analysis with MIKROMETA 2 (Czech Republic).

Results and discussion

The synthetized complex compounds $Zn(form)_2 \cdot mpc_2$, $Zn(ac)_2 \cdot mpc_2$, $Zn(but)_2 \cdot mpc_2$, $Zn(isobut)_2 \cdot mpc_2$ are white in colour, stable on air and lightproof at room temperature. They are soluble in water, methanol, ethanol and insoluble in diethylether or benzene. The experimental results of chemical analysis are presented in Table 1 and these are in good accordance with theoretical data.

Table 1 The results of chemical analysis

Compound	C/%		H/%		N/%		Zn/%	
	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
Zn(form)$_2$·mpc$_2$ $C_{16}H_{18}N_4O_8Zn$ F.W.=459.81 **(I)**	41.60	41.80	4.00	3.95	12.10	12.19	14.53	14.22
Zn(ac)$_2$·mpc$_2$ $C_{18}H_{22}N_4O_8Zn$ F.W.=487.78 **(II)**	44.05	44.31	4.15	4.54	11.40	11.48	13.40	13.40
Zn(but)$_2$·mpc$_2$ $C_{22}H_{30}N_4O_8Zn$ F.W.=543.78 **(III)**	48.70	48.60	5.49	5.56	10.15	10.30	12.33	12.03
Zn(isobut)$_2$·mpc$_2$ $C_{22}H_{30}N_4O_8Zn$ F.W.=543.78 **(IV)**	48.40	48.60	5.59	5.56	10.40	10.30	12.56	12.03

IR characteristics

The presence of individual functional groups was confirmed by IR-spectra (Table 2).

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

Assignment	**(I)**	**(II)**	**(III)**	**(IV)**
$\nu(C–H)_{pyr}$	3063 m	3022 m	3051 m	3045 m
$\nu(C–H)_{met}$	2981 w	2955 w	2958 w	2978 w
$\nu(C=O)$	1726 s	1735 s	1737 s	1732 s
$\nu(C=C)_{pyr}$	1589 m	1593 m	1587 m	1591 m
$\nu_{as}(COO^-)$	1560 s	1554 s	1559 s	1556 s
$\nu_s(COO^-)$	1325 s	1338 s	1337 s	1307 s
ΔCOO^-	235	216	222	249
$\delta(C–H)_{met}$	1428 w	1442 w	1429 w	1436 w
$\delta(C–H)_{pyr}$	1192, 1130 w	1192, 1130 w	1189, 1136 w	1192, 1130 w
$\nu(C–H)_{pyr}$	802 m	821 m	873 m	854 m
$\gamma(C–C–C)$	638 w	651 w	646 w	648 w

s – strong; m – medium; w – weak; pyr – pyridine; met – methyl
(I) – Zn(form)$_2$·mpc$_2$; (II) – Zn(ac)$_2$·mpc$_2$; (III) – Zn(but)$_2$·mpc$_2$; (IV) – Zn(isobut)$_2$·mpc$_2$

The symmetric stretching vibration of the C=O group of methyl-3-pyridyl carbamate was found at 1726 cm^{-1} for compound (**I**), at 1735 cm^{-1} for compound (**II**), at 1737 cm^{-1} for compound (**III**) and at 1732 cm^{-1} for compound (**IV**). The values of ν(C=O) are in the range 1726–1737 cm^{-1} that is in accordance with the value of ν(C=O) of free methyl-3-pyridyl carbamate (1725–1740 cm^{-1}) [14]. There is no shift in the wavelengths and therefore we propose that zinc is coordinated to methyl-3-pyridyl carbamate not via oxygen in the C=O group of methyl-3-pyridyl carbamate but probably via nitrogen of pyridine ring [14].

The position of the asymmetric vibration of the COO^- group in carboxylate chain $\nu_{as}(COO^-)$ for compounds (**I**) is 1560 cm^{-1}, for compound (**II**) is 1554 cm^{-1}, for compound (**III**) is 1559 cm^{-1} and for compound (**IV**) is 1556 cm^{-1}. Symmetric stretching vibration $\nu_s(COO^-)$ is observed at 1325 cm^{-1} for (**I**), at 1338 cm^{-1} for (**II**), at 1337 cm^{-1} for (**III**) and at 1307 cm^{-1} for (**IV**). The analysis of COO^- group band frequencies led to the determination of $\Delta\nu_{COO^-}=\nu_{as}(COO^-)-\nu_s(COO^-)$. The calculated values of $\Delta\nu_{COO^-}$ are in the range 249–216 cm^{-1} as determined from IR spectra. It shows unidentifiably bonded carboxylate structures [15]. Other characteristic absorption bands of the prepared compounds are unchanged in comparison with basic compounds and free organic ligand and are consistent with literature data [14].

Thermal behaviour

The thermal decomposition of free ligand mpc starts with its melting at 120°C and above this temperature it starts to decompose until 650°C. The process is accompanied by two exothermic peaks on the DTA curve at 405 and 590°C.

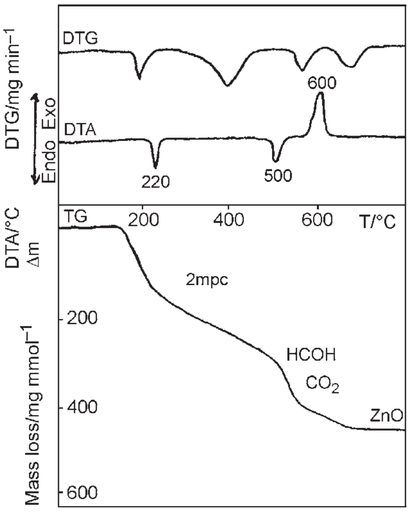


Fig. 1 Zn(form)$_2$·mpc$_2$

Zn(form)$_2$·mpc$_2$ (**I**)

The compound is stable up to 140°C (Fig. 1). Above this temperature the complex is decomposed and two molecules of methyl-3-pyridyl carbamate are lost at 220°C by an endothermic process seen on the DTA curve. The next step of the thermal decomposition is the release of volatile products formaldehyde and carbon dioxide. Zinc oxide was found as the final product of the thermal decomposition heated up to 700°C. The following mechanism of the thermal decomposition is proposed:

$$\mathrm{Zn(HCOO)_2 \cdot mpc_2 \rightarrow 2mpc + HCOH + CO_2 + ZnO}$$

Zn(ac)$_2$·mpc$_2$ (**II**)

The thermal decomposition is shown in Fig. 2. The complex is stable up to 150°C. The compound is decomposed and both molecules of methyl-3-pyridyl carbamate are lost at 260°C. It is demonstrated on the DTA curve as an endothermic effect. By further heating one molecule of acetone and carbon dioxide are released at 530°C. Zinc oxide was found as the final product of the thermal decomposition. The following reaction is proposed for the thermal decomposition:

$$\mathrm{Zn(CH_3COO)_2 \cdot mpc_2 \rightarrow 2mpc + CH_3COCH_3 + CO_2 + ZnO}$$

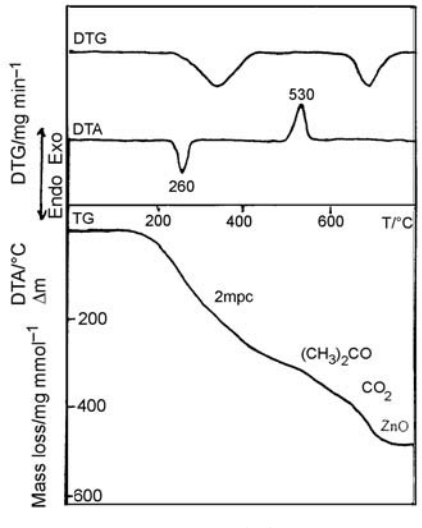


Fig. 2 Zn(ac)$_2$·mpc$_2$

Zn(but)$_2$·mpc$_2$ (**III**)

The complex compound is stable up to 140°C (Fig. 3). The first step of the thermal decomposition is accompanied with the loss of two molecules of methyl-3-pyridyl carbamate that was detected by mass spectra (M^+=152, heated up to 200°C) as demonstrated in Fig. 5. Above this temperature one molecule of dipropylketone and carbon dioxide are released. Heated up to 700°C zinc oxide was found as the final product of the thermal decomposition. Its presence was proved by X-ray patterns. The following mechanism of the thermal decomposition is proposed:

$$Zn(CH_3CH_2CH_2COO)_2\cdot mpc_2 \rightarrow 2mpc+(C_3H_7)_2CO+CO_2+ZnO$$

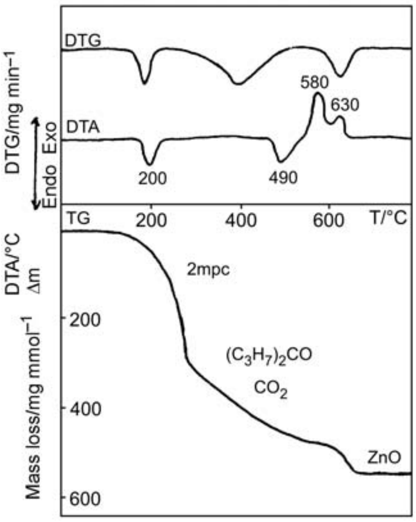


Fig. 3 $Zn(but)_2\cdot mpc_2$

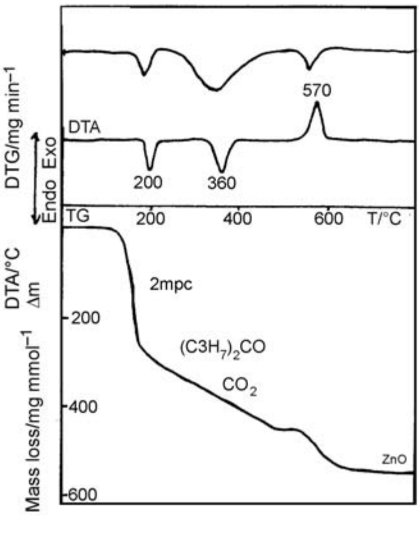


Fig. 4 $Zn(isobut)_2\cdot mpc_2$

Zn(isobut)$_2$·mpc$_2$ (**IV**)

The compound is stable up to 120°C (Fig. 4). Two molecules of methyl-3-pyridyl carbamate are released at 200°C which was detected by mass spectra ($M^+=152$, heated up to 200°C) as demonstrated in Fig. 6. The next step of thermal decomposition is the release of one molecule of dipropylketone and carbon dioxide. Zinc oxide was found as the final product of the thermal decomposition. The following reaction is proposed for the thermal decomposition:

$$Zn((CH_3)_2CHCOO)_2\cdot mpc_2 \rightarrow 2mpc+(C_3H_7)_2CO+CO_2+ZnO$$

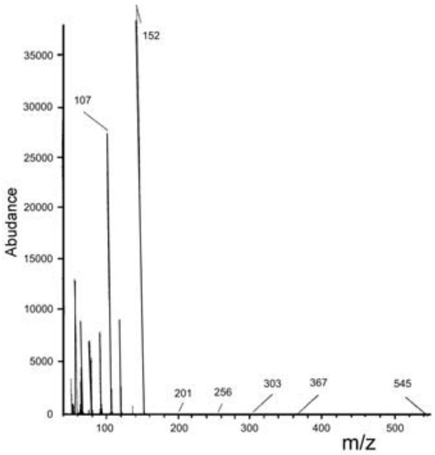


Fig. 5 Mass spectra of Zn(but)$_2$·mpc$_2$ heated to 200°C

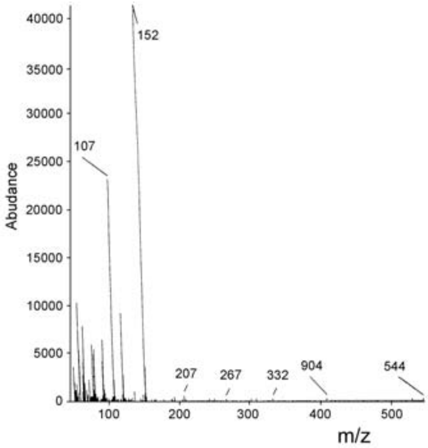


Fig. 6 Mass spectra of Zn(isobut)$_2$·mpc$_2$ heated to 200°C

All the intermediate volatile products were collected and proved by IR spectra and qualitative chemical analysis. Solid final product ZnO was confirmed by X-ray powder diffraction method.

Characterization of envolved gaseous products

In envolved gases of the thermal decomposition aldehydes and ketones were found. They were identified by characteristic IR absorption bands (for formaldehyde $\nu(C=O)_{aldehyde}$ at 1728 cm^{-1} and $\nu(C–H)_{aldehyde}$ at 2721 and 2820 cm^{-1}; for acetone $\nu(C=O)_{ketone}$ at 1708 cm^{-1} and for dipropylketone $\nu(C=O)_{ketone}$ at 1715 cm^{-1}) [14].

The presence of aldehydes and ketones was also proved by specific analytical reactions. Gases were traped into mixture solution of nitrobenzene and 15% NaOH and the presence of ketones was proved by indigo colour of the solution. Aldehydes do not give this reaction. The presence of formaldehyde was confirmed with Fehling's reagent. Aldehydes give deep blue colour and red precipitation. Ketones do not give this reaction [16].

Conclusions

By means of thermoanalytical and off-line IR- and MASS-spectroscopic measurements, the following information about thermal behaviour of zinc(II) carboxylate complex compounds have been obtained:

- The thermal decomposition begins in the temperature range 120–150°C demonstrated on TG curves.
- This decomposition is accompanied by the loss of methyl-3-pyridyl carbamate shown as an endothermic effect on the DTA curve:

$$Zn(but)_2{\cdot}mpc_2 = Zn(isobut)_2{\cdot}mpc_2 < Zn(form)_2{\cdot}mpc_2 < Zn(ac)_2{\cdot}mpc_2$$

(III) = **(IV)** < **(I)** < **(II)**

DTA, °C 200 endo 200 endo 220 endo 260 endo

The above mentioned initial temperatures of complex compounds are higher than the temperature of thermal decomposition of free methyl-3-pyridyl carbamate (120°C) indicating a higher thermal stability of the complex compounds.

- At even higher temperatures the decomposition of carboxylate anion takes place. Formaldehyde and carbon dioxide were detected as gaseous products for compound (**I**), dimethylketone and carbon dioxide for compound (**II**), and dipropylketone and carbon dioxide for compounds (**III**) and (**IV**). Zinc oxide was found as the final product of the thermal decomposition of all four studied complex compounds.
- Similar thermal behaviour was observed in case of our previously studied aliphatic zinc(II) carboxylates with caffeine, nicotinamide, thiourea, urea where the initial decomposition temperature was lower by approximately 30°C than in complexes formed with methyl-3-pyridyl carbamate [12, 17, 18]. Then carboxylate anion started to decompose and ZnO was found as final solid product of the thermal decomposition.

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