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*Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday*

# SYNTHESIS AND THERMAL BEHAVIOUR OF NEW ZINC HALOGENO COMPLEX COMPOUNDS WITH PHENAZONE AND NICOTINAMIDE

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## Abstract

New zinc complex compounds of general formula $ZnL_2,X_2$ {$X$=Cl, Br; $L$=phenazone(phen), nicotinamide(nam)} were synthesized. The new compounds were characterized by elemental analysis. IR spectroscopy and DTA, TG/DTG methods. Thermal properties of the new compounds were investigated.

It was found that nicotinamide, phenazone and $ZnCl_2$ or $ZnBr_2$ are released during the thermal decomposition of the compounds. Mass spectroscopy has been used for the determination of the thermal decomposition intermediate products.

**Keywords:** nicotinamide, phenazone, synthesis, thermal decomposition, zinc complex

## Introduction

Our previous papers [1, 2] have been dealing with synthesis and thermal properties of some zinc carboxylates and their derivates (formates, acetates, propionates, butyrates) with N-donor ligands. Some of these compounds have fungicidal effect on Trametes versicolor and Coniophora puteana [3].

The crystallographic and structural data of zinc complexes were characterized and classified in the paper [4]. In this paper the preparation and thermal behaviour of the new halogenocomplex compounds of the $ZnL_2X_2$ type are described.

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# Experimental

## *Synthesis of the compounds*

In the synthesis of zinc complex compounds following A. R. grade chemicals were used: $ZnCl_2$, NaOH (Lachema Neratovice), $CH_3CH_2CHBrCOOH$ 98%, $CH_2ClCH_2CH_2COOH$ 99% (Merck), phenazone, nicotinamide (Farmakon Hlohovec).

### Preparation of $Zn(phen)_2Br_2$

The compound was prepared by neutralization of 0.58 $cm^3$ 98% α-brombutyric acid and 0.25 g $Zn(OH)_2$ (0.0025 mol). The water solution of 0.95 g phenazone (0.005 mol) was added under stirring to the above reaction mixture after 30 minutes, filtered and the solution refluxed. After cooling the solution was again filtered. An orange product crystallized after two days. The crystals were separated by filtration, washed out with ethanol and air dried. The new compound is soluble in water and ethanol; it is insoluble in diethylether and chloroform.

### Preparation of $Zn(nam)_2Cl_2$

Water solution of 0.79 g nicotinamide (0.0064 mol) was added during stirring to the freshly prepared solution of 1 g $Zn(CH_2ClCH_2CH_2COO)_2$ (0.0032 mol). The product as white crystals appeared within three days. The new compound is soluble in water, it is insoluble in chloroform and diethylether.

### Preparation of $Zn(phen)_2 Cl_2$

The amount of 1.22 g phenazone (0.0064 mol) dissolved in 40 $cm^3$ water solution was gradually added to the water solution of 1 g $Zn(CH_2ClCH_2CH_2COO)_2$ (0.0032 mol). The reaction mixture was stirred, heated and refluxed during three hours. The solution was filtered off and left to stand at room temperature. Orange crystals precipitated from water solution after two days. This new compound is soluble in water.

## *Instrumentation*

Contents of carbon, hydrogen and nitrogen in the newly synthesized compounds were determined by means of the CHN Analyzer Perkin-Elmer 2400. Zinc content was determinated complexometrically using complexone III as agent, eriochrome black as indicator. IR spectra of the prepared compounds were measured by means of Specord IR M-80 in the range 4000–200 $cm^{-1}$ using KBr pellets.

Mass spectrometer MS 5988 was used for determination of volatiles intermediate products of thermal decomposition.

The TG/DTG and DTA measurements were carried out using Derivatograph (MOM OD-102 Hungary invented by Paulik-Paulik-Erdey) under dynamic condition in air atmosphere and in Pt crucibles; heating rate 10 K $\mathrm{min}^{-1}$, 100 mg sample.

# Results

## *Properties of the synthesized compounds*

The prepared complex compounds i.e. two compounds containing phenazone are orange in colour and one compound containing nicotinamide is white. The compounds are stable when kept on light in air at room temperature. The results of the elemental analysis are given in the Table 1. The experimental and calculated CHN-values are in a good agreement.

**Table 1** Results of chemical analysis of zinc halogeno complexes

| Compound | C% | H% | N% | Zn% |
|---|---|---|---|---|
| | exp./theor. | exp./theor. | exp./theor. | exp./theor. |
| $Zn(phen)_2Br_2$ | 44.01<br>43.08 | 3.86<br>4.02 | 9.37<br>9.31 | 10.6<br>10.92 |
| $Zn(nam)_2Cl_2$ | 38.60<br>38.69 | 3.19<br>3.17 | 15.01<br>14.99 | 16.4<br>17.1 |
| $Zn(phen)_2Cl_2$ | 51.69<br>51.49 | 4.94<br>4.72 | 11.04<br>10.93 | 13.5<br>12.8 |

## *IR characteristics*

The IR spectra were used for identification of the prepared compounds. The characteristic absorption bands of the organic ligands present in the samples are summarized in Table 2. It follows from Table 2 that in the compounds $Zn(phen)_2Br_2$ and $Zn(phen)_2Cl_2$ symmetric stretching vibration of C=O group of pyrazoline ring (1620 $\mathrm{cm}^{-1}$) shifts about 40 $\mathrm{cm}^{-1}$ towards lower wavelengths against the free phenazone molecule (1660 $\mathrm{cm}^{-1}$) [5]. This shift reflects the coordination of Zn to phenazone ligand via oxygen in the C=O group. This hypothesis was confirmed by the determination of the structure of this compound [3].

In the zinc acetate phenazone compound is $\nu_{C=O}$ value higher (1700 $\mathrm{cm}^{-1}$) [6]. Other characteristic absorption bands of the prepared compounds are remained as compared with free ligands.

**Table 2** Characteristic absorption bands ($\nu$/cm$^{-1}$) in infrared spectra

| Assignment | 1 | 2 | 3 |
|---|---|---|---|
| $\nu(C-H)_{ph}$ | 3080 | | 3080 |
| $\nu(C-H)_{pyrid}$ | | 3080 | |
| $\nu(C-H)_{met}$ | 3000, 2950 | | 3000, 2950 |
| $\delta(C-H)$ | 1450–1100 | 1200–1100 | 1430–1000 |
| $\gamma(C-H)_{ph}$ | 810– 580 | | |
| $\gamma(C-H)_{pyrid}$ | | 700– 600 | |
| $\nu(C{=}O)$ | 1620 | | 1620 |
| $\nu(C-C)_{pyrid}$ | | 1440–1400 | |
| $\nu(C-C)_{ph}$ | 1480 | | 1480 |
| $\nu(N-H)_{nam}$ | | 3390 | |
| $\nu(C-N)_{nam}$ | | 1440–1400 | |
| $\nu(Zn-Cl)$ | | 320 | 320 |

Key: 1, $Zn(phen)_2Br_2$; 2, $Zn(nam)_2Cl_2$; 3, $Zn(phen)_2Cl_2$; ph=phenyl; pyr=pyrazolone; pyrid=pyridine; met=methyl; nam=nicotinamide

## *The thermal behaviour of the prepared compounds*

In the following paragraphs the thermal behaviour of the synthesized compounds, characterized on the basis of DTA, TG/DTG and EGA (Mass spectrometric detection) is described.

### $Zn(phen)_2Br_2$

The TG/DTG and DTA curves of $Zn(phen)_2Br_2$ are shown in Fig. 1a. This compound is stable in air up to 473 K. After heating above this temperature two molecules of phenazone (373.02 mg/mmol) are released, accompanied by an exothermic effect with the DTA maximum at 693 K. The resulting $ZnBr_2$ is released in the next step of thermal decomposition, accompanied by an exothermic process peaking on the DTA curve at 973 K. The $ZnBr_2$ was detected by the mass spectra ($m/z$=224) as demonstrated in Fig. 2a. The whole amount of the sample totally decomposed by heating up to 1073 K, no solid remained.

### $Zn(nam)_2Cl_2$

It follows from Fig. 1b that this compound is stable in air up to 495 K. Above this temperature two molecules of nicotinamide (247.35 mg/mmol) are released from sample accompanied by an endothermic process peaking on the DTA curve at 603 K.

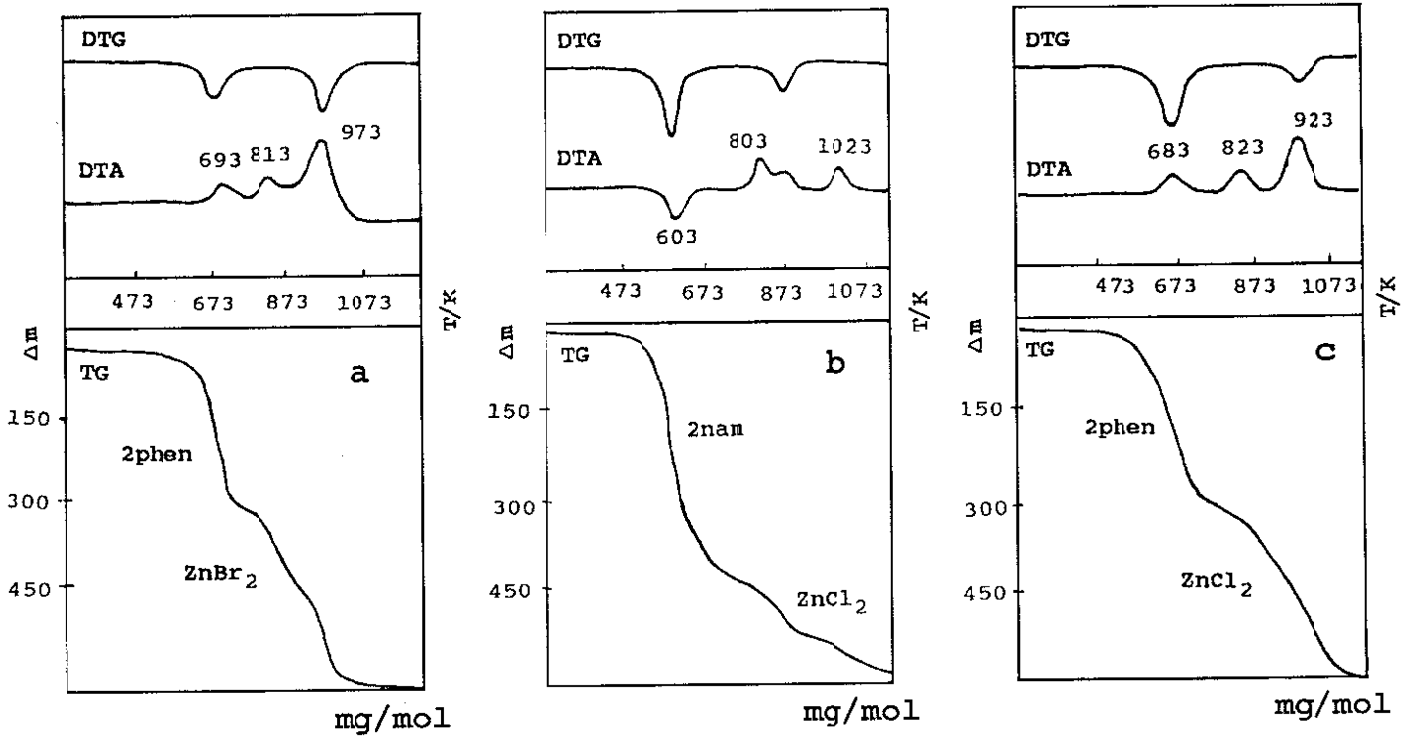

**Fig. 1** TG/DTG and DTA curves of the compound a) Zn(phen)$_2$Br$_2$, b) Zn(nam)$_2$Cl$_2$, c) Zn(phen)$_2$Cl$_2$ heated in air

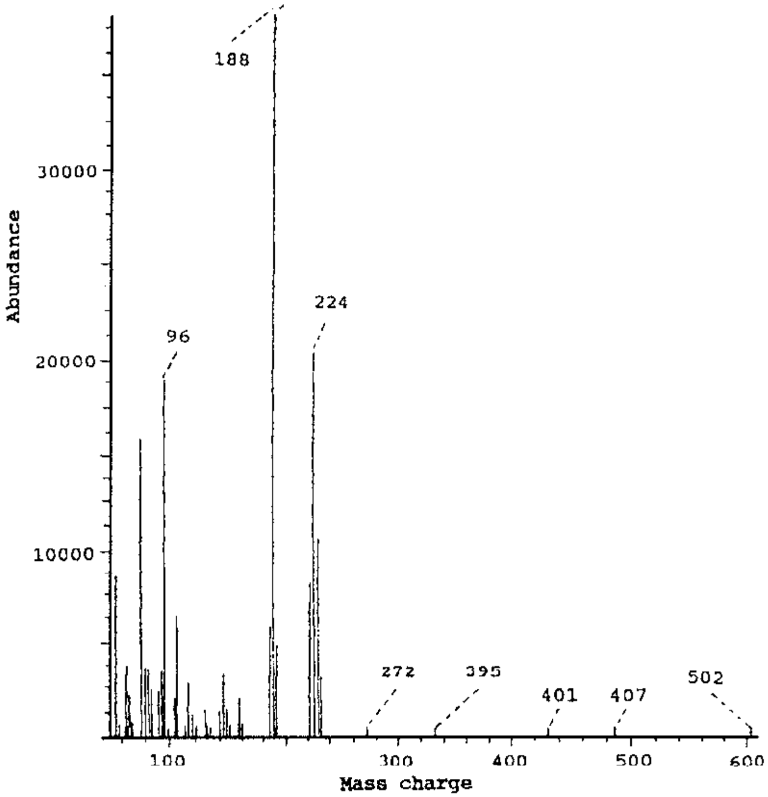

**Fig. 2a** Mass spectra of Zn(phen)$_2$Br$_2$ heated to the temperature of 473 K

The volatile ZnCl$_2$ was detected as the product of thermal decomposition by means of mass spectra ($m/z$=136) (Fig. 2b). The decomposition is accompanied by two exothermic effect, peaking on the DTA curve at 803 K and 1023 K. After the thermal decomposition the whole amount of the sample was volatilized, no solid remained.

### Zn(phen)$_2$Cl$_2$

Thermal decomposition characteristics of this compound are shown in Fig. 1c. The compound starts to decompose at 583 K as it indicated by an exothermic process peaking on the DTA curve at 683 and 823 K. The mass loss observed on the TG curve corresponds to the release of two molecules of phenazone (369.19 mg/mmol). The thermal decomposition continue by an exothermic process with maximum on the DTA curve at 923 K. As it follows from TG curve (Fig. 1c) during thermal decomposition of this compond ZnCl$_2$ is released as volatile component.

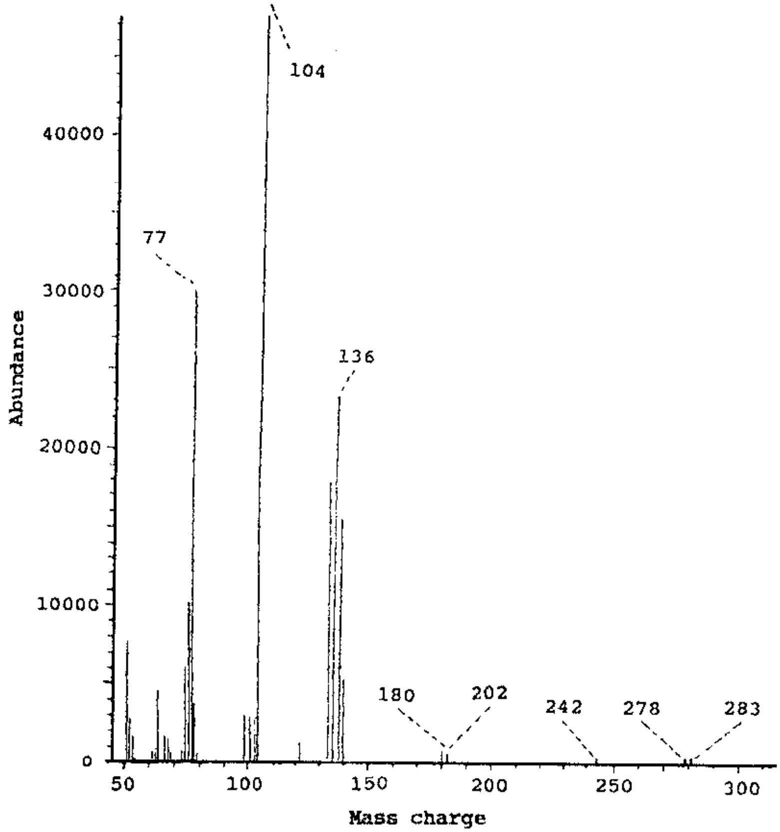

**Fig. 2b** Mass spectra of $Zn(nam)_2Cl_2$ heated to the temperature of 473 K

# Discussion and conclusions

We have demonstrated in this paper that the newly prepared compounds $Zn(phen)_2Br_2$, $Zn(nam)_2Cl_2$, $Zn(phen)_2Cl_2$ are stable in the temperature range from room temperature up to 473 K. Their thermal decomposition starts on heating in air by the release of free ligands (at 385 K phenazone and at 413 K nicotinamide). The release of nicotinamide is an endothermal process, whereas the release of phenazone ligand is an exothermal process.

Thermal stability of newly synthesized compounds increase in the following order:

| | $Zn(nam)_2Cl_2$ | < | $Zn(phen)_2Cl_2$ | < | $Zn(phen)_2Br_2$ |
|---|---|---|---|---|---|
| DTA peak: | 603 K endo | | 683 K exo | | 693 K exo |

We have observed that in the second step of the thermal decomposition the remaining inorganic part of the molecule is released from the crucible. The volatiles $ZnBr_2$ and $ZnCl_2$ were determined by mass spectrometer (for $ZnBr_2$ $m/Z=224$, for $ZnCl_2$ $m/Z=136$). It was of interest to compare the thermal behaviour of the above mentioned compounds with the thermal behaviour of the zinc complexes of the general formula $Zn(RCHXCOO)_2L_2$ [7] (where *L*-ligands represents phenazone, nicotinamide, papaverine): In the first step of the thermal decomposition of these compounds the release of organic ligands take place [7], the thermal decomposition of carboxylic anion resulting in gaseous products, such as CO, $CH_3COCH_3$ and $CH_3CH{=}CHCHO$. By comparing thermal behaviour of complex compounds and halogenacetate compounds prepared in recent years at the Institute of Inorganic Chemistry of the University of Kosice we have found a similarity in the final step of thermal behaviour of these compounds: in both cases volatile compounds of the $ZnX_2$ type have been formed, where the atom of halogen is directly bound to zinc atom [8]. The crystallographic structures of these compounds [9] confirmed this hypothesis. Therefore the mechanism of thermal decomposition of newly prepared zinc-halogenocomplex compounds is influenced by direct binding of zinc and halogen atom in the molecule.

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