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# Thermal decomposition study and biological characterization of zinc(II) 2-chlorobenzoate complexes with bioactive ligands

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**Abstract** New zinc(II) 2-chlorobenzoates of general formula $[Zn(2\text{-}ClC_6H_4COO)_2(L)_2]$ (where $L$ = caffeine—*caf*, urea—*u*, methyl-3-pyridylcarbamate—*mpc*, phenazone—*phen*, theophylline—*thp*) were synthesised and characterised by elemental analysis and IR spectroscopy. The thermal behaviour of the complexes was studied by TG/DTG and DTA methods in nitrogen and in air atmosphere. During the thermal decomposition of the studied compounds the release of organic ligands take place followed by the decomposition of 2-chlorobenzoate anion. The volatile decomposition intermediates were proved by mass spectrometry. Zinc oxide was found as the final product of the thermal decomposition performed up to 1,000 K. The antimicrobial activity of the zinc(II) complexes against various strains of bacteria, yeasts and filamentous fungi has been investigated. It was found that the prepared compounds decreased the growth of *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*, *Rhizopus oryzae* and *Microsporum gypseum*, respectively. The most resistant to all tested compounds was probiotic strain of *Lactobacillus plantarum*. The presence of zinc and ligands in the prepared compounds increased the inhibitory effect compared to sodium salt of prepared compounds and free ligands.

**Keywords** Zinc · 2-Chlorobenzoate · Thermal · Spectral properties · Bioactive ligands

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## Introduction

Zinc is necessary for normal growth and development of primates and human organism, as well as plants and microorganisms. Zinc is a relatively abundant element in biological organisms and plays an essential role in a large number of enzymatic reactions. It participates in many processes of metabolism of albuminous substances (proteins), nucleic acids, saccharides and lipides [1].

Heterocyclic compounds of zinc play important role in many biological systems, especially systems with N-donor ligands form the component of some vitamins and drugs [2]. The study of biological activity of zinc(II) carboxylates confirms their antimicrobial and anti-inflammatory effects [3, 4]. Aliphatic and aromatic carboxylates of zinc(II) with bioactive ligands, their spectral, thermal, biological properties were investigated in several works [5–9]. The thermal decomposition of aliphatic zinc(II) carboxylates, such

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as formiates, acetates, propionates and butyrates with *phen* and *thp* started with releasing of the organic ligand, then continued by the release of aldehyde or ketone [5, 6]. In the case of anhydrous zinc(II) aromatic carboxylates, such as salicylates with thiourea, *nad*, *caf* and theobromine, the thermal decomposition starts with the release of organic ligand [8]. Then, the salicylic acid is evolved. In all mentioned zinc(II) aliphatic and aromatic carboxylates ZnO was found as the final product.

Skoršepa et al. [10] studied the thermal decomposition of zinc(II) propionate, benzoate and their chloroderivative salts with thiourea. They proposed the thermal decomposition of compounds, but they did not confirm the intermediate products of the thermal decomposition.

In this article, the thermal, spectral and biological properties of new zinc(II) 2-chlorobenzoates with ligands (caffeine—*caf*, urea—*u*, methyl-3-pyridylcarbamate—*mpc*, phenazone—*phen*, theophylline—*thp*) are reported.

## Experimental

### Synthesis of the compounds

The synthesis of the compounds may be expressed by the following equations:

$$ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaCl \quad (1)$$

$$ZnCO_3 + 2(2\text{-}ClC_6H_4COOH) \rightarrow Zn(2\text{-}ClC_6H_4COO)_2 + H_2CO_3 \quad (2)$$

$$Zn(2\text{-}ClC_6H_4COO)_2 + 2L \rightarrow Zn(2\text{-}ClC_6H_4COO)_2 \cdot L_2 \quad (3)$$

where $L$ = *caf*, *u*, *nad*, *mpc*, *phen* and *thp*

For the preparation of the Zn(II) 2-chlorobenzoate complex compounds following AR grade chemicals were used: $ZnCl_2$ (Fluka), $Na_2CO_3$ (Mikrochem a.s. Pezinok), 2-chlorobenzoic acid 98% (Aldrich), *caf*, *u*, *nad*, *mpc* and *phen* (Merck).

$ZnCO_3$ was prepared by reaction of the stoichiometric amounts of $ZnCl_2$ and $Na_2CO_3$ as described in Eq. 1. Then, the ethanol solution of carboxylic acid was added to the water suspension of $ZnCO_3$ under continual stirring at 343 K and zinc(II) 2-chlorobenzoate was formed. A water solution of ligand (*caf*, *u*, *phen*) or an ethanol solution of ligand (*mpc*, *thp*) was added to the solution of zinc(II) 2-chlorobenzoate in the ratio 2:1. The reaction mixture was refluxed for 3 h, then filtered off and left to stand to crystallise at room temperature. After several days white crystals were formed. The formed Zn(II) 2-chlorobenzoate complex compounds were filtered off, washed with water and dried over silica gel. The compounds of the following formula were prepared:

$[Zn(2\text{-}ClC_6H_4COO)_2]$ (**I**) $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ (**IV**)

$[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ (**II**) $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ (**V**)

$[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ (**III**) $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2] \cdot H_2O$ (**VI**)

### Instrumentation

The infrared spectra were recorded on AVATAR 330 FTIR Thermo Nicolet spectrophotometer in the range 4,000–400 $cm^{-1}$ using KBr pellets. The content of C, H and N of the complexes were determined by means of Perkin Elmer 2400 CHN analyser and zinc content complexometrically using Complexone III as an agent and Eriochrome black as an indicator.

The thermal experiments TG/DTG, DTA were carried out up to 1,000 K by heating rate 5 K $min^{-1}$ in an air atmosphere using the NETZSCH STA 409 PC/PG thermoanalyzer (Germany) and in nitrogen atmosphere using the Perkin Elmer TGA 7 (USA). The sample (amount 20 mg) was placed in a platinum crucible. The mass spectra used for characterization of volatile intermediate products of thermal decomposition were measured on mass spectrometer MS 5988.

### Antimicrobial activity assay

The antimicrobial activity of Zn(II) 2-chlorobenzoates was evaluated by a micro-dilution method using $G^+$ bacteria *Staphylococcus aureus* CCM 3953, $G^-$ bacteria *Escherichia coli* CCM 3988 [11] . The effects of these compounds on the yeasts *Candida albicans* were determined by macro-dilution method in L-shaped tubes adapted for direct measurement of absorbance [12]. The efficiency of prepared derivatives on the growth of filamentous fungi *Rhizopus oryzae* CCM F-8284, *Alternaria alternata* CCM F-128 and *Microsporum gypseum* was observed by macro-dilution technique on Sabouraud's (dermatophytes) [13].

The antimicrobial activity of tested compounds was characterised by the $IC_{50}$ values (concentration of a derivative which in comparison to the control inhibits the growth of microorganisms to 50%) and MIC values (minimal inhibitory concentration of a derivative which inhibits microbial growth by 100%). The $IC_{50}$ and MIC values were read from toxicity curves.

The inhibitory activity was tested against $G^-$ pathogens—enterotoxigenic strain of *E. coli* O8:F4$^+$Ent$^+$ and *Salmonella enterica* Serovar Düsseldorf SA31, $G^+$ pathogen *S. aureus* SA1 and $G^+$ probiotic strain of *Lactobacillus plantarum* CCM 7102 Bacteria were cultivated as was described by Szunyogova et al. [6].

## Results and discussion

The prepared compounds are white in colour and stable in air. The results of the elemental analysis were in good agreement with theoretical values (Table 1). The solubility of the prepared compounds is changed depending on the ligand (Table 2). All prepared compounds are insoluble in $CCl_4$. The compound $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ is insoluble in polar and non-polar solvents. The other compounds are soluble in polar and also in non-polar solvents.

### Spectral behaviour

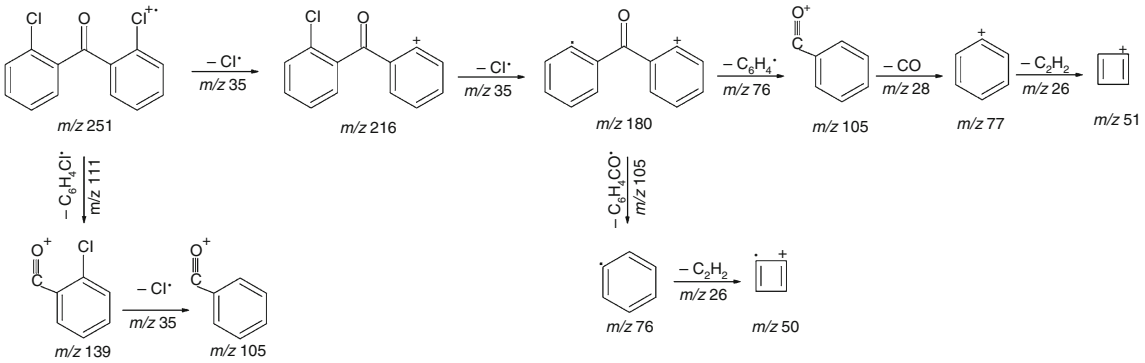
The IR spectra confirmed the presence of the characteristic absorption bands of the studied Zn(II) 2-chlorobenzoate complexes. The most characteristic absorption band $\nu$(C=N) of ligand (*caf*, *mpc*, *phen*, *thp*) in the complexes is at 1,654, 1,689, 1,641 and 1,670 $cm^{-1}$, respectively. For the (N–H) bond the stretching vibrations $\nu$(N–H) of ligand (*u*, *mpc*,*thp*) in the complexes were observed at 3,338, 3,300 and 3,379 $cm^{-1}$, respectively. The asymmetrical stretching vibrations $\nu_{as}$ of the carboxylate group were in the range 1,594–1,545 $cm^{-1}$ and symmetrical stretching vibration $\nu_s$ in the range 1,413–1,353 $cm^{-1}$. The other absorption bands are summarised in Table 3.

compounds is monodentate. This is in a good agreement with our solved crystal structure [16, 17]. The Δ value for the compounds (**III**, **IV**, **VI**) was in the range 148–164 $cm^{-1}$, so we predicted bidentate chelating coordination. It is in agreement with our solved crystal structure with methyl-3-pyridylcarbamte [18].

### Thermal behaviour

#### *[Zn(2-ClC$_6$H$_4$COO)$_2$]*

The compound $[Zn(2\text{-}ClC_6H_4COO)_2]$ (Fig. 1) is melting, which is shown on DTA curve as an endotermic effect at 523 K. In the first step of thermal decomposition in the temperature range 573–833 K $(C_6H_4Cl)_2CO$ is released (the experimental mass loss 66.65%, the theoretical mass loss 66.69%). The release of $(C_6H_4Cl)_2CO$ was also confirmed by mass spectrometry. The mass spectra in this temperature range confirmed the presence of $(C_6H_4Cl)_2CO$ (*m/z*: 251 $[C_{13}H_8OCl_2]^{+\bullet}$, 216 $[C_{13}H_8OCl]^{+}$, 180 $[C_{13}H_8O]^{+\bullet}$, 139 $[C_7H_4ClO]^{+}$, 111 $[C_6H_4Cl]^{\bullet}$, 105 $[C_6H_4CO]^{+}$, 77 $[C_6H_5]^{+}$, 76 $[C_6H_4]^{+\bullet}$, 51 $[C_4H_3]^{+}$, 50 $[C_4H_2]^{+\bullet}$). On the basis of the mass spectrum results we proposed the following fragmentation of $(C_6H_4Cl)_2CO$:




On the basis of the Δ value $[\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)]$ it is possible to predict the type of coordination of carboxylate group in the complex compounds. From the literature [14, 15], it is known that for monodentate coordination of the carboxylate group Δ value is higher than Δ value of sodium salt and for the bidentate chelating coordination the Δ value is lower than Δ value for sodium salt (Table 4).

The calculated value of Δ in prepared compounds (**I**, **II**, **V**) was in the range 185–225 $cm^{-1}$. The Δ value for sodium 2-chlorobenzoate is 183 $cm^{-1}$. According to the above mentioned criterium the carboxylate ion in these

The second step of decomposition corresponds to the releasing of $CO_2$ in the temperature range 833–933 K (the experimental mass loss 13.88%, the theoretical mass loss 11.69%). This step was accompanied by an exothermic effect at 870 K on DTA curve. The final decomposition product was ZnO (the experimental mass loss 19.47%, the theoretical mass loss 21.62%). It was confirmed by IR spectrum [$\nu$(Zn–O) 440 $cm^{-1}$] and by qualitative analysis (ZnO is dissolved in the concentrated solution of NaCl). The following mechanism is proposed for the thermal decomposition:

$$[Zn(2\text{-}ClC_6H_4COO)_2] \rightarrow (C_6H_4Cl)_2CO + CO_2 + ZnO$$

**Table 1** Analytical data of the prepared compounds

| Empirical formula | F.W. | C% | | H% | | N% | | Zn% | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $[Zn(2\text{-}ClC_6H_4COO)_2]$ | 376.53 | 44.66 | 44.50 | 2.14 | 2.09 | – | – | 17.37 | 17.92 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ | 764.92 | 47.11 | 46.52 | 3.69 | 3.63 | 14.65 | 14.90 | 8.55 | 8.31 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ | 496.65 | 38.70 | 39.10 | 3.25 | 3.17 | 11.28 | 11.15 | 13.17 | 12.59 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ | 680.83 | 49.39 | 49.40 | 3.55 | 3.62 | 8.23 | 8.25 | 9.60 | 8.37 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ | 752.99 | 57.34 | 57.13 | 4.28 | 4.29 | 7.44 | 7.66 | 8.87 | 8.15 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ | 754.86 | 45.64 | 44.74 | 3.28 | 3.40 | 15.21 | 15.28 | 8.87 | 8.70 |

**Table 2** Solubility of the prepared compounds

| Compound | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|
| | $H_2O$ | $CH_3OH$ | $C_2H_5OH$ | $(C_2H_5)_2O$ | $(CH_3)_2CO$ | $CHCl_3$ | $CCl_4$ |
| **(I)** | s.s | s.s | ins. | ins. | ins. | ins. | ins. |
| **(II)** | s.s | s | ins. | v.s. | ins. | v.s. | ins. |
| **(III)** | s | v.s. | ins. | ins. | ins. | ins. | ins. |
| **(IV)** | s.s | v.s | s.s | ins. | ins. | ins. | ins. |
| **(V)** | v.s | v.s | v.s | ins. | v.s | v.s | ins. |
| **(VI)** | ins. | ins. | ins. | ins. | ins. | ins. | ins. |

*v.s* very soluble, *s* soluble, *s.s* slightly soluble, *ins.* insoluble, $[Zn(2\text{-}ClC_6H_4COO)_2]$ **(I)**, $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ **(II)**, $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ **(III)**, $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ **(IV)**, $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ **(V)**, $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ **(VI)**

**Table 3** Characteristic absorption bands ($\nu/cm^{-1}$) of the prepared compounds in infrared spectra

| Assignement | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---|---|---|---|---|---|---|
| $\nu_{ar}$(C–H) | 3,062w | 3,056w | 3,056w | 3,066w | 3,072w | 3,009w |
| $\nu_{aliph}$(C–H) | – | 2,954w | 2,924w | 2,952w | 2,927w | 2,917w |
| $\nu$(C=O) | – | 1,701s | 1,650s | 1,731s | 1,711s | 1,714s |
| $\nu$(C=N) | – | 1,654s | – | 1,613s | 1,641s | 1,650s |
| $\nu_{as}(COO^-)$ | 1,594s | 1,552s | 1,556s | 1,545s | 1,578s | 1,562m |
| $\nu_s(COO^-)$ | 1,409s | 1,362s | 1,392s | 1,397s | 1,353m | 1,413m |
| $\Delta$ | 185 | 190 | 164 | 148 | 225 | 149 |
| $\nu(C=C)_{ar}$ | 1,578w | 1,597w | 1,574w | 1,581m | 1,598m | 1,595w |
| $\nu$(N–H) | – | – | 3,338w | 3,300w | – | 3,379m |
| $\delta(COO^-)$ | 851m | 847m | 854m | 860m | 856m | 853w |
| $\gamma(C–H)_{ar}$ | 720s | 724s | 744s | 720s | 723s | 720s |
| $\nu$(C–Cl) | 747m | 746w | 694w | 759w | 758m | 7,746w |
| $\nu$(Zn–O) | 499m | 483m | 489w | 476w | 498w | 499m |

*s* strong, *m* medium, *w* weak, *ar* aromatic, *aliph* aliphatic, $[Zn(2\text{-}ClC_6H_4COO)_2]$ **(I)**, $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ **(II)**, $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ **(III)**, $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ **(IV)**, $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ **(V)**, $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ **(VI)**

### *$[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$*

At the beginning the compound $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ melts without mass loss, which is shown on the DTA curve as an endothermic effect at 458 K (Fig. 2). Above this temperature, the release of two mole of *caf* takes place (the experimental mass loss 52.98%, the theoretical mass loss 50.77%). In the IR spectrum of solid intermediate measured up to 586 K the characteristic bands of *caf* $\nu$(C=O) at 1,704 $cm^{-1}$, $\nu$(C=N) at 1,654 $cm^{-1}$and

**Table 4** Thermal decomposition of the prepared compounds

| Compound | DTA peak/effect/K | Temperature range of decomposition/K | Products of the thermal decomposition | Mass loss/% | |
|---|---|---|---|---|---|
| | | | | Exp. | Theor. |
| $[Zn(2\text{-}ClC_6H_4COO)_2]$ | 523/melting | – | – | – | – |
| | – | 573–833 | $(C_6H_4Cl)_2CO$ | 66.65 | 66.69 |
| | 870/exo | 833–933 | $CO_2$ | 13.88 | 11.69 |
| | | $R_{933}$ | ZnO | 19.47 | 21.62 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ | 458/melting | – | – | – | – |
| | – | 478–586 | 2*caf* | 52.98 | 50.77 |
| | 591/endo | 586–730 | $(C_6H_4Cl)_2CO$ | 30.20 | 32.84 |
| | 917/exo | 730–938 | $CO_2$ | 7.92 | 5.75 |
| | | $R_{938}$ | ZnO | 8.90 | 10.64 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ | 496/endo | 426–733 | $2u + (C_6H_4Cl)_2CO$ | 73.46 | 74.75 |
| | 814/exo | 733–882 | $CO_2$ | 9.60 | 8.86 |
| | | $R_{882}$ | ZnO | 16.94 | 16.39 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ | 447/endo | 428–543 | 2*mpc* | 46.10 | 44.70 |
| | 841, 886/exo | 543–923 | $(C_6H_4Cl)_2CO + CO_2$ | 43.27 | 43.35 |
| | | $R_{923}$ | ZnO | 10.63 | 11.96 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ | 393/melting | – | – | – | – |
| | 564/endo | 463–763 | 2*phen*+ | 82.23 | 83.35 |
| | 818/exo | 763–856 | $(C_6H_4Cl)_2CO$ | 7.35 | 5.84 |
| | | $R_{856}$ | $CO_2$ | 10.42 | 10.81 |
| | | | ZnO | | |
| $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ | 353 endo | 323–383 | $H_2O$ | 2.50 | 2.38 |
| | 541/exo | 383–613 | 2*thp* | 46.84 | 47.73 |
| | 595/endo | 613–818 | $(C_6H_4Cl)_2CO$ | 33.18 | 33.27 |
| | 651,786/endo | 818–938 | $CO_2$ | 7.81 | 5.83 |
| | 925/exo | $R_{938}$ | ZnO | 9.67 | 10.79 |

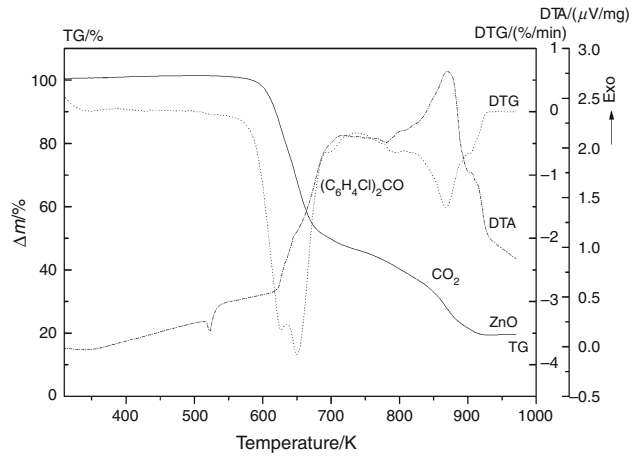



**Fig. 1** TG/DTG and DTA curves of $[Zn(2\text{-}ClC_6H_4COO)_2]$

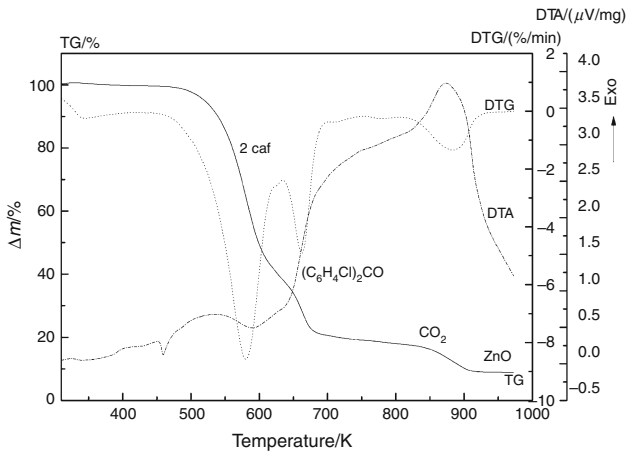
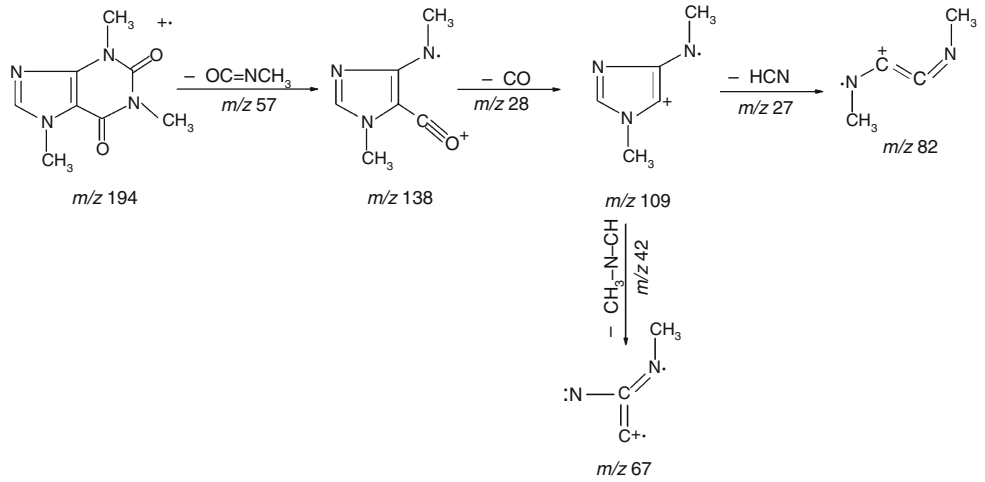



**Fig. 2** TG/DTG and DTA curves of $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$

$\nu(C\text{–}H)_{caf}$ at 2,949 $cm^{-1}$ were missing. The release of *caf* was confirmed by mass spectrometry (*m*/*z*: 194 $[C_8H_{10}N_4O_2]^{+\bullet}$, 109 $[C_5H_7N_3]^{+}$, 82 $[C_4H_6N_2]^{+\bullet}$, 67 $[C_3H_3N_2]^{+\bullet}$, 57 $[C_2H_3NO]$, 42 $[C_2H_4N]^{\bullet}$, 28 [CO]) measured up to 586 K. We proposed the following fragmentation scheme of *caf*:




Then, thermal decomposition continued with the release of $(C_6H_4Cl)_2CO$ in the temperature range 586–730 K (the experimental mass loss 30.20%, the theoretical mass loss 32.83%), which was confirmed by mass spectrum. In the third step, $CO_2$ is released in the temperature range 730–938 K (the experimental mass loss 7.92%, the theoretical mass loss 5.75%). It was accompanied by an exothermic effect at 917 K on DTA curve. ZnO is formed as the final solid product of the thermal decomposition (the experimental mass loss 8.90%, the theoretical mass loss 10.64%). The final product was confirmed by IR spectrum and qualitative analysis. The following equation for the thermal decomposition can be proposed.

$$\left[\mathrm{Zn(2\text{-}ClC_6H_4COO)_2}(caf)_2\right] \rightarrow 2caf + (C_6H_4Cl)_2CO + CO_2 + ZnO$$

*[Zn(2-ClC$_6$H$_4$COO)$_2$(u)$_2$]*

The thermal decomposition of $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ is shown on Fig. 3. The decomposition starts at 426 K with the release of two moles of *u* and $(C_6H_4Cl)_2CO$ (the experimental mass loss 73.46%, the theoretical mass loss 74.75%). The intermediate product was confirmed by IR spectra measured up to 573 K (the characteristic absorption bands *v*(N–H) at 3,456 $cm^{-1}$, 3,338 $cm^{-1}$; *v*(C=O) at 1,650 $cm^{-1}$ for *u* were missing). Mass spectrum measured up to 573 K confirmed the presence of *u* (*m/z*: 60 $[CH_4N_2O]^{+\bullet}$, 44 $[CH_2NO]^+$, 28 [CO], 16 $[NH_2]^+$) and up to 733 K $(C_6H_4Cl)_2CO$. The fragmentation of *u* is in agreement with the results of Krajníková [19]. The $(C_6H_4Cl)_2CO$ fragmentation is the same as in the case of compound (**I**). In the second step of thermal decomposition in the temperature range 733–882 K the $CO_2$ was released (the experimental mass loss 9.60%, the theoretical mass loss 8.86%). It is followed by an exothermic effect at 814 K. The final solid product of the thermal decomposition is ZnO (the experimental mass loss 16.94%, the theoretical mass loss 16.39%). The following mechanism is proposed for the thermal decomposition:

$$\left[\mathrm{Zn(2\text{-}ClC_6H_4COO)_2}(u)_2\right] \rightarrow 2u + (C_6H_4Cl)_2CO + CO_2 + ZnO$$

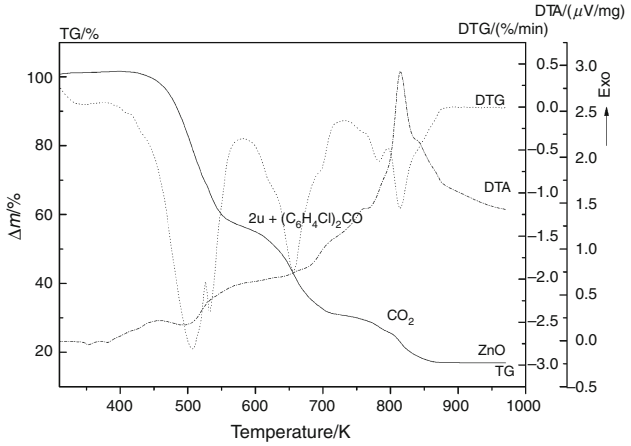
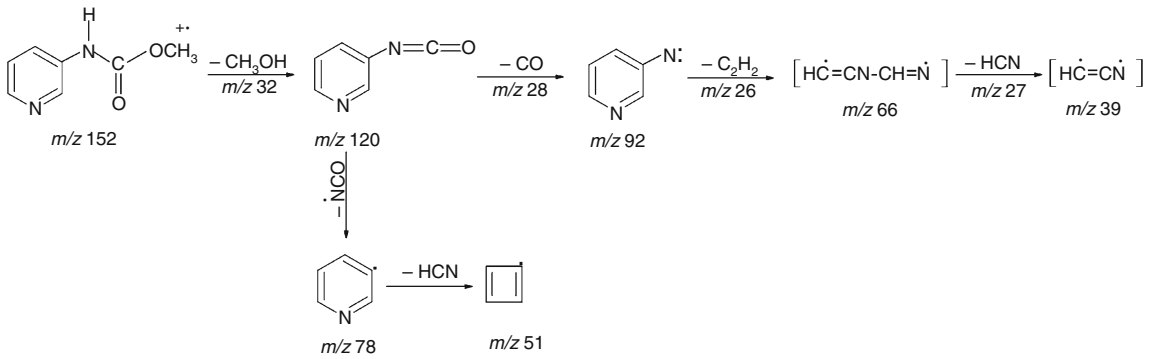



**Fig. 3** TG/DTG and DTA curves of $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$

*[Zn(2-ClC$_6$H$_4$COO)$_2$(mpc)$_2$]*

As it follows from Fig. 4, the compound starts to decompose at 428 K by evolving of two mole of *mpc* (the experimental mass loss 46.10%, the theoretical mass loss 44.70%). The IR spectrum of solid intermediate (*mpc*) measured at 543 K showed that characteristic absorption bands of *mpc* [*v*(C–H) 2,952 $cm^{-1}$, *v*(C=O) 1,736 $cm^{-1}$, *v*(C=N) 1,591 $cm^{-1}$ and *v*(N–H) 3,449 $cm^{-1}$] were missing. Mass spectrum measured up to 543 K confirmed the release of *mpc* (*m/z*: 152 $[C_7H_8N_2O_2]^{+\bullet}$, 120 $[C_6H_4N_2O]$, 92 $[C_5H_4N_2]$, 78 $[C_5H_4N]^{\bullet}$, 66 $[C_3H_2N_2]$, 51 $[C_4H_3]^{\bullet}$, 39 $[C_2HN]$, 28 [CO]) and $(C_6H_4Cl)_2CO$. On the basis of the mass spectrum results we proposed the following fragmentation of *mpc*:



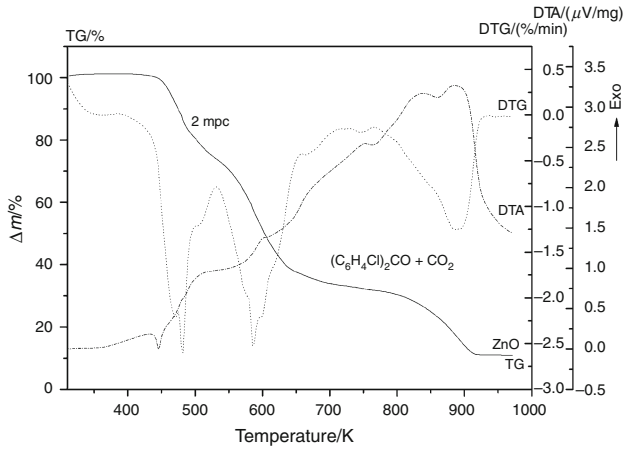




**Fig. 4** TG/DTG and DTA curves of $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$

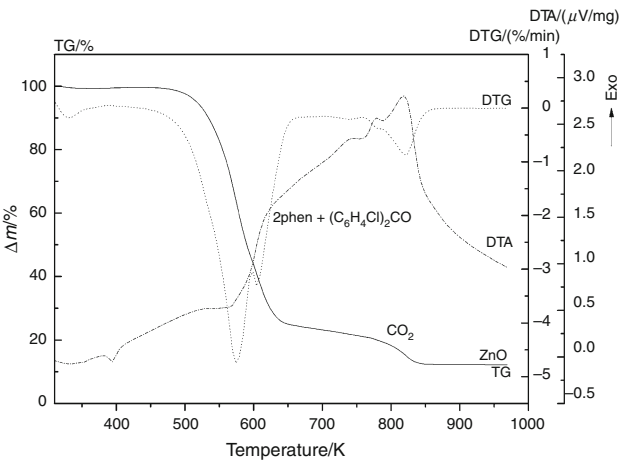


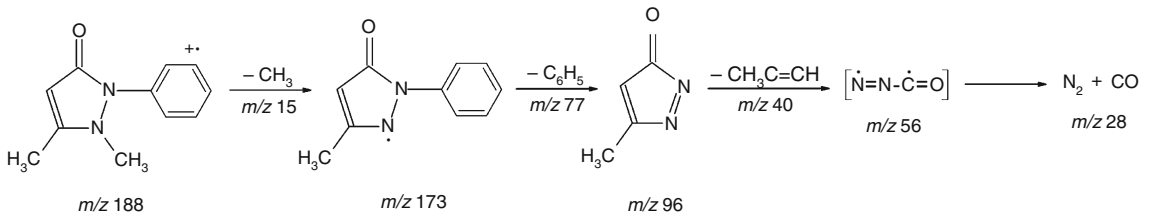

**Fig. 5** TG/DTG and DTA curves of $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$

Then, the thermal decomposition continued by the evolution of $(C_6H_4Cl)_2CO$ and $CO_2$ in the temperature range 543–923 K (the experimental mass loss 43.27%, the theoretical mass loss 43.35%). The final solid product of thermal decomposition is ZnO (the experimental mass loss 10.63%, the theoretical mass loss 11.96%). The following mechanism is proposed for the thermal decomposition:

$$\left[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2\right] \rightarrow 2mpc + CO_2 + (C_6H_4Cl)_2CO + ZnO$$

*[Zn(2-ClC$_6$H$_4$COO)$_2$(phen)$_2$]*

At the beginning the compound melts without mass loss, which is shown on the DTA curve as an endothermic effect at 393 K (Fig. 5). Above this temperature, gradual mass loss corresponding to the release of two moles of *phen* and $(C_6H_4Cl)_2CO$ is observed (the experimental mass loss 82.23%, the theoretical mass loss 83.35%). In the solid intermediate, the characteristic IR absorption bands at 593 K of *phen* ($\nu$(C–H)$_{aliph}$ at 2,936 cm$^{-1}$, $\nu$(C=O) at 1,711 cm$^{-1}$, $\nu$(C=N) at 1,616 cm$^{-1}$) were missing. Mass spectrum measured up to 593 K confirmed the presence of *phen* (*m/z*: 188 $[C_{11}H_{13}N_2O]^{+\bullet}$, 173 $[C_{10}H_{10}N_2O]^{\bullet}$, 96 $[C_4H_4N_2O]$, 77 $[C_6H_5]^{\bullet}$, 56 $[CN_2O]$, 40 $[C_3H_4]^{\bullet}$, 28 $[N_2 + CO]$) and $(C_6H_4Cl)_2CO$. The proposed fragmentation of *phen* is shown on the following scheme:

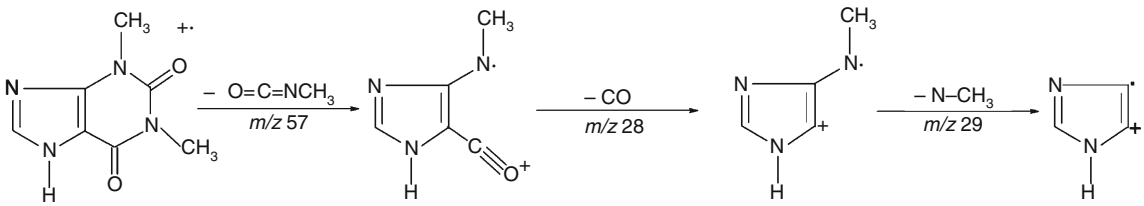


The fragmentation of $(C_6H_4Cl)_2CO$ is the same as in the case of compound (**I**). Then, $CO_2$ was released in the temperature range 763–856 K (the experimental mass loss 7.35%, the theoretical mass loss 5.84%). It was confirmed by an exothermic effect at 818 K on DTA curve. The final solid product of the thermal decomposition was ZnO (the experimental mass loss 10.42%, theoretical mass loss 10.81%). The following decomposition reaction is proposed for the decomposition process:

$$\left[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2\right] \rightarrow 2phen + CO_2 + (C_6H_4Cl)_2CO + ZnO$$

*[Zn(2-ClC$_6$H$_4$COO)$_2$(thp)$_2$]·H$_2$O*

As it can be seen from Fig. 6 the thermal decomposition starts with dehydration at 328 K (the experimental mass loss 2.50%, the theoretical mass loss 2.38%). Then in the temperature range 383–613 K two mole of *thp* are released (the experimental mass loss 46.84%, the theoretical mass loss 47.73%). In the solid intermediate at 613 K the IR absorption bands of *thp* were missing [$\nu$(C–H) at 2,917 cm$^{-1}$ $\nu$(C=O) at 1,714 cm$^{-1}$, $\nu$(C=N) at 1,670 cm$^{-1}$ and $\nu$(N–H) at 3,379 cm$^{-1}$). Mass spectrum measured up to 613 K confirmed the presence of *thp* (*m/z*: 180 $[C_7H_8N_3O_2]^{+\bullet}$, 95 $[C_4H_5N_3]^{+\bullet}$, 66 $[C_3H_2N_2]^{+\bullet}$, 57 $[C_2H_3NO]$, 28 [CO]), which fragmentation is shown on the following scheme:




In the temperature range 613–818 K $(C_6H_4Cl)_2CO$ is lost (the experimental mass loss 33.18%, the theoretical mass loss 33.27%). The thermal decomposition continued in the temperature range 818–938 K with the release of $CO_2$ (the experimental mass loss 7.81%, the theoretical mass loss 5.83%). The final solid product of thermal decomposition is ZnO (the experimental mass loss 9.67%, the theoretical mass loss 10.79%). The thermal decomposition is expressed by the following equation:

$$\left[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2\right] \cdot H_2O \rightarrow 2thp + (C_6H_4Cl)_2CO + CO_2 + ZnO$$

Antimicrobial activity

The results of antimicrobial activity are listed in Table 5. The free 2-chlorobenzoic acid and all ligands (*caf*, *u*, *phen*, *mpc*, *thp*) did not influence the growth of model bacteria, yeasts and filamentous fungi ($IC_{50} > 3$ mmol dm$^{-3}$) expected *caf* and *thp* on *M. gypseum*. The sensitivity of $G^+$ bacteria to the tested compounds **(I–VII)** was higher to the $G^-$ bacteria. It corresponds with the literature data [13]. The strongest inhibition effect against bacteria *S. aureus* was recorded for compounds [Zn(2-Clbenz)$_2$], [Zn(2-Clbenz)$_2$(*u*)$_2$], [Zn(2-Clbenz)$_2$(*nad*)$_2$], [Zn(2-Clbenz)$_2$(*thp*)$_2$]·H$_2$O,

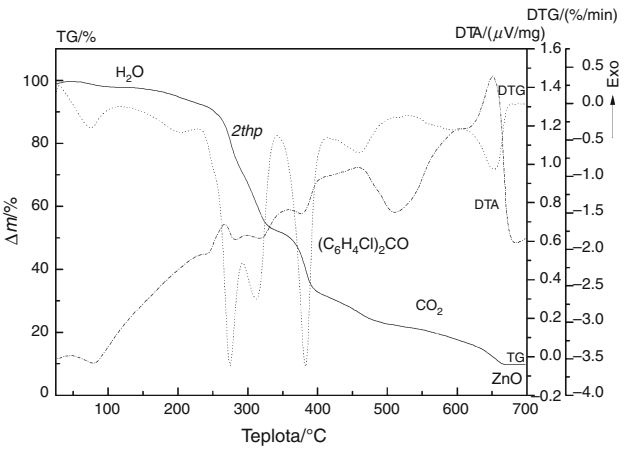



**Fig. 6** TG/DTG and DTA curves of [Zn(2-ClC$_6$H$_4$COO)$_2$(*thp*)$_2$]·H$_2$O

[Zn(2-Clbenz)$_2$(*phen*)$_2$] ($IC_{50} < 1$ mmol dm$^{-3}$), [Zn(2-Clbenz)$_2$(*caf*)$_2$] ($IC_{50} = 1.1$ mmol dm$^{-3}$), [Zn(2-Clbenz)$_2$(*mpc*)$_2$] ($IC_{50} = 1.2$ mmol dm$^{-3}$). The 100% inhibition of growth of *E. coli* was determined in the presence of [Zn(2-Clbenz)$_2$] ($IC_{50} = 2.3$ mmol dm$^{-3}$; MIC $> 3$ mmol dm$^{-3}$) and [Zn(2-Clbenz)$_2$(*thp*)$_2$]·H$_2$O ($IC_{50} = 2.1$ mmol dm$^{-3}$; MIC $> 3$ mmol dm$^{-3}$) with bacteristatic effect. From all the studied compounds the 100% inhibition with fatalness effect on the cells of yeasts *C. parapsilosis* was confirmed for compound [Zn(2-Clbenz)$_2$(*thp*)$_2$]·H$_2$O ($IC_{50} = 2.2$ mmol dm$^{-3}$; MIC $> 3$ mmol dm$^{-3}$). The antifungal activity of studied compounds against *R. oryzae* was shown for compound [Zn(2-Clbenz)$_2$(*caf*)$_2$] ($IC_{50} = 1.9$ mmol dm$^{-3}$; MIC $> 3$ mmol dm$^{-3}$). None of the studied compounds inhibited the growth of filamentous fungi *A. alternata* ($IC_{50} > 3$ mmol dm$^{-3}$). However, the compounds [Zn

**Table 5** Antimicrobial activity of Zn(II) complexes characterised by numerical values of $IC_{50}$ and MIC (mmol $L^{-1}$)

| Compound | Bacteria | | | | Yeasts | | Filamentous fungi | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *S. aureus* | | *E. coli* | | *C. parapsilosis* | | *R. oryzae* | | *A. alternata* | | *M. gypseum* | |
| | $IC_{50}$ | MIC | $IC_{50}$ | MIC | $IC_{50}$ | MIC | $IC_{50}$ | MIC | $IC_{50}$ | MIC | $IC_{50}$ | MIC |
| $[Zn(2\text{-}ClC_6H_4COO)_2]$ | <1 | 3[b] | 2.3 | >3[a] | 2.3 | >3[a] | >3 | >3 | >3 | >3 | >3 | >3 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ | 1.1 | 3[b] | 2.9 | >3 | 2.1 | >3 | 1.9 | >3 | >3 | >3 | 0.3 | 0.5[b] |
| $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ | <1 | 3[a] | >3 | >3 | 2.2 | >3[a] | >3 | >3 | >3 | >3 | 2 | 3[a] |
| $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ | 1.2 | 3[b] | >3 | >3 | 2.6 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ | <1 | >3 | >3 | >3 | 2.2 | >3[a] | >3 | >3 | >3 | >3 | >3 | >3 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ | <1 | 3[b] | 2.1 | >3[a] | 2.2 | 3[b] | >3 | >3 | >3 | >3 | 0.9 | 3[a] |
| $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ | <1 | 3[a] | 2.6 | >3 | 1.9 | >3[a] | >3 | >3 | >3 | >3 | >3 | >3 |
| $2\text{-}ClC_6H_4COOH$ | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| Caffeine (*caf*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | <1 | 3[a] |
| Urea (*u*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| Nicotinamide (*nad*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| Methyl-3-pyridylcarbamate (*mpc*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| Phenazone (*phen*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 |
| Theophylline (*thp*) | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | >3 | 2.2 | 3[a] |

[a] Microbistatical effect

[b] Microbicidal effect

**Table 6** The antimicrobial activity of tested Zn(II) complex compounds, their natrium salts and ligands against $G^-$ pathogens expressed as a difference between viable counts ($log_{10}$ cfu. $ml^{-1}$ ± sd) of control and respective compound (Δlog) ($n = 3$)

| Compound | *E. coli* | | *S. düsseldorf* | |
|---|---|---|---|---|
| | log ± sd | Δlog | log ± sd | Δlog |
| Control | 8.80 ± 0.06 | – | 9.28 ± 0.01 | – |
| $[Zn(2\text{-}ClC_6H_4COO)_2]$ | 4.29 ± 0.29 | 4.52 | 5.49 ± 0.08 | 3.79 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ | 4.60 ± 0.60 | 4.20 | 4.66 ± 0.06 | 4.62 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ | 6.22 ± 0.18 | 2.58 | 6.21 ± 0.20 | 3.07 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ | 4.21 ± 0.10 | 4.60 | 4.31 ± 0.11 | 4.97 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ | 4.99 ± 0.21 | 3.81 | 4.55 ± 0.17 | 4.73 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ | 4.02 ± 0.02 | 4.78 | 4.10 ± 0.10 | 5.18 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ | 4.96 ± 0.16 | 3.85 | 4.70 ± 0.12 | 4.58 |
| Caffeine (*caf*) | 8.08 ± 0.25 | 0.73 | 8.20 ± 0.02 | 1.08 |
| Urea (*u*) | 8.60 ± 0.00 | 0.20 | 8.79 ± 0.07 | 0.48 |
| Nicotinamide (*nad*) | 8.35 ± 0.09 | 0.46 | 8.79 ± 0.11 | 0.48 |
| Metyl-3-pyridylcarbamate (*mpc*) | 8.29 ± 0.05 | 0.52 | 8.55 ± 0.09 | 0.73 |
| Phenazone (*phen*) | 8.41 ± 0.07 | 0.40 | 8.55 ± 0.17 | 0.72 |
| Theophyline (*thp*) | 6.96 ± 0.33 | 1.84 | 8.37 ± 0.22 | 0.91 |
| $Na(2\text{-}ClC_6H_4COO)$ | 7.98 ± 0.10 | 0.82 | 8.56 ± 0.16 | 0.71 |
| $[Zn(3\text{-}ClC_6H_4COO)_2]\cdot 2H_2O$ | 0.43 ± 0.61 | 8.37 | 0.53 ± 0.75 | 8.74 |
| $[Zn(C_6H_5COO)_2]$ | 5.14 ± 0.16 | 3.67 | 4.06 ± 0.75 | 5.22 |
| $[Zn(C_6H_5COO)_2(caf)_2]$ | 4.28 ± 0.04 | 4.52 | 5.88 ± 0.06 | 3.40 |
| $Na(C_6H_5COO)$ | 7.54 ± 0.13 | 1.26 | 7.21 ± 0.21 | 2.07 |

$(2\text{-}Clbenz)_2(caf)_2]$, $[Zn(2\text{-}Clbenz)_2(thp)_2]\cdot H_2O$ has shown antifungal activity against *M. gypseum* ($IC_{50} = 0.3$ and 0.9 mmol $dm^{-3}$).

The results of biological studies against pathogens ($G^-$, $G^+$) in the concentration 0.01 and 0.02 M are presented in Tables 6, 7. More studies confirmed that this

**Table 7** The antimicrobial activity of tested Zn(II) complex compounds, their natrium salts and ligands against $G^+$ bacteria expressed as a difference between viable counts ($\log_{10}$ cfu. $ml^{-1} \pm$ sd) of control and respective compound (Δlog) ($n = 3$)

| Compound | *S. aureus* | | *L. plantarum* | |
|---|---|---|---|---|
| | Log ± sd | Δlog | Log ± sd | Δlog |
| Control | 8.58 ± 0.10 | – | 9.12 ± 0.04 | – |
| $[Zn(2\text{-}ClC_6H_4COO)_2]$ | 5.42 ± 0.15 | 3.16 | 8.47 ± 0.29 | 0.65 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2]$ | 4.27 ± 0.07 | 4.31 | 8.33 ± 0.50 | 0.80 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(u)_2]$ | 6.64 ± 0.06 | 1.94 | 8.74 ± 0.21 | 0.39 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2]$ | 4.36 ± 0.15 | 4.22 | 8.60 ± 0.28 | 0.52 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2]$ | 5.47 ± 0.13 | 3.11 | 8.60 ± 0.28 | 0.52 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2]\cdot H_2O$ | 5.45 ± 0.07 | 3.13 | 8.65 ± 0.18 | 0.47 |
| $[Zn(2\text{-}ClC_6H_4COO)_2(nad)_2]$ | 4.08 ± 0.08 | 4.50 | 8.58 ± 0.65 | 0.54 |
| Caffeine (*caf*) | 7.71 ± 0.20 | 0.87 | 8.48 ± 0.40 | 0.64 |
| Urea (*u*) | 8.29 ± 0.05 | 0.29 | 8.57 ± 0.15 | 0.56 |
| Nicotinamide (*nad*) | 7.55 ± 0.09 | 1.03 | 8.17 ± 0.01 | 0.96 |
| Metyl-3-pyridylcarbamate (*mpc*) | 8.27 ± 0.07 | 0.31 | 8.94 ± 0.11 | 0.19 |
| Phenazone (*phen*) | 8.08 ± 0.08 | 0.50 | 8.53 ± 0.19 | 0.59 |
| Theophylline (*thp*) | 8.08 ± 0.18 | 0.49 | 9.06 ± 0.02 | 0.06 |
| $Na(2\text{-}ClC_6H_4COO)$ | 7.68 ± 0.07 | 0.90 | 8.31 ± 0.13 | 0.82 |
| $[Zn(3\text{-}ClC_6H_4COO)_2]\cdot 2H_2O$ | 3.09 ± 0.09 | 5.49 | 6.03 ± 0.27 | 3.09 |
| $[Zn(C_6H_5COO)_2]$ | 4.62 ± 0.28 | 3.96 | 5.87 ± 0.14 | 3.25 |
| $[Zn(C_6H_5COO)_2(caf)_2]$ | 5.43 ± 0.17 | 3.15 | 8.16 ± 0.57 | 0.97 |
| $Na(C_6H_5COO)$ | 7.65 ± 0.17 | 0.93 | 8.86 ± 0.07 | 0.26 |

concentration of zinc possess antibacterial properties [6, 20]. The strongest inhibitive effect on all tested pathogens has shown compound $[Zn(3\text{-}ClC_6H_4COO)_2]\cdot 2H_2O$, which more or less completely inhibited the growth of *E. coli* by 8.37 log, *Salmonella düsseldorf* by 8.74 log and the growth of *S. aureus* by 5.5 log. The strongest effect against pathogens *E. coli* and *S. düsseldorf* from 2-chlorobenzoates was noted in $[Zn(2\text{-}Clbenz)_2(thp)_2]\cdot H_2O$ ($\Delta\log = 4.78$; 5.18), where *thp* can potentiate the inhibitive activity of whole compound. Similar results were achieved in previous studies performed with Zn(II) aliphatic carboxylates [6]. This is also supported by the results received from the testing of free ligands (**IX**–**XIV**), where one of the highest inhibition action against *E. coli* was noted by *thp* ($\Delta\log = 1.84$). On the other hand, *u* had only weak effect on the growth of all tested bacteria. It is well known that some bacteria use *u* as a nitrogen source for their metabolism [20]. Very similar results were received with *nad* (**XI**) which is the growth factor usually required by bacteria for the synthesis of NAD and NADP [21]. The $G^+$ bacteria were inhibited only weakly, but $G^-$ bacteria were more sensitive to $C_6H_5COO^-$ (*E. coli* were inhibited by 1.26 log and *S. düsseldorf* by 2.07 log). Received results are in agreement with studies on Zn(II) aliphatic carboxylates [6, 20].

## Conclusions

The thermal decomposition of the prepared compounds is a multistep process. During the thermal decomposition of the prepared compounds the organic ligand, bis(2-chlorophenyl)ketone and carbon dioxide were evolved. The final solid product of the thermal decomposition heated up to 1,000 K was zinc oxide in all studied compounds.

The thermal stability of studied compounds decreases in the following order:

$$\underset{573\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2\right]} > \underset{478\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2(caf)_2\right]} > \underset{463\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2(phen)_2\right]} >$$

$$> \underset{428\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2(mpc)_2\right]} > \underset{426\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2(u)_2\right]} > \underset{383\ \mathrm{K}}{\left[Zn(2\text{-}ClC_6H_4COO)_2(thp)_2\right]}$$

On the basis of measured IR spectra of the prepared compounds we assume the monodentate coordination of carboxylate group in the prepared compounds, which was confirmed by the solved structures [16, 17]. The compounds with *u*, *mpc* and *thp* have bidentate coordination.

The biological studies show that the free ligands, acids (benzoic, 2-3-chlorobenzoic) and their sodium salts did not infuence the growth of the bacteria. The presence of zinc and ligands in the prepared compounds increased the inhibitory effect.

The antimicrobial effect of the studied compounds against *E. coli*, *S. düsseldorf* and *S. aureus* is increased in the following order:

$[Zn(2\text{-}ClC_6H_4COO)_2(u)_2] < [Zn(C_6H_5COO)_2] < [Zn(2\text{-}Cl\ C_6H_4COO)_2(L)_2] < [Zn(3\text{-}ClC_6H_4COO)_2]\cdot H_2O$. The inhibition activity on filamentous fungi is lower than the antimicrobial effect on model bacteria and yeasts. In the case of *L. plantarum* the highhest inhibitory activity was found only at $[Zn(3\text{-}ClC_6H_4COO)_2]\cdot H_2O$ and $[Zn(C_6H_5COO)_2]$.

## References


1. Liljas A, Kannan KK, Bergsten PC, Waara I, Fridborg K, Strandberg B, Caribom V, Jarup L, Lovgren S, Petef M. Crystal structure of human carbonic anhydrase C. Nature New Biol. 1972;235:131–7.
2. Icbudak H, Heren Z, Ali Kose D, Necefoglu H. Bis(nicotinamide) and bis(*N*,*N*-diethyl nicotinamide)*p*-hydroxybenzoate complexes of Ni(II), Cu(II) and Zn(II) spectrothermal studies. J Therm Anal Calorim. 2004;76:837–51.
3. Martindale W. The extra pharmacopoeia. 30th ed. London: Pharmaceutical Press; 1993.
4. Sorrenson JRJ, Sodberg LSF, Chang LW, Willingtham WM, Baher ML, Barnett JB, Salari H, Bond K. Copper-, iron-, manganase- and zinc-3,5-diisopropylsalicylate complexes increase survival of gamma-irradiated mice. Eur J Med Chem. 1993;28:221–9.
5. Szunyogová E, Győryová K, Hudecová D, Piknová L, Chomič J, Vargová Z. Thermal, spectral and biological properties of Zn(II) complex compounds with phenazone. J Therm Anal Calorim. 2007;88:219–23.
6. Szunyogová E, Mudroňová D, Győryová K, Nemcová R, Kovářová J, Piknová-Findoráková L. The physicochemical and biological properties of zinc(II) complexes. J Therm Anal Calorim. 2007;88:355–61.
7. Köse DA, Necefoglu H, Sahim O, Büyükgüngör O. Synthesis, structural, spectroscopic characterization, and structural comparison of 3-hydroxybenzoate and nicotinamide/*N*,*N*-diethylnicotinamide mixed ligand complexes with Zn(II). J Therm Anal Calorim. 2011;. doi:10.1007/s1097301121340.
8. Chomič J, Győryová K, Szunyogová E, Kovářová J. Thermal study of zinc(II) salicylate complex compounds with bioactive ligands. J Therm Anal Calorim. 2004;76:33–41.
9. Refat MS, Mohamed GG, Farias RF, Powell AK, El-Garib MS, El-Korashy SA, Hussien MA. Spectroscopic, thermal and kinetic studies of coordination compounds of Zn(II), Cd(II) and Hg(II) with norfloxacin. J Therm Anal Calorim. 2010;102:225–32.
10. Skoršepa J, Godočíková E, Černák J. Comparison on thermal decomposition of propionate, benzoate and their chloroderivative salts of Zn(II). J Therm Anal Calorim. 2004;75:773–80.
11. Jantová S, Hudecová D, Stankovský Š, Špirková K, Ružeková Ľ. Antibacterial effect of substituted 4-quinazolylhydrazines and their arylhydrazones determined by a modified microdilution method. Folia Microbiol. 1995;40:611–4.
12. Dudová B, Hudecová D, Pokorný R, Mikulášová M, Palicová M, Segľa P, Melník M. Copper complexes with bioactive ligands. Folia Microbiol. 2001;46:379–84.
13. Hudecová D, Jantová S, Melník M, Uher M. New azidometalkojates and their biological activity. Folia Microbiol. 1996;41:473–6.
14. Nakamoto K. Infrared spectra of inorganic and coordination compounds. 5th ed. New York: Wiley; 1997.
15. Lewandowski W, Kalinowska M, Lewandowska H. The influence of metals on the electronic system of biologically important ligands. Spectroscopic study of benzoates, salicylates, nicotinates and isoorotates. Review. J Inorg Biochem. 2005;99:1407–23.
16. Nakacho Y, Misawa T, Fujiwara T, Wakahara A. The crystal and molecular structure of zinc complex of 2-chlorobenzoic acid. The crystal and molecular structure of bis(2-chlorobenzoato)zinc(II). Bull Chem Soc Jap. 1976;49:58–61.
17. Maroszová J, Findoráková L, Győryová K, Koman M, Melník M. Bis(2-chlorobenzoato-κO)bis(phenazone-κO)-zinc(II)0.612-hydrate. Acta Cryst. 2007;E63:1406–7.
18. Maroszová J, Findoráková L, Győryová K, Moncoľ J, Melník M. Bis(2-chlorobenzoato-κ2O, O′)bis[methyl-*N*-(pyridyl)carbamato-κ*N*]zinc(II). Acta Cryst. 2007;E63:1520.
19. Krajníková A, Győryová K, Hudecová D, Kovářová J, Vargová Z. Thermal decomposition and antimicrobial activity of zinc(II) 2-bromobenzoates with organic ligands. J Therm Anal Calorim. 2011;. doi:10.1007/s10973-010-1161-6.
20. Nancib A, Nancib N, Meziane-Cherif D, Boubendir A, Fick M, Boudrand J. Joint effect of nitrogen sources and B vitamin supplementation of date juice on lactic acid production by *Lactobacillus casei* subsp. *rhamnosus*. Biosource Technol. 2005;96:63–7.
21. Wolin J. Bacterial metabolism. In: Burrows W, editor. Textbook of microbiology. Washington: W.B. Saunders Company; 1973.