J Therm Anal Calorim (2011) 105:451–460
DOI 10.1007/s10973-010-1161-6

Thermal decomposition and antimicrobial activity of zinc(II) 2-bromobenzoates with organic ligands

Annamária Krajníková · Katarína Győryová · Daniela Hudecová · Jana Kovářová · Zuzana Vargová

ESTAC2010 Conference Special Issue

Abstract New zinc(II) 2-bromobenzoate complex compounds with general formula $Zn(2\text{-}BrC_6H_4COO)_2 \cdot nL \cdot xH_2O$ (where L = urea, nicotinamide, *N*-methylnicotinamide, *N,N*-diethylnicotinamide, isonicotinamide, phenazone $n = 0–2$, $x = 0–2$) were prepared and characterized by elemental analysis, IR spectroscopy and thermal analysis. The thermal decomposition of hydrated compounds started with dehydration process. During the thermal decomposition organic ligand, carbon dioxide and bis(2-bromophenyl)ketone were evolved. The solid intermediates and volatile products of thermal decomposition were proved by IR spectroscopy and mass spectrometry. The final solid product of the thermal decomposition heated up to 1073 K was zinc oxide. Antimicrobial activity of the prepared compounds was tested against various strains of bacteria, yeasts and filamentous fungi (*E. coli, S. aureus, C. albicans, R. oryzae, A. alternate* and *M. gypseum*). It was found that the selected bacteria were more sensitive to the studied zinc(II) complex compounds than the yeast and the filamentous fungi.

Keywords Zinc 2-bromobenzoate · Spectral properties · Thermal behaviour · Biological activity

A. Krajníková (✉) · K. Győryová · Z. Vargová
Institute of Chemistry, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovak Republic
e-mail: annamaria.erdelyiova@gmail.com

D. Hudecová
Department of Biochemistry and Microbiology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

J. Kovářová
Institute of Macromolecular Chemistry, AV CR, Heyrovského nám. 2, 162 06 Prague, Czech Republic

Introduction

Zinc is found in numerous essential enzymes which catalyze the metabolic conversion or degradation of proteins, nucleic acid, lipids and other important bioorganic compounds. Other functions are in structural stabilization of insulin, of hormone complexes or of transcription-regulating factors for the transfer of genetic information ('zinc fingers') [1]. Zinc is used in the prevention and therapy of many illnesses as a component of drugs and biopreparations [2]. It may be used in treatments of acrodermatitis enteropathica, gastrointestinal disorders, infertility, in the prevention of sickle-cell disease and other diseases [3]. Some aromatic carboxylic acids (e.g. benzoic acid, salicylic acid) are known to have antimicrobial properties. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases [4]. The synthesis and investigation of physicochemical properties and biological activity of metal carboxylate complexes are of increasing interest [5–7]. Köse [8] studied the spectral and magnetic properties of mixed-ligand *m*-hydroxybenzoate complexes of Zn(II), Co(II), Ni(II) and Cu(II) with nicotinamide. The crystal structures and spectroscopic properties of copper(II) chloroacetates with isonicotinamide, *N*-methylnicotinamide and *N,N*-diethylnicotinamide were studied by Moncol et al. [9]. Mojumdar et al. [10] studied the thermal properties of Cu(II) and Mg(II) carboxylates with *N*-donor heterocyclic ligands and proposed their structure by means of spectral analyses. Several 2-bromobenzoatocopper(II) complexes were synthesised and their spectral, structural and magnetic properties were investigated [11, 12]. In our previous works we described the preparation, thermal, spectral and biological properties of aliphatic zinc(II) carboxylates [13–15], salicylates and halogenosalicylates [16, 17] and

benzoates [18, 19]. It was found that the thermal decomposition of zinc(II) benzoate complexes with urea and caffeine starts with the release of organic ligand, which is followed by the release of carbon dioxide and diphenylketone. Carboxylato- and halogenocarboxylatozinc(II) complexes inhibited photosynthetic electron transport in spinach chloroplasts and in green alga *Chlorella vulgaris* [20]. The structural properties of zinc(II) 2-bromobenzoate and its complexes with *N*-methylnicotinamide, methyl-3-pyridylcarbamate, *N,N*-diethylnicotinamide and nicotinamide were published earlier [21–24]. In this paper the spectral, thermal and biological properties 2-bromobenzoatozinc(II) complexes with organic ligand are reported.

Experimental

Synthesis of the compounds

These A.R. grade chemicals were used for the preparation of the studied compounds: $ZnCl_2$ (Fluka, Germany), Na_2CO_3 (Mikrochem a.s., Slovakia), 2-bromobenzoic acid 97% (Aldrich, Germany), urea, *N*-methylnicotinamide, nicotinamide, isonicotinamide, *N,N*-diethylnicotinamide and phenazone (Merck, Germany).

The following compounds were prepared: $Zn(2\text{-}Brbenz)_2$ (**I**), $Zn(2\text{-}Brbenz)_2(u)_2$ (**II**), $Zn_2(2\text{-}Brbenz)_4(mnad)_2$ (**III**), $Zn(2\text{-}Brbenz)_2(inad)_2{\cdot}H_2O$ (**IV**), $Zn(2\text{-}Brbenz)_2(denad)_2{\cdot}2H_2O$ (**V**), $Zn(2\text{-}Brbenz)_2(nad)_2$ (**VI**) and $Zn_2(2\text{-}Brbenz)_4(phen)_2$ (**VII**)

The syntheses may be expressed by the following equations:

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

$$ZnCO_3 + 2(2\text{-}BrC_6H_4COOH) \rightarrow Zn(2\text{-}BrC_6H_4COO)_2 + H_2O + CO_2 \uparrow \quad (2)$$

$$Zn(2\text{-}BrC_6H_4COO)_2 + 2L \rightarrow Zn(2\text{-}BrC_6H_4COO)_2L_2 \quad (3)$$

2-Bromobenzoic acid (2.58 g, 97%, 12 mmol) dissolved in methanol (40 cm^3) was added to the excess of aqueous suspension of $ZnCO_3$ freshly prepared by the reaction of aqueous solution of $ZnCl_2$ and Na_2CO_3. The reaction mixture was stirred for 1.5 h and the excess of $ZnCO_3$ was filtered off. Then, to the filtrate of zinc 2-bromobenzoate the solution of bioactive ligands (urea, nicotinamide, isonicotinamide, *N*-methylnicotinamide, *N,N*-diethylnicotinamide and phenazone) were added in stoichiometric ratio and stirred for 2 h. The reaction mixture was reduced to a half of its volume at 343 K and left to crystallize at room temperature. In a few days, crystalline (**I**, **III**–**VII**) and powdery (**II**) complex compounds were obtained in 78–86% yields.

Instrumentation

The carbon, hydrogen and nitrogen content in the newly synthesised compounds were determined by the CHN analyzer PERKIN ELMER 2400. The zinc content was determined using Complexone III as an agent and Eriochrome black T as an indicator.

The IR spectra of the prepared zinc complex compounds and the solid intermediates of thermal decomposition were recorded on an AVATAR 330 FT-IR Thermo Nicolet spectrometer using KBr pellets (2 mg/200 mg KBr), in the range 4000–400 cm^{-1}.

Thermal decomposition was studied in nitrogen atmosphere using a Perkin-Elmer TGA7 with the heating rate of 10 K min^{-1} up to 1073 K in platinum crucibles.

Mass spectrometer GC/MS Agilent 7890A was used for determination of volatile products of the thermal decomposition.

Antimicrobial assay

The antibacterial activities of the studied Zn(II) complexes, organic ligands (urea, thiourea, methyl-3-pyridylcarbamate, phenazone, *N*-methylnicotinamide, isonicotinamide and *N,N*-diethylnicotinamide) and 2-bromobenzoic acid were evaluated by a micro-dilution method using G^+ bacteria *Staphylococcus aureus* CCM 3953, G^- bacteria *Escherichia coli* CCM 3988 [25]. The effects of these compounds on the yeasts *Candida albicans* (purchased from the *Laboratory of Medical Mycology, Slovak Medical University*, Bratislava, Slovakia) were determined by macro-dilution method in L-shapes tubes adapted for direct measurement of absorbance [26]. The cultures of bacteria (in Mueller–Hinton growth medium) and yeasts (Sabouraud′s growth medium) were incubated under vigorous shaking. The effect of tested compounds on the growth of filamentous fungi *Rhizopus oryzae* CCM F-8284, *Alternaria alternata* CCM F-128 and *Microsporum gypseum* CCM F-8342 was observed by macro-dilution technique on solidified broth medium during static culturing [27, 28] and the diameters of growing fungal colonies were measured at intervals. Strains designed "CCM" were originally obtained from the Czech Collection of Microorganisms, Masaryk University, Brno, Czech Republic.

Chromatographically pure compounds were dissolved in DMSO; its final concentration never exceeded 1.0 vol.% in either control or treated samples. Concentration of tested compounds was in the range of 0.01–2.0 mmol dm^{-3} (bacteria, yeasts) or of 0.1–3.0 mmol dm^{-3} (filamentous fungi) in all experiments. The antimicrobial activity was characterized by the IC_{50} values (concentration of a compound which in comparison to the control inhibits the growth of model microorganisms to 50%) and MIC values

(minimal inhibitory concentration of a compound which inhibits microbial growth by 100%). The IC_{50} and MIC values were read from toxicity curves. MIC experiments on subculture dishes were used to assess the minimal microbicidal concentration (MMC). Subcultures were prepared separately in Petri dishes containing appropriate agar medium and incubated at 303 K for 48 h (bacteria, yeasts) and 298 K for 96 h (filamentous fungi). The MMC value was taken as the lowest concentration which showed no visible growth of microbial colonies on the subculture dishes.

Results and discussion

The prepared compounds (**I–VII**) are white in colour, stable in air and light. Elemental analyses (Table 1) are in good agreement with the calculated ones. The solubility of the studied compounds in various solvents is presented in Table 2.

IR spectra

The characteristic IR bands for the compounds (**I–VII**) are reported in Table 3. The assignments were done according to the literature data [29, 30]. The magnitude of separation of asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching vibrations of carboxylate group, $\Delta(COO^-)$, can be used as a criterion to assign the type of the carboxylate coordination in inorganic complexes. In general the following order is proposed for divalent metal carboxylates: Δ(monodentate) $\gg \Delta$(ionic) $\geq \Delta$(bridging) $\gg \Delta$(chelating) [29, 31]. The Δ value determined from the IR spectra of sodium 2-bromobenzoate is 168 cm^{-1}. By comparing the values of $\Delta(COO^-)$ of prepared compounds with that of sodium 2-bromobenzoate we can assume a monodentate coordination of 2-bromobenzoate group in compounds (**II**) (184 cm^{-1}), (**IV**) (187 cm^{-1}), (**V**) (200 cm^{-1}), (**VI**) (211 cm^{-1}) and (**VII**) (224 cm^{-1}) and a bridging mode of binding in compounds (**I**) (168 cm^{-1}), (**III**) (168 cm^{-1}) and (**VII**) (156 cm^{-1}).

The strong absorption band of the carbonyl ν(C=O) vibration of compounds (**III**, **IV**, **V**, **VI**) at 1679, 1701, 1632 and 1682 cm^{-1}, respectively, is shifted to a higher wavenumber as compared with the free ligands (ν_{mnad}(C=O) = 1644 cm^{-1}, ν_{inad}(C=O) = 1666 cm^{-1}, ν_{denad}(C=O) = 1628 cm^{-1}, ν_{nad}(C=O) = 1679 cm^{-1}). It can be explained by the fact that the pyridine nitrogen of of these ligands is involved in coordination with zinc, therefore, the electron density is shifted towards the pyridine nitrogen, leading to

Table 1 Elemental analysis of the prepared zinc(II) compounds

Compound	C/%		H/%		N/%		Zn/%	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
$Zn(2\text{-}Brbenz)_2$ $C_{14}H_8O_4Br_2Zn$ F.W. = 465.41	36.13	36.1	1.73	1.72	0	0	14.56	14.05
$Zn(2\text{-}Brbenz)_2(u)_2$ $C_{16}H_{16}O_6N_4Br_2Zn$ F.W. = 585.53	32.77	32.82	2.76	2.75	9.83	9.57	10.84	11.12
$Zn_2(2\text{-}Brbenz)_4(mnad)_2$ $C_{42}H_{32}O_{10}N_4Br_4Zn_2$ F.W. = 1203.12	42.01	41.92	2.65	2.68	4.75	4.66	10.75	10.87
$Zn(2\text{-}Brbenz)_2(inad)_2{\cdot}H_2O$ $C_{26}H_{22}O_8N_4Br_2Zn$ F.W. = 727.68	43.16	42.92	2.94	3.05	7.71	7.7	9.15	8.93
$Zn(2\text{-}Brbenz)_2(denad)_2{\cdot}2H_2O$ $C_{34}H_{40}O_8N_4Br_2Zn$ F.W. = 857.88	48.3	47.56	4.67	4.23	6.81	6.53	8.05	7.62
$Zn(2\text{-}Brbenz)_2(nad)_2$ $C_{26}H_{20}O_6N_4Br_2Zn$ F.W. = 709.67	44.18	44	2.88	2.84	7.9	7.89	9.89	9.21
$Zn_2(2\text{-}Brbenz)_4(phen)_2$ $C_{50}H_{40}O_{10}N_4Br_4Zn_2$ F.W. = 1307.28	46.28	45.9	3.06	3.08	4.35	4.29	10.38	10

Table 2 Solubility of the prepared compounds

Compound	Solvent/solubility								
	H_2O	CH_3OH	C_2H_5OH	$(C_2H_5)_2O$	$(CH_3)_2CO$	$CHCl_3$	CCl_4	DMFA	DMSO
$Zn(2\text{-}Brbenz)_2$	w sol	sol	sol	sol	sol	insol	insol	sol	sol
$Zn(2\text{-}Brbenz)_2(u)_2$	w sol	sol	sol	w sol	sol	insol	insol	sol	sol
$Zn_2(2\text{-}Brbenz)_4(mnad)_2$	sol	sol	w sol	insol	sol	insol	insol	sol	sol
$Zn(2\text{-}Brbenz)_2(inad)_2{\cdot}H_2O$	sol	sol	w sol	insol	sol	insol	insol	sol	sol
$Zn(2\text{-}Brbenz)_2(denad)_2{\cdot}2H_2O$	sol	sol	w sol	insol	sol	insol	insol	sol	sol
$Zn(2\text{-}Brbenz)_2(nad)_2$	sol	sol	w sol	insol	sol	insol	insol	sol	sol
$Zn_2(2\text{-}Brbenz)_4(phen)_2$	sol	sol	w sol	insol	sol	insol	insol	sol	sol

sol soluble, *w sol* weakly soluble, *insol* insoluble

Table 3 Characteristic absorption bands ν/cm^{-1} in IR spectra of compounds (**I–VII**)

Assignment/compound	(**I**)	(**II**)	(**III**)	(**IV**)	(**V**)	(**VI**)	(**VII**)
ν(N–H)	–	3454s, 3350s	3360s	3379s, 3164s	–	3383s	–
ν_{ar}(C–H)	3090m, 3067m	3074w	3082–3053w	3063–3047w	3090–3035w	3063w	3101m, 3068w
ν_{aliph}(C–H)	–	–	2936w	–	2988m–2872w	–	2995vw, 2924vw
ν(C=O)	–	1633s	1679s	1701s	1632s[a]	1682s	1647s
δ(N–H)	–	1625s	1644s	1601s[a]	–	1612s	
ν(C=C)	1537s, 1467m	1551s, 1533s	1584m, 1521m	1575s, 1549m	1509w, 1495w	1556m, 1464w	1572s, 1558w
	1410sh	1489m, 1470w	1477m	1470w	1474m	1433m	1458w
$\nu_{as}(COO^-)$	1574s	1576s	1603s	1591s	1595s	1605s	1601s, 1572s
$\nu_s(COO^-)$	1406s	1392s	1435s	1404s	1395s	1394s	1377s, 1416s
$\Delta(COO^-)$	168	184	168	187	200	211	224, 156
$\delta_{as}(C-H)_{CH_3-}$	–	–	1439s	–	1444m	–	1498m
$\delta_s(C-H)_{CH_3-}$	–	–	1296m	–	1366m	–	1315m
ν(C–C)	–	–	1201m, 1163m	1230m, 1116w	1253w, 1194m	1200m, 1261w	1257w, 1151w
γ_{ar}(C–H)	750s	741m	755s	755m	752m	748m	750s
$\delta(COO^-)$	703s	710m	698s	704m	690m	696m	690m
ν(C–Br)	641m	648m	647m	644m	644m	640m	646m

(I)—$Zn(2\text{-}Brbenz)_2$, **(II)**—$Zn(2\text{-}Brbenz)_2(u)_2$, **(III)**—$Zn_2(2\text{-}Brbenz)_4(mnad)_2$, **(IV)**—$Zn(2\text{-}Brbenz)_2(inad)_2{\cdot}H_2O$, **(V)**—$Zn(2\text{-}Brbenz)_2(denad)_2{\cdot}2H_2O$, **(VI)—**$Zn(2\text{-}Brbenz)_2(nad)_2$, **(VII)**—$Zn_2(2\text{-}Brbenz)_4(phen)_2$

[a] Overlayed with $\delta(O-H)_{H_2O}$; *s* strong, *m* medium, *w* weak, *vw* very weak, *ar* aromatic, *aliph* aliphatic

the increase in the double bond character of the carbonyl group and shift the stretching vibration ν(C=O) to a higher value. On the other hand in the case of compounds **(II)** and **(VII)** the absorption band of the carbonyl ν(C=O) vibration appeared at 1633 and 1647 cm^{-1}, respectively, exhibited a shift to lower wavenumber in comparison with free ligands (ν_u(C=O) = 1670 cm^{-1}, ν_{phen}(C=O) = 1666 cm^{-1}). This phenomenon can be explained by the coordination of the carbonyl oxygen to the central zinc atom, leading to a decrease of the double bond character of the carbonyl group and shifting the stretching vibration ν(C=O) to lower values. These assumptions were proved by the results of the X-ray structural analyses of compounds (**III**, **V**, **VI**) and (**VII**) [21–24].

Thermal behaviour

Thermal decomposition of the prepared compounds is given in Table 4.

Compound Zn(2-BrC$_6$H$_4$COO)$_2$

As it follows from Fig. 1, the compound is thermally stable up to 523 K. On heating above this temperature thermal decomposition takes place. The release of bis(2-bromophenyl)ketone and carbon dioxide (exp. mass loss 84.02%, calc. mass loss 82.51%) in temperature range 523–983 K are observed on TG/DTG curve. The final solid product of thermal decomposition is ZnO (exp. 15.98%, calc.

Table 4 Thermal decomposition of the prepared compounds

Compound	Temperature range of decomposition/K	Products of the thermal decomposition	Mass loss/%	
			Exp.	Theor.
$Zn(2\text{-}Brbenz)_2$	523–973	$(C_6H_4Br)_2CO + CO_2$	84.02	82.51
	R_{973}	ZnO	15.98	17.49
$Zn(2\text{-}Brbenz)_2(u)_2$	403–1073	$2u + (C_6H_4Br)_2CO + CO_2$	86.01	86.11
	R_{1073}	ZnO	13.99	13.89
$Zn_2(2\text{-}Brbenz)_4(mnad)_2$	453–1073	$2mnad + 2(C_6H_5Br)_2CO + 2CO_2$	86.18	86.46
	R_{1073}	2ZnO	13.82	13.54
$Zn(2\text{-}Brbenz)_2(inad)_2{\cdot}H_2O$	363–393	H_2O	2.3	2.47
	393–1073	$2inad + (C_6H_5Br)_2CO + CO_2$	85.35	86.35
	R_{1073}	ZnO	12.35	11.18
$Zn(2\text{-}Brbenz)_2(denad)_2(H_2O)_2$	333–403	$2H_2O$	4.21	4.19
	403–793	$2denad + (C_6H_5Br)_2CO + CO_2$	82.94	82.12
	R_{793}	ZnO	12.85	13.69
$Zn(2\text{-}Brbenz)_2(nad)_2$	473–1073	$2nad + (C_6H_5Br)_2CO + CO_2$	88.42	88.53
	R_{1073}	ZnO	11.58	11.47
$Zn_2(2\text{-}Brbenz)_4(phen)_2$	473–1073	$2phen + 2(C_6H_5Br)_2CO + 2CO_2$	86.44	87.55
	R_{1073}	2ZnO	13.56	12.45

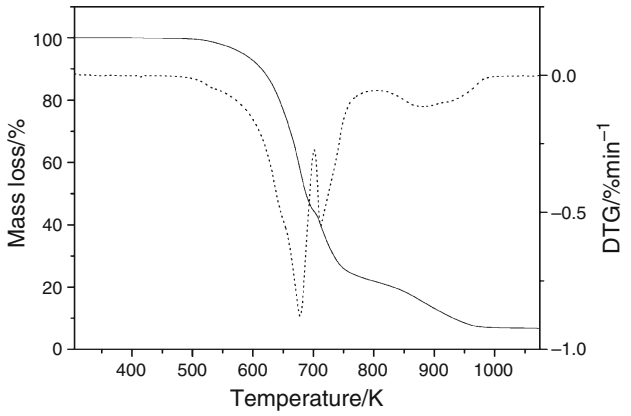


Fig. 1 Thermal decomposition of $Zn(C_6H_4COO)_2$

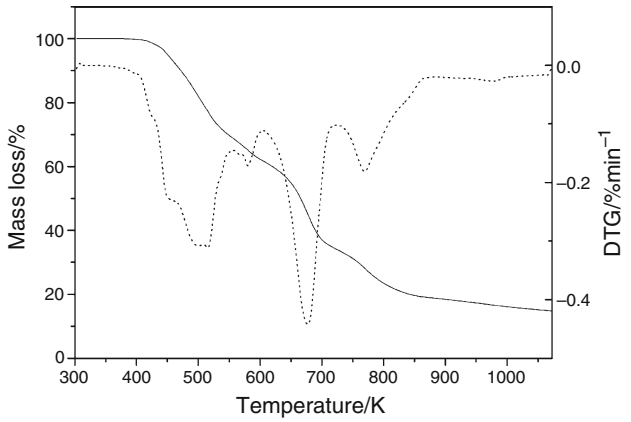


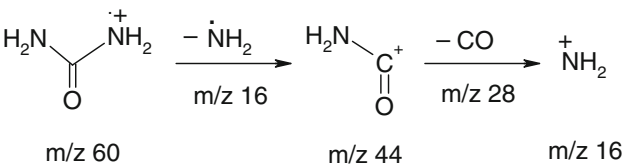
Fig. 2 Thermal decomposition of $Zn(C_6H_4COO)_2(u)_2$

17.49%). The following mechanism is proposed for the thermal decomposition:

$$Zn(2\text{-}BrC_6H_4COO)_2 \rightarrow (C_5H_4Br)_2CO + CO_2 + ZnO \quad (4)$$

Compound $Zn(2\text{-}BrC_6H_4COO)_2(u)_2$

The compound is stable up to 403 K. The thermal decomposition may be characterized as a two step reaction in temperature range from 403 to 1073 K. In the first step two moles of urea are released and than bis(2-bromophenyl)ketone and carbon dioxide (exp. mass loss 86.01%, calc. mass loss 86.11%) are evolved. The final solid product of thermal decomposition is ZnO (exp. 13.99, calc. 13.89) (Fig. 2). Mass spectrum measured at 438 K confirmed the release of urea (*m/z*: 60, 44, 16). Based on the mass spectrum we propose the following fragmentation scheme of urea:



In the IR spectrum of solid intermediate at 573 K showed that the absorption bands of urea (ν(C=O) = 1633 cm^{-1} and

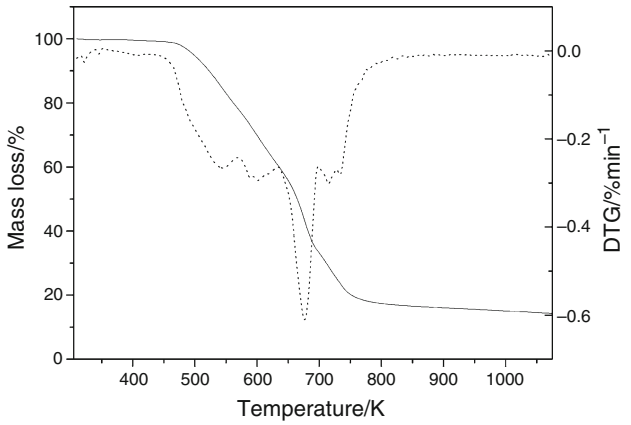


Fig. 3 Thermal decomposition of $Zn_2(C_6H_4COO)_4(mnad)_2$

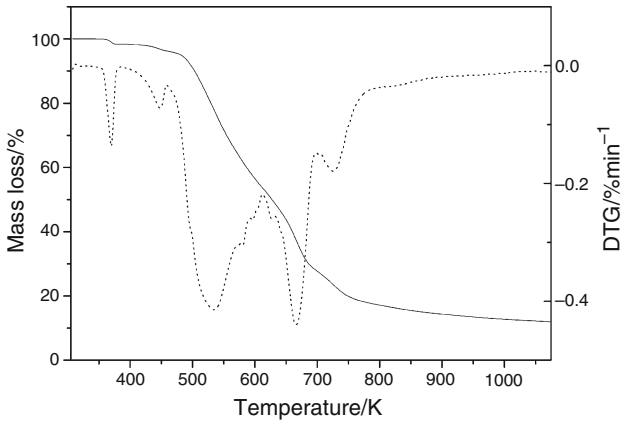


Fig. 4 Thermal decomposition of $Zn(C_6H_4COO)_2(inad)_2.H_2O$

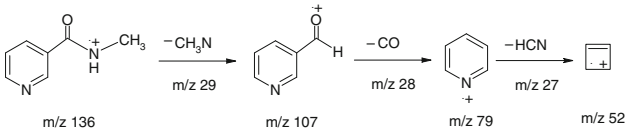
ν(N–H) = 3454, 3350 cm^{-1}) were missing. The following reaction is proposed for the decomposition process:

$$Zn(2\text{-}BrC_6H_4COO)_2(u)_2 \rightarrow 2u + (C_6H_4Br)_2CO + CO_2 + ZnO \quad (5)$$

Compound $Zn_2(2\text{-}BrC_6H_4COO)_4(mnad)_2$

The thermal decomposition starts at 453 K with the release of two moles of *N*-methylnicotinamide and in the next step the release of two moles of bis(2-bromophenyl)ketone and two moles of carbon dioxide (exp. mass loss 86.18%, calc. mass loss 86.46%) (Fig. 3) are evolved. The final solid product of thermal decomposition is ZnO (exp. 13.82%, calc. 13.54%).

The release of *N*-methylnicotinamide was confirmed by mass spectrometry (*m/z*: 136, 107, 79, 52) measured at 473 K. We propose the following fragmentation scheme of *N*-methylnicotinamide:



In the IR spectrum of the solid intermediate product at 633 K the absorption bands of *N*-methylnicotinamide (ν(C=O) = 1679 cm^{-1}, ν(N–H) = 3360 cm^{-1}, $\nu(C–H)_{aliph}$ = 2936 cm^{-1}, $\delta_{as}(C-H)_{CH_3-}$ = 1439 cm^{-1} and $\delta_s(C-H)_{CH_3-}$ = 1296 cm^{-1}) were missing.

The mechanism of thermal decomposition can be expressed as follows:

$$Zn_2(2\text{-}BrC_6H_4COO)_4(mnad)_2 \rightarrow 2mnad + 2(C_6H_4Br)_2CO + 2CO_2 + 2ZnO \quad (6)$$

Compound $Zn(2\text{-}BrC_6H_4COO)_2(inad)_2{\cdot}H_2O$

The compound is thermally stable up to 363 K (Fig. 4). Release of water takes place above this temperature (exp. mass loss 2.30%, calc. mass loss 2.47%). The thermal decomposition of anhydrous product may be characterized as a two step reaction in temperature range from 423 to 1073 K. In the first step two moles of isonicotinamide are released. In the next step bis(2-bromophenyl)ketone and carbon dioxide are lost (exp. mass loss 85.35%, calc. mass loss 86.35%). In the IR spectrum of solid intermediate product at 583 K the absorption bands of isonicotinamide (ν(C=O) = 1701 cm^{-1} and ν(N–H) = 3379, 3250 cm^{-1}) were missing. The final solid product of thermal decomposition is ZnO (exp. 12.35%, calc. 11.18%).

$$Zn(2\text{-}BrC_6H_4COO)_2(inad)_2\ H_2O \rightarrow H_2O + 2inad + (C_6H_4Br)_2CO + CO_2 + ZnO \quad (7)$$

Compound $Zn(2\text{-}Brbenz)_2(denad)_2{\cdot}2H_2O$

From Fig. 5 it followed that the thermal decomposition of $Zn(2\text{-}Brbenz)_2(denad)_2(H_2O)_2$ starts at 333 K with the dehydration process (exp. mass loss 4.21%, calc. mass loss 4.19%). In temperature range 403–823 K two moles of *N,N*-diethylnicotinamide, one mole of bis(2-bromophenyl)ketone

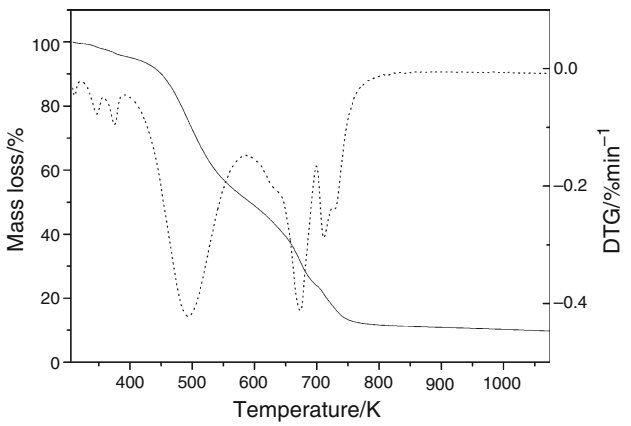


Fig. 5 Thermal decomposition of $Zn(C_6H_4COO)_2(denad)_2.2H_2O$

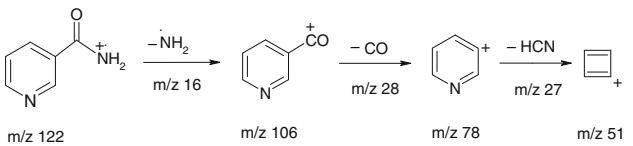
and one mole of carbon dioxide were evolved (exp. mass loss 82.94%, calc. mass loss 82.12%). In IR spectra of the solid intermediate product at 603 K the characteristic absorption bands of *N,N*-diethylnicotinamide (ν(C=O) = 1632 cm^{-1}, $\nu(C–H)_{aliph}$ = 2988 cm^{-1}, δ_{as} $(C–H)_{CH_3–}$ = 1444 cm^{-1} and $\delta_s(C–H)_{CH_3–}$ = 1366 cm^{-1}) were missing. The final product of thermal decomposition is ZnO (exp. 12.85%, calc. 13.69%). The following reaction is proposed for the decomposition process:

$$Zn(2\text{-}BrC_6H_4COO)_2(denad)_2\ 2H_2O \rightarrow\ 2H_2O + 2denad + (C_6H_4Br)_2CO + CO_2 + ZnO \quad (8)$$

Compound Zn(2-BrC$_6$H$_4$COO)$_2$(nad)$_2$

The compound is stable up to 473 K. The thermal decomposition may be characterized as a two step reaction in temperature range from 473 to 1073 K. In the first step two moles of nicotinamide release and than bis(2-bromophenyl)ketone and carbon dioxide (exp. mass loss 88.42%, calc. mass loss 88.53%) are evolved. The final solid product of thermal decomposition is ZnO (exp. 11.56%, calc. 11.47%) (Fig. 6). Mass spectrum measured at 473 K confirmed the release of nicotinamide (*m/z*: 122, 106, 78, 51).

The fragmentation scheme for nicotinamide is proposed as follows:



The absence of nicotinamide was confirmed by IR spectra in the solid intermediate product at 598 K where the absorption bands of characteristic groups of nicotinamide (ν(C=O) = 1689 cm^{-1} and ν(N–H) = 3383 cm^{-1}) were missing. The following reaction is proposed for the decomposition process:

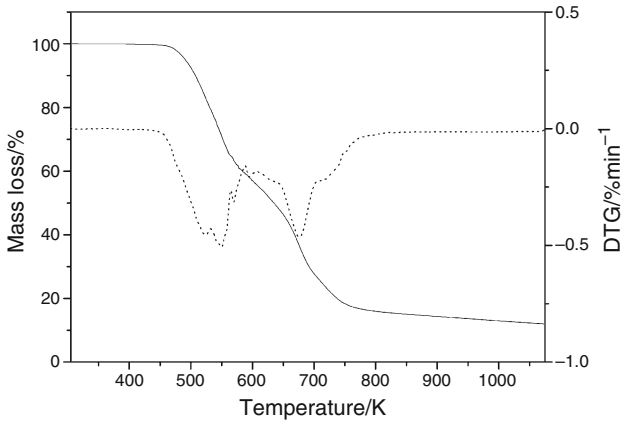


Fig. 6 Thermal decomposition of $Zn(C_6H_4COO)_2(nad)_2$

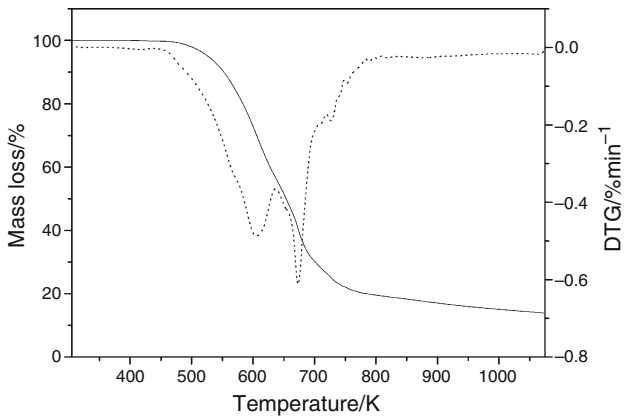
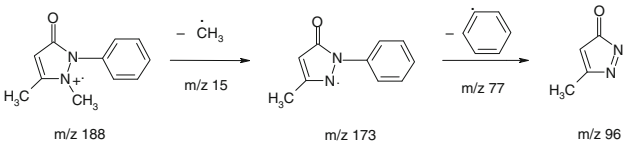


Fig. 7 Thermal decomposition of $Zn_2(C_6H_4COO)_4(phen)_2$

$$Zn(2\text{-}BrC_6H_4COO)_2(nad)_2 \rightarrow\ 2nad + (C_6H_4Br)_2CO + CO_2 + ZnO \quad (9)$$

Compound Zn$_2$(2-BrC$_6$H$_4$COO)$_4$(phen)$_2$

As it can be seen from Fig. 7, the compound is thermally stable up to 473 K. On heating above this temperature thermal decomposition takes place. The release of two moles of phenazone and than two moles of bis(2-bromophenyl)ketone and two moles of carbon dioxide (exp. mass loss 86.44%, calc. mass loss 87.55%) are observed in temperature range 473–1073 K on TG/DTG curves. The final solid product of thermal decomposition is ZnO (exp. 13.56%, calc. 12.45%). The release of phenazone was confirmed by mass spectrometry (*m/z*: 188, 173, 96) measured at 483 K. The fragmentation scheme of phenazone is as follows:



The following mechanism is proposed for the thermal decomposition:

$$Zn_2(2\text{-}BrC_6H_4COO)_4(phen)_2 \rightarrow\ 2phen + 2(C_6H_4Br)_2CO + 2CO_2 + 2ZnO \quad (10)$$

Biological properties

The results of determination of antimicrobial activity of tested compounds (characterized by the IC_{50} and MIC values [mmol dm^{-3}]) are summarized in Table 5. In general, it could be concluded that the presence of zinc(II) ion in complexes led to the increase of the inhibitory activity on the growth of bacteria, yeasts and filamentous fungi in comparison with 2-bromobenzoic acid (**XVII**), except of *A. alternata.* Neither 2-bromobenzoic acid (**XVII**) nor any

Table 5 Antimicrobial activity of zinc(II) 2-bromobenzoate complexes characterized by IC_{50} and MIC values/mmol dm^{-3}

Compound	Bacteria				Yeasts				Filamentous fungi			
	S. aureus		*E. coli*		*C. albicans*		*R. oryzae*		*A. alternata*		*M. gypseum*	
	IC_{50}	MIC	IC_{50}	MIC	IC_{50}	MIC	IC_{50}	MIC	IC_{50}	MIC	IC_{50}	MIC
(I)	0.13	1[a]	0.37	1[a]	0.71	>2	>3	>3	>3	>3	2	>3
(II)	0.21	1[a]	0.1	1[a]	0.8	>2	3	>3	>3	>3	1.9	>3
(III)	0.13	>2	0.51	1[a]	0.72	>2	2	>3	>3	>3	1.4	>3
(IV)	0.13	1[a]	0.5	2[a]	0.82	>2	3	>3	>3	>3	1.6	>3
(V)	0.12	1[a]	0.9	2[a]	0.9	>2	3	>3	>3	>3	2	>3
(VII)	0.07	1[a]	0.34	1[a]	0.5	>2	1.8	>3	>3	>3	1.5	>3
(VIII)	0.2	1[a]	0.4	2[a]	1.35	>2	2.2	>3	2.8	>3	1.3	2[b]
(IX)	0.2	2[a]	0.5	1[a]	0.88	>2	2.1	>3	>3	>3	1	>3
(X)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XI)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XII)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XIII)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XIV)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XV)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XVI)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3
(XVII)	>2	>2	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3

$Zn(2\text{-Brbenz})_2$ **(I)**, $Zn(2\text{-Brbenz})_2(u)_2$ **(II)**, $Zn_2(2\text{-Brbenz})_4(mnad)_2$ **(III)**, $Zn(2\text{-Brbenz})_2(inad)_2{\cdot}H_2O$ **(IV)**, $Zn(2\text{-Brbenz})_2(denad)_2{\cdot}2H_2O$ **(V)**, $Zn_2(2\text{-Brbenz})_4(phen)_2$ **(VII)**, $Zn(2\text{-Brbenz})_2(tu)_2{\cdot}2H_2O$ **(VIII)**, $Zn(2\text{-Brbenz})_2(mpc)_2$ **(IX)**, u **(X)**, tu **(XI)**, mpc **(XII)**, phen **(XIII)**, mnad **(XIV)**, inad **(XV)**, denad **(XVI)**, 2-bromobenzoic acid **(XVII)**

[a] Microbistatical effect

[b] Microbicidal effect

free ligand (**X–XVI**) affected the growth of selected microorganisms ($IC_{50} > 3.0$ mmol dm^{-3}, MIC > 3.0mmol dm^{-3}). In comparison with zinc(II) 2-bromobenzoate (**I**) ($IC_{50} = 0.13$ mmol dm^{-3}, MIC = 1 mmol dm^{-3}) the increase of antibacterial activity against G^+ pathogenic bacterium *S. aureus* was observed only in case of complex (**VII**) ($IC_{50} = 0.07$ mmol dm^{-3}, MIC = 1 mmol dm^{-3}); the efficiency of complexes (**IV**) and (**V**) is comparable with complex **I**. On the other hand, the inhibitory activity of compounds (**II**, **III**, **VIII**, **IX**) ($IC_{50} = 0.20$–0.21 mmol dm^{-3}, MIC = 1.0–2.0 mmol dm^{-3}) was lower than that of zinc(II) 2-bromobenzoate (**I**). In comparison with complex (**I**) ($IC_{50} = 0.37$ mmol dm^{-3}, MIC = 1.0 mmol dm^{-3}) only in case of complex (**II**) ($IC_{50} = 0.10$mmol dm^{-3}, MIC = 1.0 mmol dm^{-3}) was observed a higher antibacterial activity against *E. coli*. The inhibitory activity of complex (**VII**) ($IC_{50} = 0.34$ mmol dm^{-3}, MIC = 1.0 mmol dm^{-3}) was comparable with that of zinc(II) 2-bromobenzoate (**I**) and the remaining complexes (**III–V**, **VIII**, **IX**) have had lower inhibition efficiency than complex (**I**) ($IC_{50} = 0.40$–0.90 mmol dm^{-3}, MIC = 1.0–2.0 mmol dm^{-3}) against this G^- bacterium. Complex (**VII**) had the highest antimicrobial activity against yeast *C. albicans* (($IC_{50} = 0.50$ mmol dm^{-3}). Except of complex (**III**) ($IC_{50} = 0.72$ mmol dm^{-3}), which efficiency was comparable with that of complex (**I**) ($IC_{50} = 0.50$ mmol dm^{-3}), the remaining zinc(II) compounds (**II**, **IV**, **V**, **VIII**, **IX**) had a lower antimicrobial activity against this yeast ($IC_{50} = 0.80$–1.35 mmol dm^{-3}). The growth of *R. oryzae* was the most strongly inhibited by complex (**VII**) ($IC_{50} = 1.80$ mmol dm^{-3}), but the presence of *N*-methylnicotinamide, thiourea and methyl-3-pyridylcarbamate in complexes (**III**, **VIII**, **IX**) also increased their antifungal activity ($IC_{50} = 2.0$–2.2 mmol dm^{-3}) in comparison with zinc(II) 2-bromobenzoate (**I**) ($IC_{50} > 3.0$ mmol dm^{-3}). Neither the studied complexes (**I–VII**, **IX**), nor the free ligands (**X–XVI**) and 2-bromobenzoic acid (**XVII**) influenced the growth of filamentous fungi *A. alternata* ($IC_{50} > 3.0$ mmol dm^{-3}). Only complex (**VIII**) ($IC_{50} = 2.8$ mmol dm^{-3}) slightly inhibited the growth of this fungi. The highest antifungal activity against dermatophytic fungi *M. gypseum* was observed in the presence of complex (**IX**) ($IC_{50} = 1.0$ mmol dm^{-3}, MIC > 3.0 mmol dm^{-3}). In comparison with the inhibitory activity of compound **I** ($IC_{50} = 2.0$ mmol dm^{-3}), the inhibitory activity of compounds (**III**, **IV**, **VII**, **VIII**) was positively influenced by the ligands *N*-methylnicotinamide, isonicotinamide

phenazone and thiourea (IC_{50} = 1.3–1.6 mmol dm^{-3}). The selected bacteria *S. aureus* and *E. coli* were more sensitive to the studied zinc(II) complex compounds than yeast *C. albicans* or filamentous fungi *M. gypseum, R. oryzae* and *A. alternata*, respectively.

Conclusions

The thermal decomposition of hydrated compounds started from 333 K with dehydration process. During the thermal decomposition the organic ligand, carbon dioxide and bis(2-bromophenyl)ketone were evolved. The final solid product of the thermal decomposition heated up to 1073 K was zinc oxide. The solid intermediates and volatile products of thermal decomposition were confirmed by IR spectroscopy and mass spectrometry. It was found that zinc(II) 2-bromobenzoate starts to decompose at the highest temperature and the thermal stability of anhydrous compounds increases in the following order:

$$\underset{393\ K}{Zn(2\text{-}BrC_6H_4COO)_2\cdot(inad)_2} < \underset{403\ K}{Zn(2\text{-}BrC_6H_4COO)_2(u)_2} = \underset{403\ K}{Zn(2\text{-}BrC_6H_4COO)_2(denad)_2} < \underset{453\ K}{Zn_2(2\text{-}BrC_6H_4COO)_4(mnad)_2} < \underset{473\ K}{Zn(2\text{-}BrC_6H_4COO)_2(nad)_2} = \underset{473\ K}{Zn_2(2\text{-}BrC_6H_4COO)_4(phen)_2} < \underset{523\ K}{Zn(2\text{-}BrC_6H_4COO)_2}$$

In the case of the compounds with solved crystal structure: $Zn(2\text{-}BrC_6H_4COO)_2$ (**I**), $Zn_2(2\text{-}BrC_6H_4COO)_4(mnad)_2$ (**III**), $Zn(2\text{-}BrC_6H_4COO)_2(denad)_2{\cdot}2H_2O$ (**V**), $Zn(2\text{-}BrC_6H_4COO)_2(nad)_2$ (**VI**), $Zn_2(2\text{-}BrC_6H_4COO)_4(phen)_2$ (**VII**) the values of Δ were in agreement with the results of structural analysis:

Δ(monodentate) = 200, 211 and 224 cm^{-1} (**V**–**VII**)

Δ(bridging) = 168, 168 and 156 cm^{-1} (**I**, **III**, **VII**) [21–24].

The compound with phenazone (**VII**) had the highest inhibition activity on the growth of *S. aureus*, *C. albicans* and *R. oryzae*. The compound with urea (**II**) had the highest antibacterial activity against *E. coli*. The growth of *A. alternata* was influenced only by compound with thiourea (**VIII**). The highest antifungal activity against *M. gypseum* was observed in the presence of compound with methyl-3-pyridylcarbamate (**IX**). The presence of free organic ligands and 2-bromobenzoic acid did not affect the growth of microorganisms.

Acknowledgements This work was supported by the Slovak Ministry of Education (VEGA project 1/0122/08). The financial support is gratefully acknowledged.

References

1. Crichton RR. Biological inorganic chemistry. Amsterdam: Elsevier; 2008.
2. Warner RR, Schwartz JR, Boissy Y, Dawson TL. Dandruff has an altered stratum corneum ultrastructure that is improved with zinc pyrithione shampoo. J Am Acad Dermatol. 2001;45:897–903.
3. Cunnane SC. Zinc: clinical and biochemical significance. Florida: CRC Press; 1988.
4. Diehl KB. Topical antifungal agents: an update. Am Fam Physician. 1996;54:1687–92.
5. Ferenc W, Cristóvao B, Sarzyński J. Thermal and magnetic behaviour of 5-chloro-2-nitrobenzoates of Co(II), Ni(II) and Cu(II). J Therm Anal Calorim. 2010;101:761–7.
6. Rehman S, Arshad M, Masud K, Afzal R, Salma U. Pyrolytical characterization of transition metal complexes of cobalt, nickel, copper and zinc with ethylenediamine-N,N′-diacetate. J Therm Anal Calorim. 2010;102:715–22.
7. Olczak-Kobza M, Mrozek A. Zinc(II) and cadmium(II) complexes with o-hydroxybenzoic acid or o-aminobenzoic acid and 2-methylimidazole, IR spectra, X-ray diffraction studies and thermal analysis. J Therm Anal Calorim. 2009;96:553–60.
8. Köse AD. Synthesis and characterization of bis(nicotinamide) m-hydroxybenzoate complexes of Co(II), Ni(II), Cu(II) and Zn(II). Russ J Inorg Chem. 2007;52:1384–90.
9. Moncol J, Mudra M, Lönnecke P, Hewitt M, Valko M, Morris H, Svorec J, Melník M, Mazur M, Koman M. Crystal structures and spectroscopic behavior of monomeric, dimeric and polymeric copper(II) chloroacetate adducts with isonicotinamice, *N*-methylnicotinamice and *N*,*N*-diethylnicotinamide. Inorg Chim Acta. 2007;360:3213–25.
10. Mojumdar SC, Melník M, Jóna E. Thermal and spectral properties of Mg(II) and Cu(II) complexes with heterocyclic N-donor ligands. J Anal Appl Pyrolysis. 2000;53:149–60.
11. Moncol J, Maroszová J, Koman M, Melnik M, Valko M, Mazur M, Lis T. Self-assembly of hydrogen-bonded supramolecular structures of two copper(II) 2-bromobenzoate complexes with 4-pyridylmethanol and nicotinamide. J Chem Crystallogr. 2008; 61:3740–52.
12. Zhang YL, Chen SW, Liu WS, Wang DQ. Tetrakis(μ-2-bromobenzoato-κ^2O,O')bis[(*N*,*N*′-dimethylformamide)copper(II)], a new binuclear complex containing a metal–metal bond. Acta Crystallogr. 2004;E60:196–7.
13. Szunyogová E, Győryová K, Kovářová J, Juhászová E. Thermal behaviour of zinc(II) carboxylate complexes with methyl-3-pyridylcarbamate. J Therm Anal Calorim. 2003;71:967–76.
14. Győryová K, Kovářová J, Andogová E, Zeleňák V, Nour-El Dien FA. Thermal, spectral and antimicrobial properties of new zinc(II) isobutyrate compounds. J Therm Anal Calorim. 2002;67: 119–28.
15. Győryová K, Szunyogová E, Kovářová J, Hudecová D, Mudroňová D, Juhászová E. Biological and physicochemical study of zinc(II) propionate complexes with *N*-donor heterocyclic ligands. J Therm Anal Calorim. 2003;72:587–96.
16. Győryová K, Chomič J, Szunyogová E, Piknová L, Zeleňák V, Vargová Z. Thermal study of zinc(II) 4-chlorosalicylate complex compound with bioactive ligands. J Therm Anal Calorim. 2006; 84:727–32.
17. Bujdošová Z, Győryová K, Kovářová J, Hudecová D, Halás L. Synthesis, biological and physicochemical properties of zinc(II) salicylate and 2-chlorosalicylate complexes with theophylline and urea. J Therm Anal Calorim. 2009;98:151–9.
18. Findoráková L, Győryová K, Kovářová J, Balek V, Nour-El Dien FA, Halás L. Novel zinc(II) benzoate complex compounds with caffeine and urea. J Therm Anal Calorim. 2009;95:923–8.
19. Findoráková L, Győryová K, Večerníková E, Balek V. Use of emanation thermal analysis and evolved gas analysis in thermal study of zinc(II) benzoate complex compounds. J Therm Anal Calorim. 2009;98:765–9.
20. Kráľová K, Masarovičová E, Győryová K. Inhibition of photosynthetic electron transport in spinach chloroplasts, *Chlorella vulgaris*, reduction of *Sinapis alba* L. growth by some zinc(II) compounds. Fresen Environ Bull. 2003;12:857–60.

21. Erdélyiová A, Győryová K, Gyepes R, Halás L, Kovářová J. Synthesis, spectral, thermal and structural study of bis(2-bromobenzoato-O,O′)-bis(methyl-3-pyridylcarbamate-N)-zinc(II). Polyhedron. 2009;28:131–7.
22. Krajníková A, Gyepes R, Győryová K. Crystal structure of $[Zn(2\text{-bromobenzoato})_2]_n$ and $[Zn(2\text{-bromobenzoato})_2(N\text{-methylnicotinamide})_2$. J Chem Crystallogr. doi:10.1007/s10870-010-9712-z.
23. Hökelek T, Dal H, Tercan B, Ozbek FE, Necefoglu H. Diaquabis-(2-bromobenzoato-*O*)bis-(*N,N*-diethylnicotinamide-*N1*)zinc(II). Acta Crystallogr. 2009;E65:m481–2.
24. Hökelek T, Dal H, Tercan B, Ozbek FE, Necefoglu H. Diaquabis-(2-bromobenzoato-*O*)bis-(nicotinamide-*N1*)zinc(II). Acta Crystallogr. 2009;E65:m607–8.
25. 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.
26. Betina V, Mičeková D. Antimicrobial properties of fungal macrolide antibiotics. Z Allg Mikrobiol. 1972;5:355–64.
27. Hudecová D, Jantová S, Melník M, Uher M. New azidometalcolates and their biological activity. Folia Microbiol. 1996;40: 473–6.
28. Dudová B, Hudecová D, Pokorný R, Mičková M, Palicová M, Segľa P, Melník M. Copper complexes with bioactive ligands, part II – antifungal activity. Folia Microbiol. 2002;47:225–9.
29. Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. New York: Wiley; 1997.
30. Bellamy LJ. The infrared spectra of complex molecules. London: Methuen and Co.; 1958.
31. Zeleňák V, Vargová Z, Győryová K. Correlation of infrared spectra of zinc(II) carboxylates with their structures. Spectrochim Acta. 2007;A66:262–72.