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Thermoanalytical, spectral and biological study of 4-bromobenzoatozinc(II) complexes containing bioactive organic ligands

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Abstract New zinc(II) 4-bromobenzoate complex compounds with general formula $[Zn(4\text{-}BrC_6H_4COO)_2L_2]\cdot xH_2O$ (where L = urea, nicotinamide, phenazone or thiourea, $x = 0$–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, the neutral organic ligand, bis(4-bromophenyl)methanone and carbon dioxide 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 800 °C was zinc oxide, which was confirmed by X-ray powder diffractometry. 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. alternata* and *M. gypseum*). It was found that bacterium *S. aureus* and fungi *A. alternata* are the most sensitive to the studied compounds.

Keywords Zinc 4-bromobenzoate · IR spectroscopy · Thermal behaviour · Biological activity

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Introduction

Zinc has diverse biological functions in enzymatic catalysis, the immune system and neurons [1]. Its deficiency leads to a retardation of growth and development in children, genital development, dermatitis, poor pregnancy outcomes or decreased immune functions. Zinc deficiency is estimated to be high, with billions of people at risk, mostly in the developing world [2]. Simple zinc compounds (zinc sulphate, zinc oxide) are often used in nutritional products, pharmacy and cosmetics. They are often replaced by zinc(II) complexes, because they are not only a very good source of zinc, but also the organic ligand may have useful biological activity. Therefore, zinc(II) complexes attracted the interest of many scientists [3–5]. As a bioactive ligand in these complexes drugs (phenazone, papaverine), vitamins (nicotinamide, 2-aminobenzoic acid) or compounds with antimicrobial activity (benzoic and salicylic acid) can be used [6–9]. It was found that the substitution of hydrogen atom by halogen in aliphatic zinc(II) carboxylates increased the antibacterial activity against *S. aureus* and *E. coli* [10]. Therefore, our attention is now focused on bromobenzoatozinc(II) complexes. In our previous works, we have studied the thermal, spectral, structural and biological properties of 2-bromobenzoatozinc(II) complexes with bioactive ligands [11–13]. In the literature, 4-bromobenzoate compounds of Co(II) and

Cu(II) with nicotinamide and pyridine were prepared and characterized [14–16]. Until now from 4-bromobenzoatozinc(II) complexes, only three complexes (without additional ligand [17], with diethylnicotinamide [15] or phenantroline [18]) were prepared and their structure have been solved. Neither their thermal nor biological properties were described. This omission led us to focus our attention to 4-bromobenzoatozinc(II) complexes with bioactive ligands and as a continuation of our work the synthesis, spectral, thermal and biological properties of them are presented in this article.

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), 4-bromobenzoic acid 97% (Aldrich, Germany), urea, thiourea, nicotinamide and phenazone (Merck, Germany).

The following compounds were prepared:

$[Zn(4\text{-}Brbenz)_2(H_2O)_2]$
$[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$
$[Zn(4\text{-}Brbenz)_2(tu)_2]\cdot 2H_2O$
$[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$
$[Zn(4\text{-}Brbenz)_2(phen)_2]$

The syntheses may be expressed by the following equations:

$$ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3\downarrow + 2NaCl$$

$$ZnCO_3 + 2(4\text{-}BrC_6H_4COOH) \rightarrow Zn(4\text{-}BrC_6H_4COO)_2 + H_2O + CO_2\uparrow$$

$$[Zn(4\text{-}BrC_6H_4COO)_2] + 2L \rightarrow [Zn(4\text{-}BrC_6H_4COO)_2L_2]$$

Methanol solution of 4-bromobenzoic acid (2.58 g, 97%, 12 mmol) was added to the aqueous suspension of $ZnCO_3$, which was freshly prepared by the reaction of aqueous solution of $ZnCl_2$ (1.35 g, 0.01 mol) and Na_2CO_3 (1.06 g, 0.01 mol). The reaction mixture was stirred for 1.5 h and the excess of $ZnCO_3$ was filtered off. Then, the methanol solution of ligands (urea, thiourea, nicotinamide or phenazone) was added to the filtrate and it was refluxed for 4 h. The reaction mixture was reduced to a half of its volume at 70 °C and left to crystallize at room temperature. In a few days, crystalline complex compounds were obtained in 72–81% yields.

Instrumentation

The carbon, hydrogen and nitrogen contents in the prepared compounds was determined by the CHN analyser 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 air atmosphere using a NETZSCH STA 409 PC/PG Thermoanalyzer with the heating rate of 10 °C min^{-1} up to 800 °C in ceramic crucibles.

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

Antimicrobial assay

The antibacterial activities of the studied Zn(II) complexes, organic ligands (urea, thiourea, phenazone, methyl-3-pyridylcarbamate) and 4-bromobenzoic acid were evaluated by a micro-dilution method using G^+ bacteria *Staphylococcus aureus* CCM 3953, G^- bacteria *Escherichia coli* CCM 3988 [19]. The effects of these compounds on the yeasts *Candida albicans* were determined by macro-dilution method in L-shapes tubes adapted for direct measurement of absorbance [20]. 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 [21, 22] and the diameters of growing fungal colonies were measured at intervals.

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 30 °C for 48 h (bacteria, yeasts) and 25 °C 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 are white in colour, stable in air and light. The results of elemental analyses are in good agreement with the calculated ones (Table 1). The solubility of the studied compounds is presented in Table 2. In general, the prepared compounds are more soluble in polar solvents than in non-polar. The chemical formulas of prepared compounds were proposed on the basis of the results of analyses.

IR spectra

The characteristic IR bands for the compounds [Zn(4-Brbenz)$_2$(H$_2$O)$_2$], [Zn(4-Brbenz)$_2$(u)$_2$]·2H$_2$O, [Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O, [Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O and [Zn(4-Brbenz)$_2$(phen)$_2$] are reported in Table 3. The assignments were done according to the literature data [23, 24]. Apart from the compound with phenazone, every compound contains water. Absorption bands of ν(O–H) appeared in region 3516–3326 cm^{-1} and δ(O–H) in region 1651–1616 cm^{-1}. The presence of aromatic system was confirmed by stretching vibration ν_{ar}(C–H) in the region 3097–3032 cm^{-1}, further by ν_{ar}(C=C) at 1587–1442 cm^{-1} and γ_{ar}(C–H) in region 775–765 cm^{-1}. The absorption band of C–Br was observed at 688–618 cm^{-1} and stretching vibration ν(Zn–O) appeared at 473–454 cm^{-1}. The magnitude of separation of asymmetric and symmetric stretching vibrations of carboxylate group, Δ(COO$^-$), was used as a criterion to assign the type of the carboxylate coordination in the studied complexes. In general, the following order is proposed for divalent metal carboxylates [23, 25]: Δ(monodentate) $\gg$ Δ(ionic) $\geq$ Δ(bridging) $\gg$ Δ(chelating). The Δ value determined from the IR spectra of sodium 4-bromobenzoate is 171 cm^{-1}. By comparing the values of Δ(COO$^-$) of prepared compounds with that of sodium 4-bromobenzoate, we can assume a monodentate coordination of 4-bromobenzoate group in all compounds [Zn(4-Brbenz)$_2$(H$_2$O)$_2$] (194 cm^{-1}), [Zn(4-Brbenz)$_2$(u)$_2$]·2H$_2$O (185 cm^{-1}), [Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O (177 cm^{-1}), [Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O (193 cm^{-1}) and [Zn(4-Brbenz)$_2$(phen)$_2$] (191 cm^{-1}). The crystal structure of compound [Zn(4-Brbenz)$_2$(H$_2$O)$_2$] is known from the literature [17]. From the structural data, it can be seen that the Zn–O bond distances are significantly different (2.010(5) and 2.468(5) Å), which leads to an asymmetric chelated coordination close to the monodentate coordination. Therefore, the value of Δ(COO$^-$) in the IR spectrum indicates the monodentate binding mode. The presence of bioactive organic ligands was also confirmed by FTIR spectroscopy (Table 3). The strong absorption band of the carbonyl ν(C=O) vibration of compound [Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O appeared at 1701 cm^{-1}, which is shifted to a higher wavenumber as compared with the nicotinamide ν_{nad}(C=O) = 1679 cm^{-1}. We suppose that the pyridine nitrogen of nicotinamide is involved in coordination with zinc, therefore, the electron density is shifted towards the pyridine nitrogen, which leads to a shift of

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

Compound	C/%		H/%		N/%		S/%		Br/%		Zn/%	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
[Zn(4-Brbenz)$_2$(H$_2$O)$_2$] C$_{14}$H$_{12}$O$_6$Br$_2$Zn M_r = 501.45	32.97	33.53	2.05	2.41	–	–	–	–	31.59	31.87	13.04	13.35
[Zn(4-Brbenz)$_2$(u)$_2$]·2H$_2$O C$_{16}$H$_{20}$O$_8$N$_4$Br$_2$Zn M_r = 603.53	32.17	31.84	3.34	3.34	8.88	9.28	–	–	26.54	26.48	10.83	11.06
[Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O C$_{16}$H$_{22}$O$_7$N$_4$S$_2$Br$_2$Zn M_r = 671.70	28.93	29.40	3.35	3.39	8.88	8.57	10.02	9.81	23.09	24.44	10.00	9.74
[Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O C$_{26}$H$_{22}$O$_7$N$_4$Br$_2$Zn M_r = 727.67	42.51	42.91	3.17	3.32	7.97	7.70	–	–	21.69	21.96	8.99	9.13
[Zn(4-Brbenz)$_2$(phen)$_2$] C$_{36}$H$_{32}$O$_6$N$_4$Br$_2$Zn M_r = 841.86	51.63	51.36	4.15	3.83	6.52	6.66	–	–	19.06	18.98	7.77	7.52

Table 2 Solubility of the prepared compounds

Solvent	Compounds				
	$[Zn(4\text{-}Brbenz)_2(H_2O)_2]$	$[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$	$[Zn(4\text{-}Brbenz)_2(tu)_2]\cdot 2H_2O$	$[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$	$[Zn(4\text{-}Brbenz)_2(phen)_2]$
H_2O	w sol	w sol	sol	sol	sol
CH_3OH	sol	sol	sol	sol	w sol
C_2H_5OH	sol	sol	sol	sol	w sol
$(CH_3)_2CO$	insol	w sol	sol	sol	sol
$(C_2H_5)O$	insol	insol	w sol	insol	insol
$CHCl_3$	insol	w sol	w sol	w sol	w sol
CCl_4	insol	w sol	w sol	w sol	w sol
DMF	sol	sol	sol	sol	sol
DMSO	sol	sol	sol	sol	sol

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

Table 3 Characteristic absorption bands/cm^{-1} in IR spectra of prepared compounds

Assignment	Compound				
	$[Zn(4\text{-}Brbenz)_2(H_2O)_2]$	$[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$	$[Zn(4\text{-}Brbenz)_2(tu)_2]\cdot 2H_2O$	$[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$	$[Zn(4\text{-}Brbenz)_2(phen)_2]$
$\nu(O-H)_{H_2O}$	3326m	3446m	3496m	3516m	–
ν(N–H)	–	3345m, 3212m	3379m, 3277m	3367m	–
ν_{ar}(C–H)	3032w	3057w	3097m	3070m	3091s
$\nu(C-H)_{CH_3-}$	–	–	–	–	2961m, 2914m
ν(C=O)	–	1661s	–	1701s	1656s
$\delta(O-H)_{H_2O}$	1651s	1622m	1625s	1620s	–
δ(N–H)	–	1622m, 1179s	1616s, 1165s	1682m, 1155m	–
ν(C=C)	1543s, 1480s	1587m, 1458s	1545m, 1475m	1543s, 1485m	1486m
$\nu_{as}(COO^-)$	1591m	1589m	1591m	1593s	1587s
$\nu_s(COO^-)$	1397m	1404s	1414s	1402s	1394m
$\Delta(COO^-)$	194	185	177	191	193
$\delta_{as}(C-H)_{CH_3-}$	–	–	–	–	1454m
$\delta_s(C-H)_{CH_3-}$	–	–	–	–	1318s
γ_{ar}(C–H)	765s	767s	769s	775s	774s
$\delta(COO^-)$	723m	685m	687w	704s	694m
ν(C–Br)	688m	628w	633w	646w	618m
ν(Zn–O)	457s	470m	463s	465m	454m

ar aromatic, *as* asymmetric, *s* symmetric, *w* weak, *m* medium, *s* strong

ν(C=O) to a higher value. On the other hand, in the case of compounds $[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$ and $[Zn(4\text{-}Brbenz)_2(phen)_2]$, the stretching vibration of the carbonyl group ν(C=O) appeared at 1661 and 1656 cm^{-1}, respectively. These absorption bands are shifted to a lower wavenumber in comparison with the 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 the decrease of the double bond character of the carbonyl group and shifting the stretching vibration of ν(C=O) to a lower value.

Thermal properties

The results of thermal analysis of studied compounds are reported in Table 4.

Table 4 Thermal decomposition of the prepared compounds

Compound	Temperature range/°C	Products of thermal decomposition	Mass loss/%	
			Calc.	Exp.
$[Zn(4\text{-}Brbenz)_2(H_2O)_2]$	120–190	$2H_2O$	7.19	6.73
	250–630	$(4\text{-}BrC_6H_4)_2CO + CO_2$	76.58	76.77
	R_{630}	ZnO	16.23	16.50
$[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$	85–180	$2H_2O$	5.80	4.53
	180–450	$2u + (4\text{-}BrC_6H_4)_2CO$	74.03	76.30
	450–550	CO_2	7.08	6.58
	R_{550}	ZnO	13.09	12.59
$[Zn(4\text{-}Brbenz)_2(tu)_2]\cdot 2H_2O$	95–160	$2H_2O$	5.51	4.66
	160–360	$2tu + (4\text{-}BrC_6H_4)_2CO$	75.30	75.45
	360–640	CO_2	6.74	8.13
	R_{640}	ZnO	12.45	11.76
$[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$	100–165	H_2O	2.47	2.30
	165–750	$2nad + (4\text{-}BrC_6H_4)_2CO + CO_2$	86.35	86.52
	R_{750}	ZnO	11.18	11.05
$[Zn(4\text{-}Brbenz)_2(phen)_2]$	200–450	$2phen + (4\text{-}BrC_6H_4)_2CO$	85.10	82.10
	450–720	CO_2	5.23	5.88
	R_{720}	ZnO	9.67	12.02

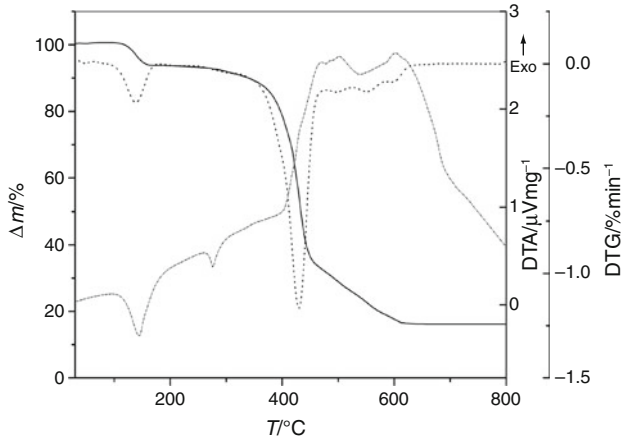


Fig. 1 TG–DTG–DTA curves of $[Zn(4\text{-}Brbenz)_2(H_2O)_2]$

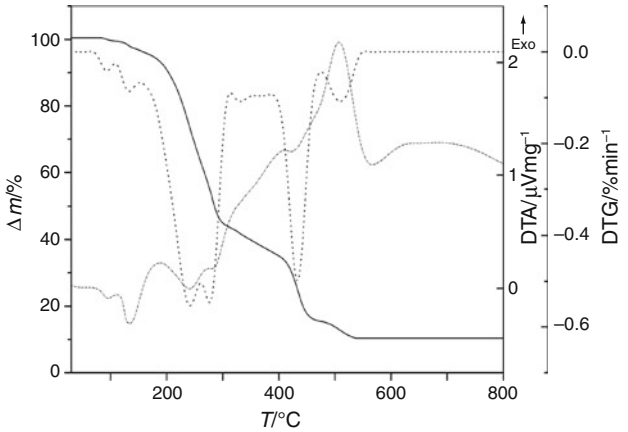


Fig. 2 TG–DTG–DTA curves of $[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$

$[Zn(4\text{-}Brbenz)_2(H_2O)_2]$

The thermal decomposition starts with the release of water, which is accompanied by endothermic effect at 140 °C (exp. 6.73%, calc. 7.19%) (Fig. 1). In the next step, above 250 °C, the release of $(4\text{-}BrC_6H_4)_2CO$ (*m/z* 338, 260, 183, 155) and CO_2 (exp. 76.77%, calc. 76.58%) takes place, which is accompanied with an exothermic effect in temperature range 400–670 °C. The final solid product of thermal decomposition is ZnO. It was confirmed by XRD analysis and IR spectroscopy (ν(Zn–O) = 442 cm^{-1}).

The following equation is proposed for the decomposition process:

$$[Zn(4\text{-}BrC_6H_4COO)_2(H_2O)_2] \xrightarrow{120-190\,^{\circ}C} 2H_2O + [Zn(4\text{-}BrC_6H_4COO)_2]$$

$$[Zn(4\text{-}BrC_6H_4COO)_2] \xrightarrow{250-630\,^{\circ}C} (4\text{-}BrC_6H_4)_2CO + CO_2 + ZnO$$

$[Zn(4\text{-}Brbenz)_2(u)_2]\cdot 2H_2O$

As it can be seen in Fig. 2, in the first stage of the thermal decomposition, the dehydration process occurs in two steps with endothermic effects on DTA curve at 90 and 130 °C (exp. 4.53%, calc. 5.80%). Above 180 °C, the release of urea (*m/z* 60, 44, 16) and $(4\text{-}BrC_6H_4)_2CO$ (*m/z* 338, 260,

183, 155) occurs (exp. 76.30%, calc. 74.03%) with endothermic effects at 240 and 280 °C and exothermic effect at 505 °C. Apart from the mass spectrometry, the release of urea was confirmed by IR spectroscopy of solid intermediate at 250 °C. The absence of characteristic absorption bands of urea was observed (ν(N–H) = 3345, 3212 cm^{-1}, ν(C=O) = 1665 cm^{-1}). In the final step of thermal decomposition, the release of CO_2 (exp. 6.58%, calc. 7.08%) takes place. The solid product is zinc(II) oxide, which was confirmed by XRD analysis and IR spectroscopy (ν(Zn–O) = 490 cm^{-1}).

The decomposition process can be expressed by the following reactions:

$$[Zn(4\text{-}BrC_6H_4COO)_2(u)_2] \cdot 2H_2O \overset{85-180\,^\circ C}{\longrightarrow} 2H_2O + [Zn(4\text{-}BrC_6H_4COO)_2(u)_2]$$

$$[Zn(4\text{-}BrC_6H_4COO)_2(u)_2] \overset{180-550\,^\circ C}{\longrightarrow} (4\text{-}BrC_6H_4)_2CO + CO_2 + ZnO$$

[Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O

Dehydration process takes place in one step up to 160 °C (exp. 4.66%, calc. 5.51%), which is accompanied with an endothermic effect at 140 °C on DTA curve (Fig. 3). In the next step, thiourea (*m*/*z* 76, 60, 16) releases in endothermic effect at 220 °C and (4-$BrC_6H_4)_2CO$ (*m*/*z* 338, 260, 183, 155) with a small endothermic peak at 310 °C (exp. 8.13%, 6.74%). The release of thiourea up to 230 °C was confirmed by IR spectroscopy of the solid intermediate (absence of (ν(N–H) = 3379, 3277 cm^{-1}, δ(N–H) = 1616 cm^{-1}). In the last step of thermal decomposition, the release of CO_2 takes place (exp. 8.13%, calc. 6.74%) with exothermic effect at 510 and 600 °C. The final solid product of thermal decomposition is ZnO (exp. 11.76%, calc. 12.45%) (confirmed by IR spectroscopy (ν(Zn–O) = 440 cm^{-1}).

The following equation expresses the thermal decomposition:

$$[Zn(4\text{-}BrC_6H_4COO)_2(tu)_2] \cdot 2H_2O \overset{95-160\,^\circ C}{\longrightarrow} 2H_2O + [Zn(4\text{-}BrC_6H_4COO)_2(tu)_2]$$

$$[Zn(4\text{-}BrC_6H_4COO)_2(tu)_2] \overset{160-640\,^\circ C}{\longrightarrow} 2tu + (4\text{-}BrC_6H_4)_2CO + CO_2 + ZnO$$

[Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O

The thermal decomposition of this compound is shown in Fig. 4. As it can be seen, this compound is thermally stable up to 100 °C, when the release of H_2O (exp. 2.43%, calc. 2.47%) occured with endothermic effect at 125 °C on the DTA curve. The dehydration step was followed by the release of nicotinamide (*m*/*z* 122, 106, 78) and (4-$BrC_6H_4)_2CO$ (*m*/*z* 338, 260, 183, 155) in endothermic effect at 300 °C, which was followed by the release of CO_2 in a broad exothermic effect in region 400–800 °C on the DTA

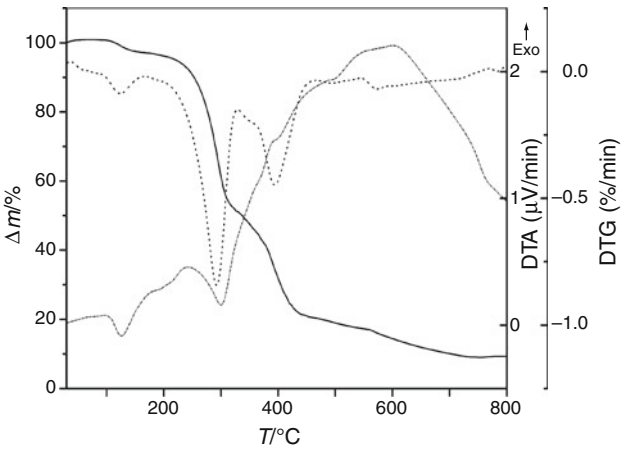


Fig. 4 TG–DTG–DTA curves of [Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O

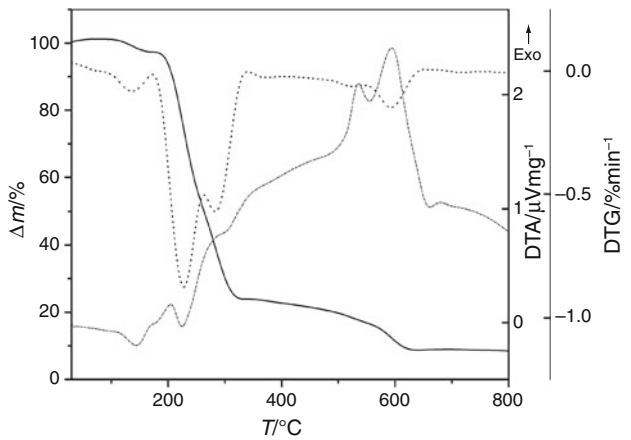


Fig. 3 TG–DTG–DTA curves of [Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O

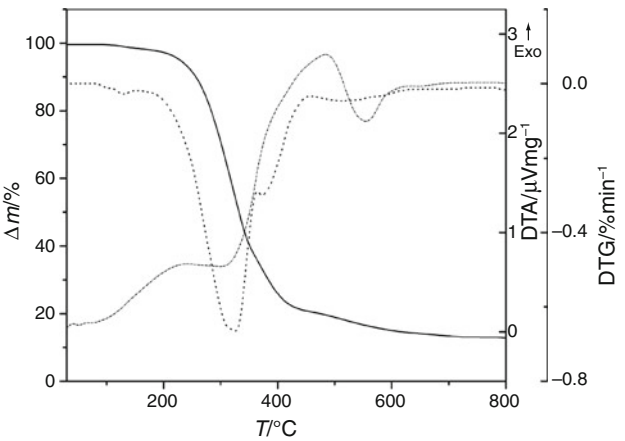
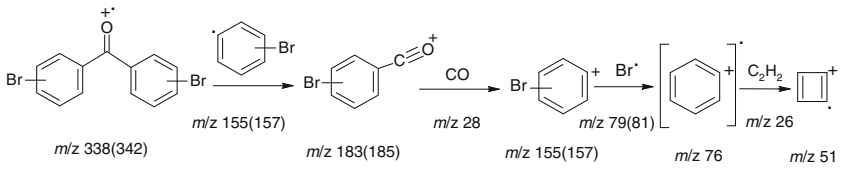


Fig. 5 TG–DTG–DTA curves of [Zn(4-Brbenz)$_2$(phen)$_2$]

Scheme 1 Fragmentation of bis(4-bromophenyl)methanone based on the mass spectrum



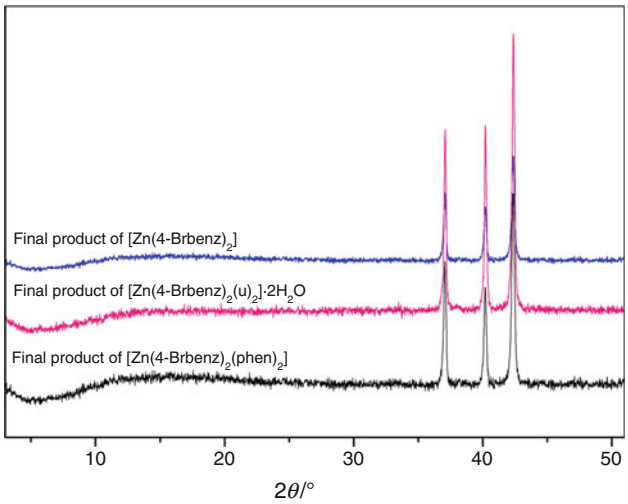


Fig. 6 Results of powder diffractometry

curve. The final solid product of thermal decomposition was ZnO (exp. 11.05%, calc. 11.18%), which was confirmed by XRD analysis and IR spectroscopy (ν(Zn–O) = 488 cm^{-1}). The release of nicotinamide up to 290 °C was confirmed by IR spectroscopy of the intermediate (absence of (ν(N–H) = 3367 cm^{-1}, ν(C=O) = 1701 cm^{-1}).

The thermal decomposition can be expressed as follows:

$$[Zn(4\text{-}BrC_6H_4COO)_2(nad)_2]\cdot H_2O \overset{100-165\,^\circ C}{\longrightarrow} H_2O + [Zn(4\text{-}BrC_6H_4COO)_2(nad)_2]$$

$$[Zn(4\text{-}BrC_6H_4COO)_2(nad)_2] \overset{165-750\,^\circ C}{\longrightarrow} 2nad + (4\text{-}BrC_6H_4)_2CO + CO_2 + ZnO$$

[Zn(4-Brbenz)$_2$(phen)$_2$]

Thermal decomposition of this compound starts above 200 °C by the release of phenazone (*m/z* 188, 173, 96) and (4-BrC$_6$H$_4$)$_2$CO (*m/z* 338, 260, 183, 155) with endothermic effect at 330 °C (Fig. 5). The release of phenazone up to 300 °C was confirmed by IR spectrum of the solid intermediate product of thermal decomposition, where the absorption bands of phenazone (ν(C=O) = 1656 cm^{-1}, δ(C–H) = 1454, 1318 cm^{-1}) were missing. Above 450 °C, carbon dioxide released (exp. 5.88%, calc. 5.23%) and the final solid product of thermal decomposition was ZnO (exp. 12.02%, calc. 9.67%). It was confirmed by IR spectroscopy (ν(Zn–O) = 481 cm^{-1}) and XRD analysis.

The following equation expresses the thermal decomposition:

$$[Zn(4\text{-}BrC_6H_4COO)_2(phen)_2] \overset{200-720\,^\circ C}{\longrightarrow} 2phen + (4\text{-}BrC_6H_4)_2CO + CO_2 + ZnO$$

Table 5 Antimicrobial activity of prepared compounds, bioactive ligands and 4-bromobenzoic acid characterized by the values of IC_{50} and MIC/mmol dm^{-3}

Compound	Bacteria				Yeast		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
[Zn(4-Brbenz)$_2$(H$_2$O)$_2$]	0.23	1[a]	0.73	2[a]	0.50	2[a]	0.70	1[b]	0.52	1[b]	0.60	1[b]
[Zn(4-Brbenz)$_2$(u)$_2$]·2H$_2$O	0.31	1[a]	1	>2	0.60	2[a]	0.35	1[b]	0.50	1[b]	0.70	1[b]
[Zn(4-Brbenz)$_2$(tu)$_2$]·2H$_2$O	0.20	1[a]	0.90	>2	0.68	3[a]	0.45	1[b]	0.30	1[b]	0.62	1[b]
[Zn(4-Brbenz)$_2$(nad)$_2$]·H$_2$O	0.14	1[a]	0.70	2[a]	2.60	>3	0.50	1[b]	0.60	1[b]	0.70	1[b]
[Zn(4-Brbenz)$_2$(phen)$_2$]	0.35	1[a]	1	>2	0.78	2[a]	0.50	1[b]	0.34	1[b]	0.72	1[b]
u	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3	>3	>3
tu	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3	>3	>3
nad	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3	>3	>3
phen	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3	>3	>3
4-Bromobenzoic acid	>2	>2	>2	>2	>3	>3	>3	>3	>3	>3	>3	>3

[a] Microbistatical effect

[b] Microbicidal effect

On the basis of mass spectrum patterns the following mechanism of the fragmentation of bis(4-bromophenyl) methanone was proposed (Scheme 1).

The fragmentations of neutral ligands (urea, phenazone, nicotinamide and thiourea) were proposed in our last paper [13].

The results of XRD analysis correspond with the structural data of ZnO from the literature [26] and are presented in Fig. 6.

Biological properties

Biological activity of compounds were characterized by the IC_{50} and MIC values [mmol dm^{-3}]. The results of microbiological tests are summarized in Table 5. It was found that neither 4-bromobenzoic acid nor any free ligand affected the growth of selected microorganisms ($IC_{50} >$ 3.0 mmol dm^{-3}, MIC > 3.0 mmol dm^{-3}). Thus, it can be concluded that the presence of zinc(II) ion in complexes led to the increase of the inhibitory activity on the growth of selected bacteria, yeasts and filamentous fungi. In comparison with zinc(II) 4-bromobenzoate (IC_{50} = 0.23 mmol dm^{-3}, MIC = 1 mmol dm^{-3}), only the complex with thiourea $[Zn(4\text{-}BrC_6H_4COO)_2(tu)_2]\cdot 2H_2O$ (IC_{50} = 0.20 mmol dm^{-3}, MIC = 1 mmol dm^{-3}) and with nicotinamide $[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$ (IC_{50} = 0.14 mmol dm^{-3}, MIC = 1 mmol dm^{-3}) had a higher inhibitory activity against G^+ bacterium *S. aureus.* Compound $[Zn(4\text{-}Brbenz)_2(nad)_2]\cdot H_2O$ (IC_{50} = 0.70 mmol dm^{-3}, MIC = 2 mmol dm^{-3}) had a higher inhibitory activity against *E. coli* than compound $[Zn(4\text{-}Brbenz)_2(H_2O)_2]$ without neutral ligand (IC_{50} = 0.73 mmol dm^{-3}, MIC = 2 mmol dm^{-3}). The presence of neutral bioactive ligands decreased the biological activity of complexes (IC_{50} = 0.6–2.6 mmol dm^{-3}, MIC = 2–3 mmol dm^{-3}) in comparison with compound $[Zn(4\text{-}Brbenz)_2(H_2O)_2]$ (IC_{50} = 0.5 mmol dm^{-3}, MIC = 2 mmol dm^{-3}) against *C. albicans*. The antifungal activity of compounds with bioactive ligands (IC_{50} = 0.35–0.5 mmol dm^{-3}, MIC = 1 mmol dm^{-3}) is higher than in zinc(II) 4-bromobenzoate (IC_{50} = 0.70 mmol dm^{-3}, MIC = 1 mmol dm^{-3}) against *R. oryzae*. The highest antifungal activity against *A. alternata* was found in the case of compound with thiourea $[Zn(4\text{-}BrC_6H_4COO)_2(tu)_2]\cdot 2H_2O$ (IC_{50} = 0.3 mmol dm^{-3}, MIC = 1 mmol dm^{-3}). Dermatophytic fungi *M. gypseum* was the most sensitive to compound without neutral bioactive ligand $[Zn(4\text{-}Brbenz)_2(H_2O)_2]$ (IC_{50} = 0.6 mmol dm^{-3}, MIC = 1 mmol dm^{-3}).

Conclusions

The thermal decomposition of hydrated compounds started with dehydration process. During the thermal decomposition, the neutral organic ligand, carbon dioxide and bis(4-bromophenyl)metanone were evolved. The final solid product of the thermal decomposition 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) 4-bromobenzoate starts to decompose at the highest temperature and the thermal stability of anhydrous compounds decreases in the following order:

$$[Zn(4\text{-}BrC_6H_4COO)_2] \underset{250\,^\circ C}{>} [Zn(4\text{-}BrC_6H_4COO)_2(phen)_2] \underset{200\,^\circ C}{>} [Zn(4\text{-}BrC_6H_4COO)_2(u)_2] \underset{180\,^\circ C}{>} [Zn(4\text{-}BrC_6H_4COO)_2(nad)_2] \underset{165\,^\circ C}{>} [Zn(4\text{-}BrC_6H_4COO)_2(tu)_2] \underset{160\,^\circ C}{>}$$

On the basis of values of Δ from IR spectra, the monodentate coordination of 4-bromobenzoate group was proposed in all compounds.

It was found that the filamentous fungi are more sensitive to the studied compounds as the selected bacteria. Compound with nicotinamide had the highest antibacterial activity. The presence of neutral ligands decreased the biological activity against *C. albicans* and *M. gypseum*. On the other hand, thiourea and phenazone increased the antifungal activity of 4-bromobenzoatozinc(II) complex compounds against *A. alternata*.

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