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Preparation, characterisation and crystal structure of two zinc(II) benzoate complexes with pyridine-based ligands nicotinamide and methyl-3-pyridylcarbamate

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Abstract

Two benzoate complexes namely tetrakis(μ_2 -benzoato-O,O')-bis(μ_2 -benzoato-O,O)-bis(nicotinamide-N)-tri-zinc(II), [Zn₃(benz)₆-(nia)₂] (I) and bis(benzoato-O)-bis(methyl-3-pyridylcarbamate-N)-zinc(II), [Zn(benz)₂(mpcm)₂] (II) (benz = benzoate anion, nia = nicotinamide, mpcm = methyl-3-pyridylcarbamate) were prepared and characterised by elemental analysis, IR spectroscopy, thermal analysis and X-ray structure determination. The structure of the complex I is centrosymmetric, formed by a linear array of three zinc atoms. The central zinc atom shows octahedral coordination and is bridged to each of the terminal zinc atoms by three benzoate anions. Two of them act as bidentate, one as monodentate ligand. By additional coordination of the nia ligand, the terminal Zn atoms adopt tetrahedral surrounding. The structure of complex II contains two crystallographically independent [Zn(benz)₂(mpcm)₂] molecules. In each molecule, the zinc atom is tetrahedrally coordinated by two monodentate benzoate and two methyl-3-pyridylcarbamate ligands. Intermolecular hydrogen bonds of the N–H…O type connect molecules in the structures of complexes I and II to form a two-dimensional network. The three different types of carboxylate binding found in the complexes were distinguished also by values of carboxylate stretching vibrations in FT-IR spectra as well as by thermal decomposition of the complexes in nitrogen.

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1. Introduction

Aromatic carboxylic acids are widely used in medicine as non-steroidal anti-inflammatory drugs (e.g., ibuprofen, naproxen, diclophenac and fenclofenac) [1– 4]. Moreover, some of the simple aromatic carboxylic acids (benzoic acid and cinnamic acid) are known to have anti-bacterial and anti-fungal properties. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment (Whitfield's ointment) for fungal skin diseases (ringworm) [5]. It can be found in cosmetics, deodorants and toothpastes [6,7]. More widespread is the use of benzoic acid and its salts

^{*} Corresponding author. Tel.: +6228114; fax: +6222124. *E-mail address:* zelenak@kosice.upjs.sk (V. Zeleňák). to preserve food from growth of microorganisms and it can be found in beverages, fruit products, chemically leavened baked goods, condiments as well as in the drink industry (E-codes 210–213) [8–12].

The carboxylic group of the carboxylic acids is available for interactions with metals which can have synergetic or antagonistic effect to the biological activity. It was found that anti-inflammatory and antibacterial activity of metal complexes was higher than in the parent carboxylic acids [3,13]. Moreover, the anti-bacterial effect of some drugs could be enhanced when they are chelated to a metal [14]. Therefore, for the preparation of effective anti-microbial species it is very important to gain knowledge about the structure and bonding relations of the complexes. On the contrary, undissociated benzoic acid is a more effective

anti-microbial agent than its sodium salt, however, sodium benzoate is still used preferably due to its higher solubility in water [12,15].

It is of our interest to study the interaction of the carboxylic acids with zinc, which is an essential and beneficial element in human growth. This element is known to regulate activity over 300 metalloenzymes and it is a component of special proteins, called "zinc fingers" which participate in the reliable transfer of genetic information [16–18]. Zinc and its compounds have antibacterial and anti-viral activity and the wound-healing effect of zinc-containing ointments has been known for several centuries [3,19–23]. Zinc may be used as a therapeutic agent, it may act as an anti-sickling agent and play a role in the prevention of pain crisis in sickle-cell disease. Zinc was successfully used in the treatment of acrodermatitis enteropathica, Wilson's disease, gastrointestinal disorders, infertility and other diseases [24]. Complex of zinc(II) acetate with erythromycin is used in clinical medicine for acne therapy [25,26].

In our previous works, we have described physicochemical properties, crystal structures and biological activity of aliphatic carboxylic acid zinc(II) complexes containing additional N-donor ligands [27]. As a part of our ongoing research with aromatic carboxylic acids, we report in the present study synthesis, crystal structure, thermal and spectral properties of two benzoate complexes, namely tetrakis(μ_2 -benzoato-O,O')-bis(μ_2 -benzoato-O,O)-bis(nicotinamide-N)-tri-zinc(II), [Zn₃(benz)₆ (nia)₂] (I) and bis(benzoato-O)-bis(methyl-3-pyridylcarbamate-N)-zinc(II) [Zn(benz)₂(mpcm)₂] (II) (benz = benzoate anion, nia = nicotinamide, mpcm = methyl-3pyridylcarbamate). The biological activity of these complexes against common bacterial strains is under investigation.

2. Experimental

2.1. Syntheses

All reagents were purchased from Aldrich and used as received.

2.1.1. $[Zn_3(benz)_6(nia)_2]$ (**I**)

About 25 cm³ of aqueous solution of sodium benzoate (0.500 g; 3.47 mmol) was mixed with 25 cm³ of an aqueous solution of zinc sulfate (0.280 g; 1.73 mmol). The pH of the solution was adjusted to 6 using free benzoic acid. After 30 min stirring, the solution was filtered and 20 cm³ of an aqueous solution of nicotinamide (0.141 g; 1.16 mmol) was added to the filtrate. The reaction mixture was stirred for 3 h, then filtered and left to stand at room temperature. After two days, colourless prisms of the complex crystallised. The crystals were filtered off, washed with water and dried. Yield 71%. Anal. Calc. for $C_{54}H_{42}N_4O_{14}Zn_3$: C, 55.57; H, 3.63; N, 4.80; Zn, 16.81. Found: C, 55.49; H, 3.45; N, 4.93; Zn, 16.1%. IR(KBr disk): 3376 s, 3200 s, 3066 w, 3027 vw, 1670 vs, 1630 vs, 1600 vs, 1568 vs, 1541 vs, 1492 w, 1448 m, 1401 vs, 1343 vs, 1308 m, 1204 m, 1176 w, 1157 w, 1133 m, 1097 w, 1071 ww, 1062 m, 1024 m, 1002 w, 942 m, 843 w, 822 w, 802 w, 723 vs, 695 s, 680 m, 660 vw, 639 w, 548 vw, 523 vw, 477 w, 462 w, 422 w, cm⁻¹.

2.1.2. $[Zn(Benz)_2(MPCM)_2]$ (II)

A solution of 0.280 g zinc(II) sulfate (1.73 mmol) in 40 cm^3 of water was added to a solution of 0.500 g (3.47) mmol) of sodium benzoate in 40 cm³ of water. The pH of the solution was adjusted by free benzoic acid to 6. The reaction mixture was stirred for 30 min and filtered. Then, 25 cm³ of an aqueous solution of methyl-3-pyridylcarbamate (0.528 g, 3.47 mmol) was added to this mixture. After stirring for 2 h, the solution was filtered and left to crystallise at room temperature. After two days, needle-like crystals appeared, which were filtered off, washed with water and dried in air. Yield 80%. Anal. Calc. for C₂₈H₂₆N₄O₈Zn: C, 54.96; H, 4.28; N, 9.16; Zn, 10.68. Found: C, 54.72; H, 4.47; N, 9.35; Zn, 10.15%. IR(KBr disk): 3249 m, 3134 w, 3067 m, 2952 w, 1736 vs, 1610 vs, 1556 vs, 1491 s, 1439 s, 1427 s, 1389 s, 1335 m, 1300 w, 1259 s, 1236 vs, 1193 w, 1134 w, 1110 vw, 1076 m, 1056 m, 1025 w, 955 vw, 939 vw, 910 vw, 876 w, 845 w, 808 m, 770 w, 721 s, 698 m, 650 vw, 639 vw, 566 w, $450 \text{ w}, 417 \text{ w}, 389 \text{ w}, \text{ cm}^{-1}$.

2.2. Physical measurements

The infrared spectra of the complexes were recorded with a EQUINOX 55 (Bruker) FT-IR spectrophotometer as KBr discs (complex/KBr mass ratio 1:100). Thermogravimetric (TG) measurements were carried out in dynamic nitrogen atmosphere (sample flow rate 60 ml/min) using Hi-Res mode (G) and an initial heating rate of 5 °C/min by means of TGA Q500 apparatus (TA Instruments). Elemental analyses were performed with a Perkin–Elmer 2400 CHN Elemental Analyser. Zinc content was determined spectrophotometrically by the dithiazone method with a Varian 635 spectrophotometer. The final solid products of the thermal decomposition were analysed by Siemens a D5005 XRD diffractometer using Cu K α radiation.

2.3. Structure determination and refinement

Complex I crystallises as air-stable colourless prisms, whereas complex II forms needle-like crystals. The crystallographic data for both complexes are given in Table 1. Diffraction experiments were performed on IPDS area detector systems (Mo K α radiation, $\lambda = 0.71070$ Å) equipped with graphite monochroma-

Table 1 Crystal data and structure refinement

Empirical formula $C_{y}H_{z}N_{y}O_{x}Zn_{y}$ $C_{z}H_{z}N_{y}O_{z}Zn_{y}$ Formula weight1167.02611.90Crystal parametersrismflat needleCrystal size (mm)0.30 × 0.24 × 0.200.60 × 0.30 × 0.13Crystal size (mm)0.30 × 0.24 × 0.200.60 × 0.30 × 0.13Crystal size (mm)0.30 × 0.42 × 0.200.60 × 0.30 × 0.13Crystal systemorthorhombicorthorhombicSpace groupPbc (No. 61) $P2_12_12$ (No. 19)Unit-cell dimensions u $24_3303(12)$ a (Å)10.1343(4)10.2866(4) b (Å)20.3514(11)22.3253(8) c (Å)24.3803(12)24.4093(15) c (Å)20.3514(1)22.3253(8) c (Å)20.3514(1)23.3253(8) c (Å)20.3514(1)23.351(8) b (Å)20.3514(1)23.353(8) c (Å)24.3803(12)24.4093(15) r_{i} (Å)1.5421.450Molecules per cell, Z48 D_{i} (g cm ⁻¹)1.5421.450Measurement of intensity dataInstrumentInstrumentIPDS (Stoc)IPDS-II (Stoc)Temperature (K)193(1)153(1)Range (°)2.17-28.01.82-29.44Scan mode o o o o o 0 drange (°)2.17-28.01.5376Independent reflections59631.5376Independent reflections59631.5376Independent reflections238422	Formula	$[Zn_3(benz)_6(nia)_2]$	[Zn(benz) ₂ (mpcm) ₂]
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Temperature (K)193(1)153(1)Radiation λ (Å)0.710730.71073MonochromatorgraphitegraphiteScan mode ω ω θ range (°)2.17–28.01.82–29.44Reflections measured34 59315 376Independent reflections596315 376Reflections observed4512 ($I \ge 2\sigma(I)$)10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits -12 to 12 -13 to 14 k -26 to 26 -30 to 30 l -28 to 32 -22 to 33 RefinementgraphitegraphiteRefinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	Instrument	IPDS (Stoe)	IPDS-II (Stoe)
Radiation λ (Å)0.710730.71073MonochromatorgraphitegraphiteScan mode ω ω θ range (°)2.17–28.01.82–29.44Reflections measured34 59315 376Independent reflections596315 376Reflections observed4512 ($I \ge 2\sigma(I)$)10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits h -12 to 12 -13 to 14 k -26 to 26 -30 to 30 -22 to 33 RefinementRefinementFull-matrix least-squares on F^2 full-matrix least-squares on F^2 as racemic twin	Temperature (K)	193(1)	153(1)
MonochromatorgraphitegraphiteScan mode ω ω θ range (°)2.17–28.01.82–29.44Reflections measured34 59315 376Independent reflections596315 376Reflections observed4512 ($I \ge 2\sigma(I)$)10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits-12 to 12-13 to 14 k -26 to 26-30 to 30 l -28 to 32-22 to 33Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	Radiation λ (Å)	0.71073	0.71073
Scan mode ω ω θ range (°)2.17–28.01.82–29.44Reflections measured34 59315 376Independent reflections596315 376Reflections observed4512 ($I \ge 2\sigma(I)$)10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits-12 to 12-13 to 14 k -26 to 26-30 to 30 l -28 to 32-22 to 33Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	Monochromator	graphite	graphite
$\begin{array}{lll} \theta \ \text{range} \ (^{\circ}) & 2.17-28.0 & 1.82-29.44 \\ \text{Reflections measured} & 34593 & 15376 \\ \text{Independent reflections} & 5963 & 15376 \\ \text{Reflections observed} & 4512 \ (I \ge 2\sigma(I)) & 10592 \\ \text{Linear absorption coefficient } \mu \ (\text{mm}^{-1}) & 1.492 & 0.933 \\ F(000) & 2384 & 2528 \\ \text{Reflections for cell measurement} & 8000 \ \text{with} \ 2.25 \le \theta \le 27.95 & 37641 \ \text{with} \ 1.73 \le \theta \le 29.41 \\ \hline \textit{Indices limits} & & \\ h & -12 \ \text{to} \ 12 & -13 \ \text{to} \ 14 \\ k & -26 \ \text{to} \ 26 & -30 \ \text{to} \ 30 \\ l & -28 \ \text{to} \ 32 & -22 \ \text{to} \ 33 \\ \hline \textit{Refinement} \\ \hline \textit{Refinement} \\ \hline \textit{Refinement method} & \text{full-matrix least-squares on } F^2 \\ \hline \text{full-matrix least-squares on } F^2 \\ \hline \end{array}$	Scan mode	ω	ω
Reflections measured34 59315 376Independent reflections596315 376Reflections observed4512 ($I \ge 2\sigma(I)$)10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits-12 to 12-13 to 14 k -26 to 26-30 to 30 l -28 to 32-22 to 33Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	θ range (°)	2.17-28.0	1.82–29.44
Independent reflections596315 376Reflections observed4512 $(I \ge 2\sigma(I))$ 10 592Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits-12 to 12-13 to 14 k -26 to 26-30 to 30 l -28 to 32-22 to 33RefinementFull-matrix least-squares on F^2 full-matrix least-squares on F^2	Reflections measured	34 593	15376
Reflections observed $4512 \ (I \ge 2\sigma(I))$ 10592 Linear absorption coefficient $\mu \ (mm^{-1})$ 1.492 0.933 $F(000)$ 2384 2528 Reflections for cell measurement $8000 \ with \ 2.25 \le \theta \le 27.95$ $37641 \ with \ 1.73 \le \theta \le 29.41$ Indices limits $-12 \ to \ 12$ $-13 \ to \ 14$ h $-26 \ to \ 26$ $-30 \ to \ 30$ l $-28 \ to \ 32$ $-22 \ to \ 33$ RefinementRefinementfull-matrix least-squares on F^2 Refinementfull-matrix least-squares on F^2	Independent reflections	5963	15 376
Linear absorption coefficient μ (mm ⁻¹)1.4920.933 $F(000)$ 23842528Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37 641 with $1.73 \le \theta \le 29.41$ Indices limits-12 to 12-13 to 14 h -26 to 26-30 to 30 l -28 to 32-22 to 33RefinementFull-matrix least-squares on F^2 full-matrix least-squares on F^2	Reflections observed	4512 $(I \ge 2\sigma(I))$	10 592
$F(000)$ 23842528Reflections for cell measurement 8000 with $2.25 \le \theta \le 27.95$ 37641 with $1.73 \le \theta \le 29.41$ Indices limits -12 to 12 -13 to 14 h -26 to 26 -30 to 30 l -28 to 32 -22 to 33 RefinementRefinement methodfull-matrix least-squares on F^2	Linear absorption coefficient μ (mm ⁻¹)	1.492	0.933
Reflections for cell measurement8000 with $2.25 \le \theta \le 27.95$ 37641 with $1.73 \le \theta \le 29.41$ Indices limits -12 to 12 -13 to 14 h -26 to 26 -30 to 30 l -28 to 32 -22 to 33 Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	F(000)	2384	2528
Indices limits h -12 to 12 -13 to 14 k -26 to 26 -30 to 30 l -28 to 32 -22 to 33 RefinementRefinement methodfull-matrix least-squares on F^2	Reflections for cell measurement	8000 with $2.25 \leq \theta \leq 27.95$	37 641 with $1.73 \le \theta \le 29.41$
h -12 to 12 -13 to 14 k -26 to 26 -30 to 30 l -28 to 32 -22 to 33 Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2	Indices limits		
k -26 to 26 -30 to 30 l -28 to 32 -22 to 33 Refinementfull-matrix least-squares on F^2 full-matrix least-squares on F^2 as racemic twin	h	-12 to 12	-13 to 14
<i>l</i> -28 to 32 -22 to 33 <i>Refinement</i> Refinement method full-matrix least-squares on F^2 full-matrix least-squares on F^2 as racemic twin	k	-26 to 26	-30 to 30
Refinement method full-matrix least-squares on F^2 full-matrix least-squares on F^2 as racemic twin	l	-28 to 32	-22 to 33
Refinement method full-matrix least-squares on F^2 full-matrix least-squares on F^2 as received twin	Refinement		
	Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2 as racemic twin
(twin ratio 0.483(5))		-	(twin ratio 0.483(5))
Parameters 346 741	Parameters	346	741
Goodness-of-fit on F^2 0.922 0.803	Goodness-of-fit on F^2	0.922	0.803
R_1 0.0263 (observed); 0.0421 (all) 0.0275 (observed); 0.0463 (all)	R_1	0.0263 (observed); 0.0421 (all)	0.0275 (observed); 0.0463 (all)
wR_2 0.0584 (observed); 0.0617 (all) 0.0527 (observed); 0.0556 (all)	wR_2	0.0584 (observed); 0.0617 (all)	0.0527 (observed); 0.0556 (all)
Maximum and minimum height in final 0.405 and -0.237 0.255 and -0.394	Maximum and minimum height in final	0.405 and -0.237	0.255 and -0.394
difference synthesis (e Å ⁻³)	difference synthesis (e Å ⁻³)		

tors. The details about determination of unit cell parameters and data collection are in Table 1. Data were corrected for Lorentz and polarisation factors. A numerical absorption correction based on indexed faces was applied for both crystals [28]. In both structures the zinc atoms were located from Patterson synthesis using the SHELXS 97 program [29]. Fourier maps, calculated using SHELXL 97 [30], enabled the location of all nonhydrogen atoms. Full-matrix least-squares refinements on F^2 were carried out with anisotropic thermal parameters. Hydrogen atoms were located from difference Fourier syntheses but kept riding on idealised positions [30]. The H atoms of the NH_2 group of complex I only were refined without any constraints. The isotropic thermal parameters were fixed to $1.2U_{eq}$ of the parent atom for all H atoms. All structure drawings were performed using DIAMOND [31]. Selected bond distances and angles are listed in Tables 2 and 3.

3. Results and discussion

3.1. Synthesis

Generally in the preparation of zinc(II) carboxylates, the reaction between carboxylic acid and zinc(II) carbonate or hydroxide is often used and this procedure is also applicable for the preparation of aromatic zinc(II) carboxylates [32–34]. However, due to the lower solubility of aromatic carboxylic acids in water, the synthetic procedure involving the sodium salt of the acid is often used [35,36]. For the preparation of copper(II)

Table 2				
Selected bond	distances (Å) and	angles (°) in the	complex [Zi	13(benz)6(nia)2]

Bond distances			
Zn1-O12	2.061(1)	O22–C20	1.228(2)
Zn1-O21	2.201(1)	C20–C21	1.500(3)
Zn1-O32	2.050(1)	O31–C30	1.275(2)
Zn2011	1.962(1)	O32–C30	1.247(2)
Zn2O21	1.996(1)	C30–C31	1.501(2)
Zn2-O31	1.933(1)	N1-C1	1.342(2)
Zn2–N1	2.023(1)	N1-C5	1.344(2)
O11–C10	1.270(2)	C2–C6	1.504(2)
O12-C10	1.257(2)	O1–C6	1.232(2)
C10-C11	1.499(2)	N12-C6	1.326(2)
O21–C20	1.306(2)		
Bond angles			
O31–Zn2–O11	117.24(6)	Zn2–O21–Zn1	98.57(5)
O31–Zn2–O21	116.47(5)	C1-N1-C5	118.8(1)
O11–Zn2–O21	95.73(5)	N1-C1-C2	122.7(1)
O31–Zn2–N1	105.09(5)	C1–C2–C6	118.2(1)
O11–Zn2–N1	103.13(5)	O1-C6-N12	122.3(1)
O21–Zn2–N1	118.80(5)	O1-C6-C2	120.2(1)
O32 ⁱ –Zn1–O12	84.72(5)	N12-C6-C2	117.4(1)
O32–Zn1–O12	95.28(5)	O12-C10-O11	124.1(1)
O32–Zn1–O12 ⁱ	84.72(5)	O12-C10-C11	119.2(1)
O32 ⁱ –Zn1–O21 ⁱ	91.95(5)	O11-C10-C11	116.6(1)
O32–Zn1–O21 ⁱ	88.05(5)	O22-C20-O21	121.1(2)
O12–Zn1–O21 ⁱ	92.95(4)	O22-C20-C21	121.7(2)
O12 ⁱ –Zn1–O21 ⁱ	87.05(4)	O21-C20-C21	117.1(2)
O32 ⁱ -Zn1-O21	88.05(5)	O32-C30-O31	125.5(2)
O32-Zn1-O21	91.95(5)	O32-C30-C31	118.1(2)
O12–Zn1–O21	87.05(4)	O31-C30-C31	116.5(2)
O12 ⁱ -Zn1-O21	92.95(4)		

i, 1 - x, -y, -z.

complexes of aromatic carboxylic acids containing additional N-donor ligands, Melnik et al. used a two-step synthesis. They prepared crystalline copper carboxylates in a first step, which were consequently used in the second step in the reaction with the N-donor ligand [37,38]. The complexes in this study were prepared by a modified procedure – direct one-step reaction of the sodium benzoate with zinc sulfate and nicotinamide or methyl-3-pyridylcarbamate.

3.2. Description of the structure

3.2.1. Complex $[Zn_3(benz)_6(nia)_2]$ (I)

A view of the structure is shown in Fig. 1, principal bond lengths and angles are summarised in Table 2. The complex crystallises in the orthorhombic space group *Pbca* with four formula units in the unit cell. The structure is formed by a centrosymmetric linear array of three zinc ions, which are coordinated by six benzoate anions and two neutral nicotinamide ligands. The middle zinc atom occupies a special position and lies on a crystallographic inversion centre. This atom is octahedrally coordinated by six oxygen atoms of the benzoate groups. Each of the two terminal zinc ions is coordinated tetrahedrally by three oxygen atoms of benzoate groups and by the nitrogen atom of the pyridine ring of the nicotinamide molecule.

Two different types of carboxylate coordination were found in this complex. Four benzoate ligands are coordinated bidentately by both oxygen atoms of carboxylate group, forming *syn-syn* bridges between central and terminal zinc ions. The other two benzoate ligands are coordinated monodentately and function as *monatomic* Zn–O–Zn bridges with one oxygen atom which remains uncoordinated and involved only in a weak interaction with the zinc atom $(Zn2\cdots O22 = 2.780(1) \text{ Å})$.

Similar structures of a linear array of three metal ions bridged by carboxylate ligands were reported by Clegg et al. [39,40]. They reported the crystal structures of complexes of general formula $[MZn_2(crot)_6(base)_2]$, where M = Zn, Mn, Co, Ni, Cd, Mg, Ca, Sr; crot = crotonate = CH₃CHCHCOO⁻ and base = quinoline = C₉H₇N or 6-methylquinoline = C₁₀H₉N. In this series, the structures of complexes with M = Zn, Mn, Co, Ni, Cd contained, as with complex I, four *syn–syn* and two monodentate *monatomic* crotonate bridges.

Moreover, to *monatomic* crotonate, *monatomic* acetate ligands were also found in zinc complexes, namely $[Zn_3(CH_3COO)_6(py)_2]$, $[Zn_3(CH_3COO)_6(bppz)_2]$, where

Table 3

Selected bond distances	(\mathbf{A})	and angles	(°)	in the	e crystall	ogra	phicall	v inde	pendent	molecul	les of	the con	nplex	[Zn(benz) ₂ (r	npcm)2]
	· · ·		· ·										- ·	L \		· · · /	/4.

Bond distances			
Zn1–O41	1.935(1)	Zn2–O71	1.936(1)
Zn1-O31	1.960(1)	Zn2–O81	1.954(1)
Zn1-N21	2.017(1)	Zn2-N51	2.008(1)
Zn1–N11	2.052(1)	Zn2-N61	2.052(1)
O31–C30	1.282(2)	O82–C80	1.238(2)
O41–C40	1.279(2)	C70–O72	1.242(2)
N22–C26	1.354(3)	C70–O71	1.285(2)
N22–C22	1.398(2)	C70–C71	1.497(3)
C30–O32	1.243(2)	O81–C80	1.285(2)
C30–C31	1.499(3)	C80–C81	1.500(3)
O21–C26	1.212(3)	N62–C66	1.374(2)
O42–C40	1.236(2)	N62-C62	1.383(2)
C12-N12	1.397(2)	O61–C66	1.202(2)
N12-C16	1.370(3)	C66–O62	1.337(2)
C40–C41	1.498(3)	O52–C56	1.352(3)
C26–O22	1.341(2)	C52–N52	1.402(2)
O12-C16	1.346(2)	N52-C56	1.361(3)
O11–C16	1.197(2)	O51–C56	1.196(3)
O12-C17	1.441(3)	O52–C57	1.438(3)
O22–C27	1.442(3)	O62–C67	1.443(2)
Bond angles			
O41–Zn1–O31	108.91(6)	O71–Zn2–O81	109.09(6)
O41–Zn1–N21	121.16(7)	O71–Zn2–N51	118.51(7)
O31–Zn1–N21	112.74(6)	O81–Zn2–N51	111.96(6)
O41–Zn1–N11	109.94(6)	O71–Zn2–N61	111.62(6)
O31–Zn1–N11	95.56(6)	O81–Zn2–N61	94.92(6)
N21–Zn1–N11	105.38(6)	N51-Zn2-N61	108.24(6)
C26-N22-C22	127.2(2)	O72–C70–O71	123.7(2)
O32–C30–O31	123.2(2)	O72–C70–C71	120.1(2)
O32–C30–C31	120.5(2)	O71–C70–C71	116.2(2)
O31-C30-C31	116.2(2)	O82–C80–O81	124.1(2)
C16-N12-C12	125.9(2)	O82–C80–C81	120.6(2)
O42-C40-O41	123.7(2)	O81-C80-C81	115.2(2)
O42-C40-C41	120.5(2)	C66–N62–C62	127.1(2)
O41-C40-C41	115.9(2)	O61–C66–O62	126.0(2)
O21–C26–O22	124.7(2)	O61-C66-N62	126.0(2)
O21-C26-N22	126.7(2)	O62-C66-N62	108.0(2)
O22-C26-N22	108.6(2)	C66–O62–C67	114.9(2)
C26–O22–C27	115.7(2)	C56–O52–C57	114.3(2)
C16-O12-C17	114.5(2)	C56–N52–C52	126.3(2)
O11-C16-O12	125.7(2)	O51-C56-O52	125.2(2)
O11-C16-N12	126.4(2)	O51-C56-N52	127.4(2)
O12-C16-N12	107.8(2)	O52-C56-N52	107.4(2)

py = pyridine, bppz = 2,5-bis(2-pyridyl)pyrazine) [41, 42]. However, to our knowledge, the structure presented is the first where a trinuclear array of zinc ions is formed by aromatic carboxylate species. Such structures formed by benzoate anions were reported with cobalt [43], but not with zinc. Although Clegg et al. [44] successfully synthesised the complex $[Zn_2Co(benz)_6(quinoline)_2]$, which on the basis of spectral data has probably a similar structure, however, the structure of this complex was not solved.

The Zn–O bonds in carboxylate ligands of complex I range from 1.933(1) to 2.201(1) Å and, on an average, they are somewhat longer than values observed for a series of structurally characterised zinc benzoate complexes [32–36,45,46]. Four oxygen atoms of the biden-

tate carboxylate groups form an equatorial plane of the octahedron around Zn1, with distances $2 \times 2.050(1)$ and $2 \times 2.061(1)$ Å, respectively. Apical positions of the octahedron are occupied by oxygen atoms from *monatomic* benzoates (Zn1–O21 distances $2 \times 2.201(1)$ Å). The angles in this octahedron differ only slightly from the ideal 90° value (see Table 2). The tetrahedron around the terminal zinc atoms is formed by two oxygen atoms of two bidentate benzoate groups (Zn2–O31 = 1.933(1) and Zn2–O11 = 1.962(1) Å, respectively), one oxygen atom of *monatomic* benzoate (Zn2–O21 = 1.996(1) Å) and the nitrogen atom of the pyridine ring of nicotinamide (Zn2–N1 = 2.023(1)). The tetrahedron is slightly deformed, due to the *monatomic* binding mode of the carboxylate group and weak



Fig. 1. The structure of the complex $[Zn_3(benz)_6(nia)_2]$.

interaction of the non-bonded carboxylate oxygen with the zinc atom $(Zn2\cdots O22 = 2.780(1) \text{ Å})$. The interatomic $Zn\cdots Zn$ distance (3.1845(2) Å) is somewhat shorter than $Zn\cdots Zn$ distance in trinuclear complexes formed by aliphatic carboxylates [40–42].

The trinuclear molecules are linked by two sets of intermolecular N-H···O hydrogen bonds. In the first of these sets, hydrogen bonds are formed between the hydrogen atom of the amino group of nicotinamide and uncoordinated carboxylate oxygen O22 of monatomic carboxylate bridge. This set of hydrogen bonds connects the trinuclear molecules into chains in the c-axis direction. The second set of hydrogen bonds is formed between the second hydrogen of the amino group of nicotinamide and an oxygen atom O1 of an adjacent nicotinamide molecule. This set of hydrogen bonds is running along the *a*-axis. Considering both sets of hydrogen bonds, trinuclear molecules are interconnected forming a plane parallel with the *ac*-plane (Fig. 2(a)). However, this plane is not "flat" but possesses sinusoidal-like shape (Fig. 2(b)). No hydrogen bonds were found between such planes in the *b*-axis direction. The important parameters of the hydrogen bonding geometry are listed in Table 4.

3.2.2. Complex $[Zn(benz)_2(mpcm)_2]$ (II)

The complex crystallises in an orthorhombic space group $P2_12_12_1$ with eight formula units in the unit cell. The formula unit contains two crystallographically independent $[Zn(benz)_2(mpcm)_2]$ molecules differing strongly in the arrangement of the ligand molecules. A view of the structure is given in Fig. 3. The bond lengths and angles in both molecules differ only slightly and they are summarised in Table 3.

The structure of the complex is molecular. The zinc ion is tetrahedrally coordinated by two monodentate benzoate anions and two neutral methyl-3-pyridylcarbamate molecules. The tetrahedron around the zinc atom is distorted due to the presence of a weak interaction between the uncoordinated carboxylate oxygens and the zinc atoms. The maximum deviations from the ideal value of 109°28' have the angles O31-Zn1-N11 and O81-Zn2-N51 of 95.56(6)° and 94.92(6)°, respectively. The distances of the uncoordinated oxygens from the zinc atoms vary from 2.847(1) to 2.946(1) A. These distances are longer than the distances of non-bonded carboxylate oxygen in complex I and are comparable to the other zinc(II) benzoate complexes with monodentate coordination of the benzoate group and containing an additional organic ligand [46-48]. In each of these two crystallographically independent molecules, the Zn-O distances are not the same (see Table 3). A similar behaviour can be observed in the Zn–N bond lengths. This is a consequence of the hydrogen bonding geometry discussed below. The bond lengths in the methyl-3pyridylcarbamate molecule are within the distances observed for similar complexes containing this ligand [49,50].



Fig. 2. Hydrogen bonding geometry in the complex $[Zn_3(benz)_6(nia)_2]$. Zinc atoms are displayed as black spheres, oxygen atom as dashed and nitrogen atoms as grey spheres. (a) View of two-dimensional network parallel with *ac*-plane. Benzene rings are omitted for clarity purposes. (b) View along *a*-axis displaying sinusoidal-like shape of the formed planes.

The molecules are held together by hydrogen bonds formed by the hydrogen atoms of the imino groups in the methyl-3-pyridylcarbamate ligands and non-coordinated oxygens of the benzoate anions. These bonds run along the a and b axes forming a two-dimensional network parallel to the ab-plane and connect as well crystallographically same and crystallographically independent molecules. No hydrogen bonds were found between these planes, in the *c*-direction. These hydrogen bonds significantly influence the Zn–O and Zn–N bond lengths in both molecules. If the hydrogen atom and oxygen atom, which form the intermolecular hydrogen bond, are in the crystallographically same molecules (see bonds N12–H12···O42ⁱ and N62–H62···O72ⁱⁱ in Table 4), the Zn–N distances have longer values (Zn1– N11 = 2.052(1) and Zn2–N61 = 2.052(1) Å, respectively)

D–H	D–H (Å)	H···A (Å)	DHA (°)	$D \cdots A$ (Å)	А
Complex I					
N12-H12B	0.85(2)	2.07(2)	159(2)	2.880(2)	O1 $[x - 1/2, y, -z + 1/2]$
N12-H12A	0.88(2)	1.97(2)	173(2)	2.847(2)	O22 $[x - 1/2, y, -z + 1/2]$
Complex II					
N12-H12	0.880	2.04	160	2.887(2)	O42 $[1/2 + x, 5/2 - y, -z]$
N22-H22	0.879	1.99	165	2.845(2)	O82
N52–H52	0.879	1.96	164	2.820(2)	O32
N62–H62	0.880	2.04	168	2.905(2)	O72 $[-1/2 + x, 3/2 - y, -z]$

and the Zn–O distances have shorter values (Zn1– O41 = 1.935(1) and Zn2–O71 = 1.936(1) Å, respectively) than in the case when the intermolecular hydrogen bonds (N22–H22···O82 and N52–H52···O32 in Table 4) are formed between crystallographically independent molecules. The details of this hydrogen bonding geometry are shown in Fig. 4 and are summarised in Table 4.

3.3. Spectroscopic studies

The IR data of the complexes are listed in Section 2. In the spectra of both complexes, the stretching vibrations of N–H and C–H groups are observed in the region above 3000 cm⁻¹. The stretching vibrations of aliphatic C–H groups of methyl-3-pyridylcarbamate are at 2952 cm⁻¹. Moreover, the presence of N-donor organic ligands of nicotinamide and methyl-3-pyridylcarbamate is evident from the presence of strong absorption bands of the carbonyl v(C=O) vibration at 1670 and 1732 cm⁻¹, respectively.

For the IR spectra of carboxylates, the stretching vibrations of the carboxylate group $v_{as}(COO)$ and $v_{\rm s}({\rm COO})$ are characteristic. In the studied complexes, their assignment has to be made carefully due to the presence of aromatic rings in both benzoate and N-donor organic ligands, whose stretching vibrations fall in the same region of the spectrum as the stretching vibrations of the carboxylate group. Therefore, we have compared the spectra of these complexes with the data presented in the literature for related complexes [34,44] as well as with the spectrum of zinc benzoate, nicotinamide and methyl-3-pyridylcarbamate. The anti-symmetric carboxylate stretches $v_{as}(COO)$ were found at 1630, 1568 cm⁻¹ in complex I and at 1610 cm⁻¹ in complex II. The symmetric $v_s(COO)$ stretches were found at 1448 and 1401 cm⁻¹ in complex I and 1427 cm^{-1} in complex II. In accordance with the literature data, we suppose that the bands at 1630 and 1448 cm^{-1} in complex I are due to anti-symmetric and symmetric stretching vibrations of the two monodentate benzoate



Fig. 3. The two crystallographically independent molecules of [Zn(benz)₂(mpcm)₂].



Fig. 4. Two-dimensional network formed by hydrogen bonds (dashed lines) in the complex [Zn(benz)₂(mpcm)₂]. View along the *c*-crystallographic axis. The zinc atoms in crystallographically independent molecules are displayed as black and hatched spheres, respectively. The other atoms in the crystallographically independent molecules are displayed as grey and white spheres, respectively. The benzene rings as well as hydrogen atoms not involved in the intermolecular hydrogen bonds are omitted for clarity.



Fig. 5. TG/DTG curves of the complexes $[Zn_3(benz)_6(nia)_2]$ (curve 1) and $[Zn(benz)_2(mpcm)_2]$ (curve 2) during heating in N₂.

groups and the bands at 1568 and 1401 cm^{-1} are due to stretches of the four *syn–syn* bidentate benzoate ligands [34,44]. It is important to notice the trend of the change of the values of the carboxylate stretches in both complexes. The lowest values of $v_{as}(COO)$ and $v_s(COO)$ (1568 and 1401 cm⁻¹, respectively) are observed for *syn*syn benzoate groups in complex I, in which the similar distribution of electron density is expected for both C-O bonds. These values are higher in complex II (1610 and 1427 cm^{-1}), where only monodentate carboxylate coordination occurs and the electron density distribution in both C-O bonds is different. As a consequence, the frequencies of the carboxylate stretches are shifted to higher values, closer to the region of v(C=O) vibration in free carboxylic acids. Finally, the vibrations of monodentate benzoate groups occur at the highest values (1630 and 1448 cm⁻¹, respectively). The coordinated oxygen atom is simultaneously bonded to two zinc ions, which probably leads to the higher electron withdrawing from unbounded oxygen and to the shift in

anti-symmetric as well symmetric vibrations of the carboxylate group.

In the region below 1300 cm⁻¹, a number of bands due to deformation vibrations of C–H and N–H groups as well as vibrations of aromatic ring were observed and respective values are listed in Section 2.

3.4. Thermal studies

The results of the thermogravimetric analysis are presented in Fig. 5. The thermal decomposition of the complex $[Zn_3(benz)_6(nia)_2]$ well reflects its crystal structure. The sample is thermally stable up to 165 °C. Above this temperature, in the range 165-210 °C, two molecules of nicotinamide are evolved (calc. mass loss 20.9%, observed 20%). This decomposition takes place in one step, which is in accordance with the symmetry of the complex and the equivalence of the nicotinamide molecules through the inversion centre. Further heating leads to the decomposition of the zinc(II) benzoate, which takes place in two different steps. In the first step in the range 210–305 °C, decomposition of two benzoate anions takes place and we suppose that the two monodentately bonded bridging benzoate ligands are evolved in this step. Heating above 320 °C leads to very rapid and complete pyrolysis of the rest of the organic part of the molecule, i.e., decomposition of four syn-syn benzoate bridges. The white colour of the final solid residue was in accordance with the results of XRD, which confirmed a hexagonal *wurtzite* structure.¹ The careful inspection of the weight losses during the last two thermal decomposition steps enabled us to make some further conclusions about the decomposition of benzoate ligands and formation of final solid residue. From the observed weight loss in the range 210-305 °C, we suppose that in the *monatomic* benzoate bridges fracture of C-O bonds between carbon atoms of carboxylate group and bridging oxygen atoms took place to form two free radicals $C_6H_5C(O)$, which were liberated and probably further reacted to form benzil C₆H₅CO-COC₆H₅ (calc. mass loss 18.1%, observed 18%). Such formation of radicals was observed also by Sun et al. [51] in zinc phthalate. The two oxide atoms formed by this fracture remained bonded to zinc atoms and used in zinc oxide formation found in the final solid residue. Similar fracture of one of the four *syn–syn* carboxylate bridges also probably took place in the final decomposition step above 320 °C, while the other three syn-syn benzoate ligands decompose by another mechanism and we suppose that they are liberated entirely. The calculated weight loss considering this proposal is 40.1% and observed weight loss was 42%. The amount of the final solid residue (20%) is in accordance with the value 20.9% calculated for ZnO.

The thermal decomposition of the sample $[Zn(benz)_2(mpcm)_2]$ significantly differs from complex I described above. The first striking difference can be found already by visual comparison of the solid residues. Instead of a white zinc oxide observed after the thermal analysis of the complex $[Zn_3(benz)_6(nia)_2]$, a black powder was found after the thermal analysis of [Zn(benz)₂(mpcm)₂]. The powder XRD showed the presence of zinc² as well as an amorphous component, which we suppose to be carbon. The thermogravimetric curves of the thermal decomposition of this complex are shown in Fig. 5. The complex is thermally stable up to 130 °C. We suppose that in the first step the benzoate ligands are broken in the temperature range 130–200 °C. The temperature 130 °C is approximately 80 °C lower than the decomposition temperature of the benzoate ligands in complex I. We suppose that this is due to the fact that in complex I each of the benzoate ligands is bonded to zinc atoms by two bonds, instead of one bond formed by the monodentate coordination in complex II. Moreover, considering the composition of the solid residue, we suppose that no fracture of C–O bonds took place. The calculated weight loss, considering the release of two benzoate ligands, is 39.6% and observed weight loss in the range 130-200 °C is 37%. The release and pyrolysis of methyl-3-pyridylcarbamate ligands starts at 200 °C. This temperature is similar to that observed by Mojumdar et al. [52] for the release of methyl-3-pyridylcarbamate from magnesium complexes. The pyrolysis of mpcm ligands took place in two steps in the temperature ranges 200-310 and 310-450 °C. However, the release of the ligands was not complete and some carbonisation occurred during the pyrolysis. Due to this carbonisation, the amount of solid residue (22 wt%) is higher than the value calculated for zinc or zinc oxide (10.7% and 13.3%, respectively).

4. Supplementary material

Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 211577 (complex I) and CCDC 211576 (complex II), respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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