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Synthesis, spectral, thermal and structural study of bis(2-bromobenzoato-*O*,*O*')-bis(methyl-3-pyridylcarbamate-*N*)-zinc(II)

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ABSTRACT

The new complex bis(2-bromobenzoato-O,O')-bis(methyl-3-pyridylcarbamate-N)-zinc(II), [Zn(2-BrC₆H₄COO)₂mpc₂] (**1**), has been prepared and characterized by elemental analysis, IR spectroscopy, thermal analysis and single-crystal X-ray diffraction. The bonding between the ligands and the central atom was investigated by DFT studies. The theoretical infrared spectrum of **1** was compared with the experimental data. The complex proved to be thermally stable up to 165 °C. Volatile intermediate products of its thermal decomposition were identified by mass spectrometry. The coordination environment of the zinc atom consists of two nitrogen atoms of two methyl-3-pyridylcarbamate ligands and is chelated by four oxygen atoms of two 2-bromobenzoate ligands (ZnO₄N₂ – chromophore).

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1. Introduction

Several aromatic carboxylic acids (e.g. benzoic acid, salicylic acid) are known to have antibacterial and antifungal properties [1,2]. For metal carboxylate complexes it has been found that their antibacterial activity is higher than that of the parent carboxylic acid [3].

Our interest is aimed at studying compounds of halogenobenzoic acids with zinc, which can have a considerable effect on many biological processes. Zinc(II) complexes with organic ligands have proved to be useful in clinical medicine, e.g. for acne therapy [4]. Moreover, organic ligands can contribute to a better transport of metal ions through the lipophylic regions of cell membranes [5]. In addition, heterocyclic compounds play a significant role in many biological systems, e.g. vitamins. Therefore heterocyclic compounds such as nicotinamide, methyl-3-pyridylcarbamate and theophylline, incorporated in complexes as ligands have been investigated by many authors and their biological activities have been examined [6]. The thermal behaviour of several aliphatic zinc(II) carboxylate complexes with methyl-3-pyridylcarbamate was investigated by Szunyogová et al. [7]. Győryová et al. studied the thermal, spectral and structural properties of aliphatic zinc(II) carboxylates and halogenocarboxylates [8–11], and zinc(II) halogenosalicylates [12] with different bioactive ligands.

For the preparation of effective antimicrobial species it is important to gain information about the structure of the com-

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pound. It has been observed that the antibacterial effect can be enhanced when the ligands are chelated to the metal [13]. Zeleňák et al. [14] investigated Zn(II) benzoate complexes with pyridine based ligands. They found that for the zinc(II) benzoate complex with methyl-3-pyridylcarbamate, the metal atom is tetrahedrally coordinated by two monodentate benzoate and two heterocyclic ligands. Intermolecular hydrogen bonds connect the molecules to form a two-dimensional network. Maroszová et al. [15] studied the structural properties of a zinc(II) 2-chlorobenzoate complex with methyl-3-pyridylcarbamate. They found that the zinc atom is coordinated by two nitrogen atoms from two methyl-3-pyridyl-carbamate ligands and four oxygen atoms from two bidentate 2-chlorobenzoate anions in a pseudo-octahedral geometry. The molecules are linked into a chain by hydrogen bonds.

The present work deals with the structural and bonding characterization, thermal and spectral properties of the new monomeric complex $[Zn(2-BrC_6H_4COO)_2mpc_2]$.

2. Experimental

2.1. Materials and instrumentation

The following A. R. grade chemicals were used for the preparation of the studied compound: $ZnCl_2$ (Fluka), Na_2CO_3 (Mikrochem a.s. Pezinok), 2-bromobenzoic acid 97% (Aldrich), methyl-3-pyridylcarbamate (Merck) (Scheme 1).

The carbon, hydrogen and nitrogen content in the newly synthesised compound was determined on a CHN analyser PERKIN EL-

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Scheme 1. Methyl-3-pyridylcarbamate (mpc).

MER 2400. The zinc content was determined by complexometry using Complexone III as an agent and Eriochrome black T as an indicator. The IR spectrum of the prepared zinc complex compound was recorded on an AVATAR 330 FT-IR Thermo Nicolet spectrometer using KBr pellets (2 mg/200 mg KBr), operating in the range 4000–400 cm⁻¹. The thermal measurements were carried out in air using ceramic crucibles under dynamic conditions on a NET-ZSCH STA 409 PC/PG Thermoanalyzer (heating rate 9 °C min⁻¹) with a sample mass of 24.970 mg, in the temperature range 26–900 °C. A GC/MS Agilent 7890A mass spectrometer (heating rate 30 °C min⁻¹ from 100 °C up to 280 °C) was used for determination of volatile intermediate products of the thermal decomposition.

2.2. Synthesis

Compound 1 was synthesised as follows: ZnCO₃ was prepared by the reaction of an aqueous solutions of 1.35 g (10 mmol) ZnCl₂ and 1.06 g (10 mmol) Na₂CO₃. The freshly prepared aqueous suspension of ZnCO₃ was added in excess to the methanol solution of 2.58 g 97% 2-bromobenzoic acid under continual stirring. The reaction mixture was stirred for 1 h at 70 °C. Excess ZnCO3 was filtered off using an S4 frit and the filtrate was left for crystallization at room temperature. After several days a white powdery compound of $[Zn(2-BrC_6H_4COO)_2]$ was formed (2.46 g, 5 mmol, yield: 83%). Afterwards, 1.61 g (10 mmol) of methyl-3-pyridylcarbamate was dissolved in methanol and added gradually to the methanol solution of zinc(II) 2-bromobenzoate. The reaction mixture was stirred for 2 h at 50 °C and the solution was reduced in volume at 70 °C in a water bath and left to crystallise at room temperature. After a few days colourless crystals of 1 were formed (2.69 g, 3.5 mmol, yield: 70%).

Anal. Calc. for C₂₈H₂₄O₈N₄Br₂Zn (MW: 769.70): C, 43.66; H, 3.14; N, 7.28; Zn, 8.49. Found: C, 43.93; H, 3.13; N, 7.25; Zn, 8.46%.

IR (KBr, cm⁻¹): 3310s [ν (N–H)]; 3098m, 3066m [ν_{ar} (C–H)]; 2951 m [ν (C–H)_{–CH3}]; 1732 s [ν (C=O)]; 1613s [δ (N–H)]; 1593s, 1491s, 1467m [ν (C=C, C=N)]; 1542s [ν_{as} (COO⁻)]; 1437s [δ_{as} (C–H)_{–CH3}]; 1398s [ν_{s} (COO⁻)]; 1335m [δ_{s} (C–H)_{–CH3}]; 1028s, 641m [ν (C–Br)]; 756s [γ (C–H)]; 709m [γ (N–H)]; 695s [δ (COO⁻)].

GC/MS (m/z): 152 [$C_7H_8N_2O_2$], 120 [$C_6H_4N_2O$], 107 [$C_5H_4N_2O$], 92 [$C_5H_4N_2$], 78 [C_5H_4N], 51 [$C_4H_3^+$], 42 [\cdot NCO], 32 [CH₃OH], 28 [CO], 27 [HCN].

2.3. X-ray crystallographic study

Diffraction data for a suitable single crystal of **1** were collected on a Nonius Kappa CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å) and processed by the HKL program package [16]. The phase problem was solved by direct methods (SIR97) [17], and refined by full-matrix least-squares on F^2 (SHELX97) [18]. Hydrogen atoms were refined isotropically, while all the other atoms anisotropically. The hydrogen atom on N17 was located from difference Fourier maps and refined without any constraints. Hydrogen atoms on the aromatic rings were included in ideal positions with C–H bonds fixed to 0.95 Å and U_{iso} (H) assigned to 1.2 U_{eq} of the adjacent carbon atom; terminal methyl group hydrogen atoms were included in ideal positions with C–H bonds fixed to 0.98 Å and U_{iso} (H) assigned to 1.5 U_{eq} of the pivot atom (Table 1).

Tab	le	1				
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Crystal data and structure refinement for **1**

Empirical formula	$C_{28}H_{24}Br_2N_4O_8Zn$
Formula weight	769.70
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system, space group	orthorhombic, Pccn (No. 56)
Unit cell dimensions	
a (Å)	15.8880(4)
b (Å)	13.2252(3)
<i>c</i> (Å)	13.4622(2)
$V(Å^3)$	2828.70(10)
$Z, D_{\text{calc}} (\text{Mg/m}^3)$	4, 1.807
Absorption coefficient (mm ⁻¹)	3.752
F(000)	1536
Crystal size (mm ³)	$0.48 \times 0.08 \times 0.05$
θ Range for data collection	2.00-27.47
Refinement method	full-matrix least-squares on F ²
Data/restraints/parameters	3237/0/200
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0300, wR_2 = 0.0581$
R indices (all data)	$R_1 = 0.0491, wR_2 = 0.0640$
Largest difference peak and hole ($e Å^{-3}$)	0.435 and -0.413

2.4. Computational details

DFT studies have been carried out at the fermi cluster at the I. Hevrovský Institute of Physical Chemistry, Academy of Sciences of Czech Republic, using GAUSSIAN 03, Revision E.01 [19]. All calculations used the Becke exchange [20] and the Perdew/Wang 91 correlational [21] functionals. For a proper elucidation of the theoretical infrared spectrum, the solid-state structure has been optimized using the 6-311+G(3d,p) basis set [22] employed for all atoms and an analytical Hessian determined before the first step of the optimization procedure. Numerical integration was done on a pruned grid having 99 radial shells each of 590 angular points. The IR spectrum was computed after the optimization step yielded a proper stationary point where no imaginary frequencies were present. No scaling was employed for the obtained bands. Natural bonding analysis [23] was carried out by the NBO 3.1 [24] program integrated in Gaussian. To remove any side effects of possible near linear dependencies in the basis set due to the incorporation of diffuse functions, the NBO analysis and Mayer bond order [25] determination were carried out employing only the 6-311G(3d,p) basis set on the optimized geometry. Visualization and examination of molecular orbitals was accomplished by MOLDEN [26].

3. Results and discussion

3.1. Synthesis and properties of the prepared compound

Several methods of preparing zinc(II) carboxylate compounds are described in the literature [14,27,28]. Methods involving either the reaction of the sodium salt of the carboxylic acid with zinc sulfate, or the reaction between carboxylic acid and zinc(II) carbonate can be used.

The compound **1** was synthesised according to the following reactions:

$$\begin{split} &ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 \downarrow + 2NaCl \\ &ZnCO_3 + 2(2\text{-}BrC_6H_4COOH) \rightarrow [Zn(2\text{-}BrC_6H_4COO)_2] + H_2O + CO_2 \uparrow \\ &[Zn(2\text{-}BrC_6H_4COO)_2] + 2 \text{ mpc} \rightarrow [Zn(2\text{-}BrC_6H_4COO)_2\text{mpc}_2] \end{split}$$

The prepared complex, $[Zn(2-BrC_6H_4COO)_2mpc_2]$, is colourless, and is stable to light and air at ambient temperature. It exhibits a very good solubility in methanol, acetone and DMSO, and is insoluble in chloroform and water.

3.2. Crystallographic characterization

Compound **1** crystallized with an orthorhombic lattice (space group *Pccn*) and with an exact molecular twofold symmetry, thus only one half of the molecule is located in the asymmetric part of the unit cell. The symmetrically dependent part of the molecule is generated by a twofold rotation around the axis passing through the central atom. The whole molecule is depicted in Fig. 1; selected bond distances and angles are listed in Table 2.

The coordination environment of the zinc atom consists of two nitrogen atoms from the mpc ligand and four oxygen atoms from the two 2-bromobenzoate carboxylate groups, making up an octahedral environment. This octahedron is however significantly distorted. Although the two least-squares planes, both containing one nitrogen and three oxygen atoms (cf. Table 3) do not suffer from large deviances of their constituent atoms, the geometry constrains imposed by the presence of the rather rigid carboxylate group leads to a large deflection of the oxygen atoms from the ideal positions at the octahedron vertices.

The driving force of the solid state packing is the presence of an infinite network of hydrogen bridges, chaining the hydrogen atom of one mpc NH group and one carboxylate oxygen atom from one neighbouring molecule (Table 4, Fig. 2).

3.3. Spectroscopic and thermal properties

In the case of carboxylate compounds, the values of the asymmetric and symmetric vibrations of COO⁻ are important. In the

Table 2

Selected bond lengths [Å] and angles [°] for 1

$Zn(1)-N(11); Zn(1)-N(11)^{i}$	2.1151(19)
$Zn(1)-O(9); Zn(1)-O(9)^{i}$	2.1389(17)
$Zn(1)-O(8); Zn(1)-O(8)^{i}$	2.2208(17)
$Zn(1)-C(7); Zn(1)-C(7)^{i}$	2.508(2)
$C(7)-O(8); C(7)^{i}-O(8)^{i}$	1.256(3)
$C(7)-O(9); C(7)^{i}-O(9)^{i}$	1.263(3)
$N(11)-Zn(1)-N(11)^{i}$	95.37(10)
$N(11)-Zn(1)-O(9); N(11)^{i}-Zn(1)-O(9)^{i}$	97.89(7)
$N(11)^{i}-Zn(1)-O(9); N(11)-Zn(1)-O(9)^{i}$	90.98(7)
$O(9)-Zn(1)-O(9)^{i}$	166.83(9)
$N(11)^{i}-Zn(1)-O(8); N(11)-Zn(1)-O(8)^{i}$	150.91(7)
$N(11)-Zn(1)-O(8); N(11)^{i}-Zn(1)-O(8)^{i}$	91.86(7)
$O(8)-Zn(1)-O(9); O(8)^{i}-Zn(1)-O(9)^{i}$	60.09(6)
$O(8)^{i}$ -Zn(1)-O(9); O(8)-Zn(1)-O(9)^{i}	110.14(6)
$O(8) - Zn(1) - O(8)^{i}$	95.38(9)
$N(11)^{i}-Zn(1)-C(7); N(11)-Zn(1)-C(7)^{i}$	121.21(8)
$N(11)-Zn(1)-C(7); N(11)^{i}-Zn(1)-C(7)^{i}$	93.29(7)
$O(9)-Zn(1)-C(7)^{i}$	139.99(7)
$O(8) - Zn(1) - C(7)^{i}$	106.88(7)
$C(7)-Zn(1)-C(7)^{i}$	129.39(11)

Symmetrically equivalent atoms generated by:

prepared compound, $[Zn(2-BrC_6H_4COO)_2mpc_2]$, the stretching vibrations of the aromatic rings of 2-bromobenzoate and the heterocyclic ligand fall in the same region of the spectrum as the stretching vibrations of the carboxylate group, therefore the IR spectrum of $[Zn(2-BrC_6H_4COO)_2mpc_2]$ has been compared with the spectrum of $[Zn(2-BrC_6H_4COO)_2]$ and methyl-3-pyridylcarba-



Fig. 1. Solid state structure of 1. Displacement ellipsoids are drawn at the 30% probability level. Symmetrically dependant atoms are labelled with a terminal 'a'.

⁽i): -x + 1/2, -y + 1/2, z.

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Table 3

Least-squares planes and deviations of individual atoms from them

Plane 1		Plane 2	
Atom	Deviation	Atom	Deviation
09	0.0251(6)	O9 ⁱ	0.0251(6)
N11	-0.0308(7)	N11 ⁱ	-0.0308(7)
O8 ⁱ	-0.0383(10)	08	0.0383(10)
09 ⁱ	0.0440(11)	09	0.0440(11)

The distance of Zn1 from both planes is 0.1379(9) Å, the angle between the two planes is $89.39(4)^{\circ}$.

Table 4

Hydrogen bonds with H - A < r(A) + 2.000 Å and DHA > 110° in solid state

D-H	d(D–H)	$d(H \cdots A)$	∠DHA	<i>d</i> (D…A)	А
N17-H17	0.774 Å	2.115 Å	150.12°	2.813 Å	O8 [− <i>x</i> + 1/2, <i>y</i> , <i>z</i> − 1/2

D denotes the donor and A the acceptor atom.

mate. The vibration observed at 1541 cm^{-1} was assigned as $v_{as}(COO^{-})$ and that at 1397 cm^{-1} as $v_{s}(COO^{-})$.

The strong absorption band of the carbonyl v(C=O) vibration at 1732 cm⁻¹ is slightly shifted to a higher wavenumber as compared with the free methyl-3-pyridylcarbamate (1727 cm⁻¹). This is in agreement with the results of Bellamy and Akbar Ali [29,30]. It can be explained by the fact that the pyridine nitrogen of methyl-3-pyridylcarbamate ligand is involved in coordination with zinc, therefore the electron density in the ligand is shifted towards the pyridine nitrogen, leading to the increase in the double bond character of the carbonyl group and shift the stretching vibration v(C=O) to a higher value.

The most significant stretching and deformation vibrations are listed in Section 2.

Table 5

Comparison of the experimental and the theoretical values of the IR absorption bands

ssignment Experimental (KBr) [cm ⁻¹]		Theoretical [cm ⁻¹]
v(N–H)	3310s	3530
var(C-H)	3098m, 3066m	3164-3102
$(v(C-H)_{-CH_2})$	2951m	2990
v(C=0)	1732s	1749
v(C=C, C=N)	1593s, 1491s, 1467m	1596, 1527, 1476
$v_{as}(COO^{-})$	1542s	1563
$(\delta_{as}(C-H)_{-CH_2})$	1437s	1456
v _s (COO ⁻)	1398s	1376
v(C-Br)	1028s, 641m	1008, 637
δ(COO ⁻)	695s	697

The experimentally obtained and calculated IR spectra of $[Zn(2-BrC_6H_4COO)_2mpc_2]$ are in good agreement (Table 5), with the notable exception of the N–H vibration. However, this particular hydrogen atom is part of a hydrogen bridge in the solid state (see above), which leads to a prolongation of the N–H bond. The latter phenomenon could not be reflected by the computational studies as these were performed on one single molecule only.

The results of thermogravimetric analysis are presented in Fig. 3. It was found that the studied complex compound is thermally stable up to 165 °C. Above this temperature the thermal decomposition is accompanied by the loss of methyl-3-pyridylcarbamate and CO_2 (calc. mass loss 51.07%, exp. 51.44%). The released methyl-3-pyridylcarbamate was confirmed by mass spectrometry (Fig. 4). The next step of the thermal decomposition is the release of bromobenzene (calc. mass loss 40.79%, exp. 42.67%). Zinc is the solid product of the thermal decomposition (calc. 8.49%, exp. 7.75%). The following reaction is proposed for the thermal decomposition of the investigated compound:



Fig. 2. Solid state packing of 1. View along [100].



Fig. 4. Mass spectrum of [Zn(2-BrC₆H₄COO)₂mpc₂] heated up to 280 °C.

 $[Zn(2\text{-}BrC_6H_4COO)_2mpc_2] \rightarrow 2\ mpc + 2\ CO_2 + 2\ C_6H_5Br + Zn$

Based on the mass spectrum pattern, we propose the following fragmentation scheme for methyl-3-pyridylcarbamate:



This assumption is in a good agreement with the results of pyridine fragmentation proposed by Smith [31].

3.4. Computational studies

The IR spectrum of 1 (discussed above) and the nature of the bonding between the central atom and its ligands was investigated by DFT calculations. As expected for a Zn(II) compound, the calculations suggest a predominantly ionic character of the ligand coor-

dination, with only a slight covalent contribution. The overall low ratio of the covalent contribution from the ligands can be conveniently deduced by examination of the crystal orbital overlap population (COOP) diagram (Fig. 5), depicting the value of the overlap integral between the ligands and the central atom versus orbital energies. In accordance with their lower electronegativity, an increased covalency ratio was observed for the two nitrogen atoms, since the total contribution from the 2-bromobenzoate ligand has to be partitioned among four oxygen atoms.

The apparent proximity of the carboxylate carbon atom and the central zinc atom could suggest a partial (covalent) bonding between them; however, Mayer bond order [25] analysis disproved any such possibility (Table 6). The carboxylate oxygen atoms thus coordinate as separate entities and the coordination environment of the central atom cannot be described as pseudotetrahedral by considering the centre of gravity of the carboxylate group only.

According to the results of natural bonding analysis [23], the electronic configuration of the central zinc atom is [Ar] $4s^{0.42}3d^{9.96}4p^{0.02}$, proving the presence of a zinc divalent cation, calling for primarily electrostatic interactions with the ligands.



Fig. 5. The COOP diagram of 1.

Table 6

Mayer bond orders between the central zinc atom and selected donors

Atoms	Mayer bond order(s)
Carboxylate oxygens	0.222, 0.204
Carboxylate carbons	0.015
mpc nitrogens	0.223

4. Conclusion

The present work describes the synthesis and characterization of $[Zn(2-BrC_6H_4COO)_2mpc_2]$. It was found out that the zinc is coordinated by two nitrogen atoms from two methyl-3-pyridylcarbamate ligands and by four oxygen atoms from two bidentate 2-bromobenzoates in a pseudo-octahedral geometry. The molecules are linked into a chain by hydrogen bridges between the NH group of methyl-3-pyridylcarbamate and one carboxylate oxygen atom from a neighbouring molecule.

According to our computational studies, the prevalence of an electrostatic interaction between the zinc divalent cation and two carboxylate anions of 2-bromobenzoate ligands was proved. A somewhat greater covalent contribution was observed only for the two nitrogen atoms of the methyl-3-pyridylcarbamate ligands. A notable bonding interaction between the two carboxylate carbon atoms and the central atom was disproved.

Acknowledgements

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Appendix A. Supplementary data

CCDC 686772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.09.017.

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