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SYNTHESIS AND CHARACTERIZATION OF BIS(CARBOXYLATO)ZINC(II) (C_6 - C_8) - CRYSTAL STRUCTURE OF BIS(HEXANOATO)ZINC(II), $Zn(O_2CC_5H_{11})_2$ - FORM A[#]

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Abstract

Different synthetic routes were used for the preparation of zinc(II) alkyl carboxylates with 6 - 8 carbon atoms. Isolated products were characterised by standard physicochemical methods. Powder diffraction patterns, IR spectra, DTA curves and ^{13}C solid state NMR spectra indicate presence of two different polymorphic forms in the case of hexanoate and heptanoate. No fungicidal activity of isolated compounds was observed.

Crystal structure of $Zn(O_2CC_5H_{11})_2$ - form **A** was determined by X-ray single-crystal method. Each Zn atom is coordinated tetrahedrally by oxygen atoms of four different hexanoate ligands while each hexanoate ligand is bridging two tetrahedral zincs in *syn-anti* mode thus forming a typical layered structure.

Introduction

Carboxylate complexes of transition metals have been subject of many studies. Besides their practical importance in industry, these compounds exhibit very interesting physicochemical properties which also make them a challenge to fundamental investigation [1]. Recent studies on the formation of zinc carboxylates revealed that the structures of the

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[#] Dedicated to the memory of Prof. Dr. Jože Šiftar compounds formed depend mainly on the R group of the carboxylic acid and only partly on reaction conditions [2] and suggested that the alkyl chain has a much more important role in the formation and stability of the structure through the interactions between neighbouring chains than previously believed [3]. Our interest in metal carboxylates evolves from their biological implications with emphasis on possible correlation between chemical and biological properties of synthesised compounds.

Experimental

Commercially available substances as ZnO, $ZnSO_4 \cdot 7H_2O$, $Zn(O_2CCH_3)_2 \cdot 2H_2O$, hexanoic, heptanoic and octanoic acid and all solvents were used without further purification. The zinc contents of weighed samples were determined by EDTA titration after fuming the samples twice with a 1 : 2 mixture of concentrated sulphuric and nitric acids.

Synthesis

Bis(hexanoato)zinc(II), $Zn(O_2CC_5H_{11})_2$ *- form* **A**

0.814 g ZnO and 5.0 mL hexanoic acid (100 % excess) were added to 25 mL of ethanol and the obtained suspension was refluxed. After one hour the solution became transparent, but reflux was continued for one hour. The solution was left at room temperature for 20 h. The colourless plate-like crystals were filtered off, washed with ethanol and dried in evacuated desiccator over KOH. Average yield 96 %. *Anal.* Calcd. for $Zn(O_2CC_5H_{11})_2$ (M_r=295.7): Zn 22.11 %; found 22.4 %. From X-ray powder data the following *d* spacings (Å) were observed (relative intensities in parentheses): 8.1 (4), 5.4 (4), 4.72 (1), 4.58 (3), 4.38 (10), 4.16 (5), 4.00 (2), 3.88 (8), 3.83 (7).

The same form of bis(hexanoato)zinc(II) was obtained by alternative methods: from $ZnSO_4 \cdot 7H_2O$ with hexanoic acid and KOH in ethanol by already described procedure [4], from $ZnSO_4 \cdot 7H_2O$ with sodium hexanoate in water and from $Zn(O_2CCH_3)_2 \cdot 2H_2O$ with sodium hexanoate in water. In all cases the obtained yields are lower therefore the details of the procedures are not given.

Monocrystals of $Zn(O_2CC_5H_{11})_2$ - form **A** were obtained by following procedure: 0.5 g of crude product was added to 100 mL of water, warmed and left at boiling temperature for one minute. The undissolved product was filtered off and the solution was cooled to room temperature and left in refrigerator at 0 ºC for one week. 100 mL of ethanol were added and the solution was left at 0 ºC. Monocrystals suitable for structure determination were collected from solution after another week.

Bis(hexanoato)zinc(II), $Zn(O_2CC_5H_{11})_2$ - form **B**

0.90 g of form **A**, obtained from ZnO by reaction with hexanoic acid in ethanol, were dissolved in 125 mL of benzene at boiling temperature. The undissolved starting material was filtered off and the solution was cooled slowly to room temperature and left in the refrigerator over night. Transparent colourless crystalline product was filtered, dried on air without washing and then over KOH for 24 hours. Average yield 33.5 %.

Anal. Calcd. for $Zn(O_2CC_5H_{11})_2$ (M_r= 295.7): Zn 22.11 %; found 22.2 %. The following *d* spacings (Å) were observed (relative intensities in parentheses): 8.1 (4), 5.4 (3), 4.59 (7), 4.38 (8), 4.13 (10), 3.98 (3), 3.90 (8), 3.84 (2), 3.63 (6).

Bis(heptanoato)zinc(II), $Zn(O_2CC_6H_{13})_2$ - **A** *and* **B**, *and bis(octanoato)zinc(II), $Zn(O_2CC_7H_{15})_2$*

Similar synthetic procedures were used for reactions with heptanoic and octanoic acid. While in the case of bis(heptanoato)zinc(II) the formation of two polymorphic forms was observed - form **A** after different synthetic routes described above, and form **B** with recristallization from benzene, only one form of bis(octanoato)zinc(II) was obtained. Measured *d*-values with relative intensities for three isolated products are given in Table 1. Results of Zn analysis were within expected experimental errors.

Table 1. Measured *d*-values in Å (with relative intensities in parentheses) for $Zn(O_2CC_6H_{13})_2$ - form **A (2A)**, $Zn(O_2CC_6H_{13})_2$ - form **B (2B)**, and $Zn(O_2CC_7H_{15})_2$ **(3)**.

2A	9.3(4)	6.15(3)	4.61(2)	4.52(2)	4.45(7)	4.37(8)	4.19(1)	4.07(1)	4.00(8)
	3.9(1)	3.77(6)	3.72(9)						
2B	9.3(3)	6.2(3)	4.62(5)	4.53(6)	4.25(8)	4.2(1)	3.87(2)	3.78(6)	3.72(8)
3	10.5(3)	7.0(3)	4.63(2)	4.59(2)	4.35(6)	4.28(5)	4.07(1)	3.93(8)	3.9(1)
	3.79(1)	3.52(3)	3.47(3)						

Physical Measurements

Interplanar spacings were obtained with HUBER GUINIER CAMERA 620 using CuK_α radiation (Johansson monochromator). Infrared spectra were measured on Nujol or Fluorolube mulls between CsI plates using Perkin-Elmer FT-IR 1720X spectrometer in the range 4000-400 cm^{-1}. DTA curves were obtained using a Mettler 2000 C thermoanalyzer. Experimental conditions: platinum crucibles 7.0 mm in diameter, sample weights 20 mg, heating rate 2 °C min^{-1}, atmosphere of dry argon., α-Al_2O_3 as a reference substance for DTA measurements. ^{13}C solid state NMR spectra were recorded with Varian Unity-plus 300 at the National NMR Center of Slovenia. Experiments were carried out at 75.41 MHz using cross-polarization (CP) and magic-angle spinning (MAS) at 3.5-4.0 kHz with high-power ^1H decoupling, 1.9 ms CP contact time and a 5 s recycle time, using 7 mm probe from Doty. Typically 1000-5000 accumulations were acquired. Spinning sidebands were eliminated using the TOSS technique.

Single crystal diffraction measurements were carried out on an Enraf-Nonius CAD-4 diffractometer with MoK_α radiation (graphite monochromator). Cell parameters were obtained from refinement of 75 reflections in θ range 8.53 - 15.56 ° using PARAM [5]. Common data corrections for variations in reference reflections and Lorentz-polarization effects were applied (DATRD2 in NRCVAX) [6]. Absorption correction was preformed by

Gaussian integration method (ABSORP in NRCVAX) [6]. SHELXS [7] was used to solve and SHELXL [8] to refine the structure. Details of crystal data and data collection are presented in Table 2.

All H atoms were placed at calculated positions with isotropic thermal displacement parameters taken from the parent non-H atoms and multiplied by 1.2. Scattering factors of all atoms were taken from the reference [9]. Final values of R_1 (wR_2) factors are 0.0302 (0.0719) for 2670 observed reflections and 0.0512 (0.0785) for all 3466 data.

Table 2. Crystal and data collection summary for $Zn(O_2CC_5H_{11})_2$ - form **A**

Asymmetric Unit Formula	$Zn(O_2CC_5H_{11})_2$
Crystal System	monoclinic
Space Group	$P2_1/c$ No.14
a (Å)	32.395(3)
b (Å)	4.7914(2)
c (Å)	9.3450(8)
β (°)	93.661(1)
Volume (Å^3)	1447.5(2)
Z	4
D_x (Mg/m^3)	1.357
μ (mm^{-1})	0.1697
Crystal Colour	colourless
Crystal Shape	plate
Crystal Size (mm)	0.15x0.61x0.69
Intensity Decay (%)	1.1
T_{min}/T_{max}	0.3774/0.8171
Radiation	MoK_α, $\lambda = 0.710930$ Å
Diffractometer	Enraf-Nonius CAD-4
Scan Type	ω/2θ
Measured Reflections	3466
Observed Reflections [I>2(σ)I]	2670
R_{int}	0.0441

Results and Discussion

Different synthetic routes were used for the preparation of bis(carboxylato)zinc(II) complexes with 6-8 carbon atoms. Reproducible, although small differences in powder patterns were the first indication for the presence of two modifications in the case of hexanoato and heptanoato ligands. The most prominent features of the IR spectra are the carboxylate stretching frequencies characterised by strong bands between 1650 and 1400 cm^{-1}. Very similar patterns for antisymmetric ($\nu_{as}CO_2$) and symmetric (ν_sCO_2) stretching modes of carboxylate groups and almost identical values of differences Δ between them (Table 3) are the consequence of the bidentate bridging positions of carboxylate ligands in all isolated compounds [10]. Small differences in the structure of strong band centered at 1460 cm^{-1} corresponding to the antisymmetric deformations of CH_3 and scissoring modes of CH_2 groups (Figure 1) indicate different interactions of alkyl chains in different polymorphic forms. This proposal is confirmed with the observed values of ^{13}C chemical shifts in the solid state NMR spectra (Table 4).

Table 3. IR absorption bands in carboxylate stretching region for $Zn(O_2CC_5H_{11})_2$ - form **A (1A)**, $Zn(O_2CC_5H_{11})_2$ - form **B (1B)**, $Zn(O_2CC_6H_{13})_2$ - form **A (2A)**, $Zn(O_2CC_6H_{13})_2$ - form **B (2B)**, and $Zn(O_2CC_7H_{15})_2$ **(3)**.

Compound	$\nu_{as}(CO_2)$, cm^{-1}	$\nu_s(CO_2)$, cm^{-1}	$\Delta\nu$, cm^{-1}
1A	1548, 1532	1409, 1398	136
1B	1548, 1537, 1532	1408, 1398	136
2A	1548, 1531	1409, 1399	136
2B	1546, 1532	1409, 1399	135
3	1549, 1532, 1527	1408, 1398	133

Table 4. ^{13}C NMR chemical shift data (ppm relative to TMS)

Compound	**$\delta(CH_3)$**	**$\delta(CH_2)$**	**$\delta(CO)$**
$Zn(O_2CC_5H_{11})_2$ - **A**	15.3	27.4, 30.2, 36.3, 38.5	186.3
$Zn(O_2CC_5H_{11})_2$ - **B**	15.3	26.1, 28.5, 37.3[a]	185.2
$Zn(O_2CC_6H_{13})_2$ - **A**	16.9	27.4, 30.2, 34.9, 37.7	186.4
$Zn(O_2CC_6H_{13})_2$ - **B**	16.7	27.4, 30.0, 34.9, 37.5	186.0
$Zn(O_2CC_7H_{15})_2$	16.8	27.2, 30.2, 37.2[a]	186.3

[a] Broad

Figure 1. IR spectra of $Zn(O_2CC_6H_{13})_2$ - form **A**, (A) and $Zn(O_2CC_6H_{13})_2$ - form **B**, (B) in carboxylate stretching region.

There are three types of carbon for each carboxylate ligand. A single resonance at 185.8 ∀ 0.6 ppm in all spectra corresponds to carboxyl carbon and another at 16.1 ∀ 0.8 ppm to methyl carbon. Significant differences in the positions and shapes of resonances corresponding to methylen carbons in the range 26.1 - 38.5 ppm in the case of two polymorphic forms of hexanoato and heptanoato complexes also indicate possible differences in interactions between carboxylate chains or their different orientations. All observed values of chemical shifts are in agreement with published results for other metal carboxylate complexes [11].

Although thermal decomposition of isolated compounds has not been studied in details, two stage decomposition leading to ZnO as the only obtained solid residue was proved by powder pattern. Symmetrical ketones and carbon dioxide are the most probable gaseous products in all cases in agreement with observed thermal decomposition for salts of many carboxylic acids [12]. The only significant difference is observed in DTA curves of two polymorphic forms of hexanoato and heptanoato complexes in low temperature range, where no mass loss was observed (Figure 2). Polymorphism was observed in some other metal carboxylates, with different crystalline modifications being formed on crystallisation from solution and on cooling from melt [12, p. 4]. In the case of zinc carboxylates the differences in DTA curves, indicating different phase changes on heating premelted samples or samples obtained by recrystallisation from benzene was already described [13]. The irreversible transformation of $Zn(O_2CC_5H_{11})_2$ - form **B** and $Zn(O_2CC_6H_{13})_2$ - form **B** to form **A** was observed in both cases, when the samples were repeatedly heated to 155 °C (slightly over melting point) and cooled to room temperature. The observed changes in DTA curves were confirmed by powder patterns of solid residues after the third cycle. The presence of two polymorphic forms was confirmed in the case of bis(acetato)zinc(II) [14a,b] and bis(propionato)zinc(II) [14c,d] by X-ray structure determination.

All isolated compounds were screened for fungicidal activity by preliminary tests described previously [15]. All of them showed no significant fungicidal activity against *Trametes versicolor.*

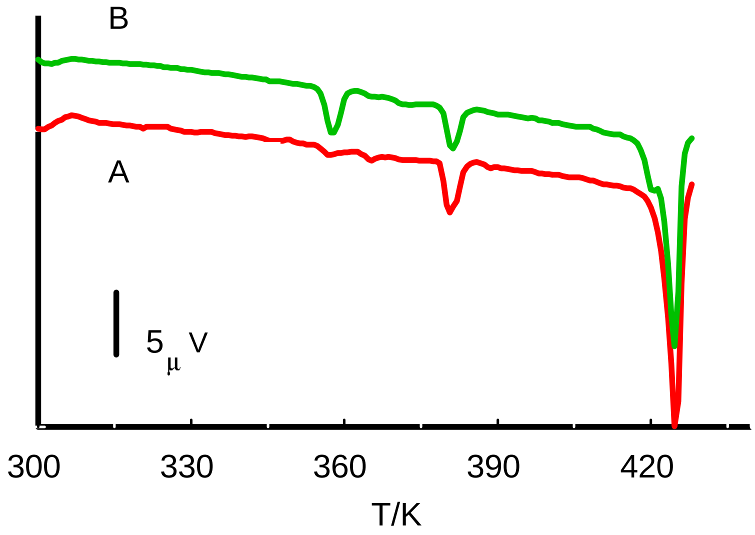

Figure 2. DTA curves of two polymorphic forms of $Zn(O_2CC_5H_{11})_2$ in temperature range, where no mass loss was observed: form **A** - (A), and form **B** - (B).

Crystal structure of $Zn(O_2CC_5H_{11})_2$ - form A

The title compound belongs to the family of polymeric anhydrous zinc(II) carboxylates and crystallizes in monoclinic space group $P2_1/c$. It is isostructural with the previously published Zn(II) propionate [14d]. Each Zn atom is tetrahedrally coordinated by carboxylate O atoms from four different monodentate hexanoato ligands as illustrated in Figure 3. Selected bond lengths and angles are presented in Table 5.

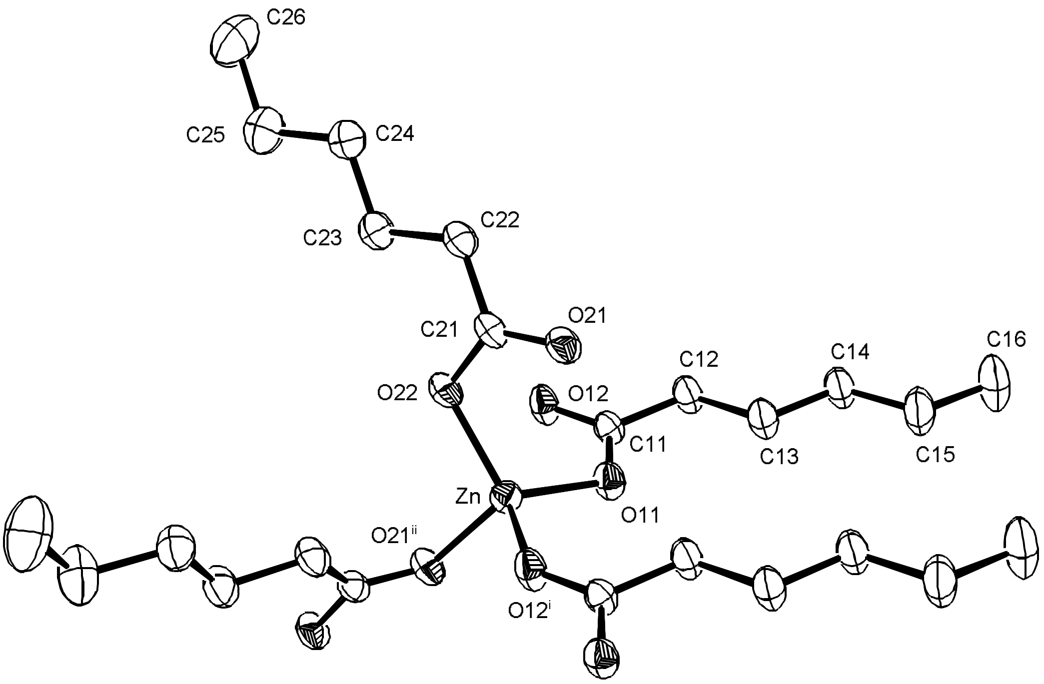

Figure 3. ORTEP-III view of the coordination around zinc. Thermal ellipsoids are drawn with 30% probability level. Hydrogen atoms are omitted for clarity.

It is noticeable that the Zn-O distances are significantly different in two crystallographicaly different hexanoate groups. Zn-O21 and Zn-O22 are lengthened slightly compared to Zn-O11 and Zn-O12. Similar discrepancy was observed in Zn(II) propionate [14d]. Alkyl chains are in fully extended, all-trans configuration. Mean value of C-C bond lengths is 1.516(7) Å which is common for similar systems.

Table 5. Interatomic Distances (Å) and Angles (°) with Estimated Standard Deviations

Bond lengths and angles			
Zn-O11	1.954(1)	Zn-O21^{ii}	1.964(1)
Zn-O12^{i}	1.952(1)	Zn-O22	1.964(1)
O11-C11	1.261(2)	O21-C21	1.270(2)
O12-C11	1.262(2)	O22-C21	1.263(2)
C11-C12	1.502(2)	C21-C22	1.507(3)
C12-C13	1.519(3)	C22-C23	1.511(3)
C13-C14	1.525(3)	C23-C24	1.526(3)
C14-C15	1.520(3)	C24-C25	1.518(3)
C15-C16	1.521(3)	C25-C26	1.516(4)
O11-C11-O12	120.9(2)	O21-C21-O22	120.5(2)

Symmetry code: i) x, y-1, z and ii) x, 0.5-y, 0.5+z

Zn atoms are linked with *syn-anti* hexanoate bridges forming two-dimensional polymer sheets paralel to bc plane. A similar sheet structure is observed not only for isostructural propionate [14d], but also for monoclinic form of Zn(II) acetate [14b] . There is no covalent bonding between sheets (Figure 4). The closest contacts between alkyl chains of hexanoate groups are: 4.105(3) Å for C12-C13 (x,1+y,z), 4.139(3) Å for C14-C15(x,1+y,z), 4.072(3) Å for C22-C24 (x, y-1,z) and 4.115(4) Å for C23-C25(x, y-1,z) which might be characterized as weak hydrophobic interactions.

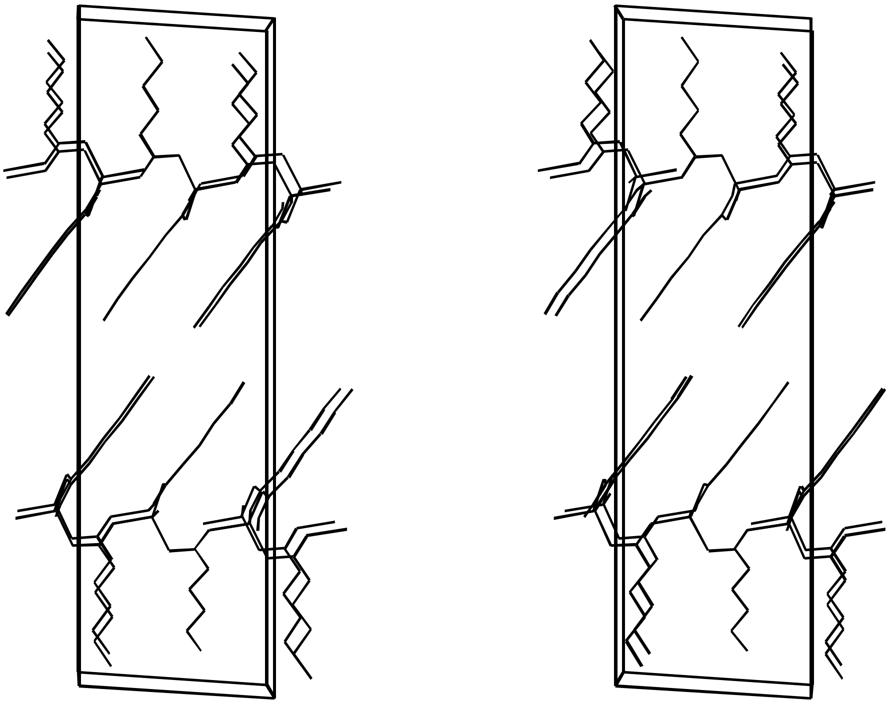

Figure 4. The PLUTON [16] stereoview of the packing in the unit cell.

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Povzetek

Po različnih sintetskih poteh smo pripravili cinkove soli karboksilnih kislin s 6 - 8 C atomi. Vse izolirane spojine so bile okarakterizirane s standardnimi fizikalno kemijskimi metodami. Praškovni posnetki, IR spektri, DTA krivulje in ^{13}C spektri v trdnem kažejo na prisotnost dveh polimorfnih oblik v primeru koordinacijski spojin s heksanoato in heptanoato ligandom. Nobena od sintetiziranih spojin ne kaže fungicidne aktivnosti.

Kristalna struktura $Zn(O_2CC_5H_{11})_2$ - oblika A je bila določena z rentgensko strukturno analizo. Cinkovi atomi so tetraedrično koordinirani s kisikovimi atomi štirih različnih heksanoato ligandov. Heksanoato skupine kot mostovni ligandi povezujejo po dva cinkova atoma na *syn-anti* način, pri čemer nastane tipična plastovita struktura.