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Preparation, Structure and Thermal Decomposition of Zinc(II) Complex with 2,5-Dichlorobenzoic Acid

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Zinc(II) carboxylates adopt a variety of structures. Features common to all so far reported compounds are a tetrahedral coordination of Zn atoms and a bridging function for the carboxylate ligands. The benzoate [1] and crotonate [2] form polymeric chains, in which $Zn_2(carboxylate)_3^+$ binuclear units with three syn-syn bridges are connected by single syn-anti carboxylates. Only syn-syn bridges occur in the structure of the 2-chlorobenzoate [3,4]. In 4-chlorobenzoate [5] with Zn atom placed on a two fold axis and the coordination polyhedron around it forms a very deformed tetrahedron with four normal Zn–O bonds. The same type of very deformed tetrahedral coordination, as well as similar additional weak interactions, was found in both the salicylate complex [6] and the nitrobenzoate complex [7]. Tetrahedral coordination of the Zn atom was also observed in the aminobenzoate complex [8]. As a part of our study on the synthesis, crystal structure, properties and biological activity of zinc carboxylates with and without additional ligands, the title complex was isolated and its crystal structure determined.

The dichlorobenzoate of Zn(II) was obtained by adding hot 0.1 M ammonium 2,5-dichlorobenzoate solution (pH = 5.5) to a 0.2 M solution of Zn(II) nitrate. The precipitate formed was heated in its mother liquor for 1 h, filtered off, washed with water to remove NH_4^+ ions, and dried at 303 K to constant mass. The analytical results agree with the calculated data.

IR spectra were recorded over the range of 4000–400 cm^{-1}. The spectra of free dichlorobenzoic acid, Zn(II) and Na(I) dichlorobenzoates are summarized in Table 1. In the IR spectrum of the free acid there is a single strong absorption band at 1704 cm^{-1} (COOH group). In the IR spectrum of the Zn(II) complex, this absorption band disappears and a split band of symmetrical OCO vibrations (ν_s) appears at 1410 and 1371 cm^{-1}, as well as a band of asymmetrical vibrations (ν_{as}) at 1581 cm^{-1}. The broad absorption bands of ν(OH) can be found at 3431 cm^{-1} and a narrow band of $\delta(H_2O)$ at 1593 cm^{-1} confirms the presence of crystal water. The bands of ν(C–Cl) appear at 760 and 798 cm^{-1} and are insignificantly displaced compared to ν(C–Cl) of the free acid, suggesting that the Cl atoms do not participate in the metal ligand bonding. The split band of ν_s(OCO) suggests a different way of coordination of OCO^- groups in the complex. This suspicion was confirmed by the X-ray analysis. The separation values

($\Delta\nu$) of ν_{as}(OCO) and ν_s(OCO) amount to 210 and 171 cm^{-1}, suggesting that carboxylate groups act as bridging and ionic bonded ligands, respectively. The C$\cdots$C and C–H vibrational bands of the Zn(II) complex change their frequencies only insignificantly, compared to the corresponding bands of the sodium salt and the free acid. This means that the Zn(II) ion in the complex does not deform the aromatic ring, an assumption which was confirmed by the crystal structure determination.

Table 1. Frequencies for characteristic absorption bands in the IR spectra of 2,5-dichlorobenzoic acid and its Zn(II) and Na(I) complexes (cm^{-1}).

HL	NaL	ZnL$_2$	Assignment
512_v		472_v	φ(CC)
529_v	521_w	520_v	φ(CC)
616_w	604_w	614_w	φ(CC)
666_w	665_v	666_w	γ(CC)
742_m	763_m	760_m	ν(C–Cl)
784_v	813_s	798_m	ν(C–Cl)
866_m	878_w	885_v	β_s(OCO)
1053_w	1052_m	1052_s	β(CH)
1109_m	1099_s	1100_s	β(CH)
1256_s	1246_v	1253_v	ν(C...C)
1295_s	1275_v	1273_v	ν(C...C)
		1371_s	ν_s(OCO)
	1408_s	1410_s	ν_s(OCO)
1438_v	1438_w		ν(C...C)
1458_w	1459_m	1463_w	ν(C...C)
1508_w	1495_s		ν(C...C)
1559_w	1554_s	1555_m	ν(C...C)
	1581_s	1581_s	ν_{as}(OCO)
	1635_m	1595_{vs}	δ(H$_2$O)
1704_{vs}			ν(OCO)
	3459_m	3431_m	ν(OH)

s – strong, m – medium, w – weak, v – very.

The thermal stability of the Zn(II) complex was determined by TG, DTG and DTA. Zn(II)2,5-dichlorobenzoate is stable in air at room temperature. It decomposes during a heating rate of 10 K min^{-1} and 5 K min^{-1} (Fig. 1). 2,5-Dichlorobenzoate of Zn(II) is stable up to 393 K and then loses two crystal water molecules. Heated above 613 K, the tetrahydrated complex decomposes to gaseous products. Similary behave Zn(II) complexes with 2,3- [9], 2,4- [10] and 3,4-dichlorobenzoic acids [11].

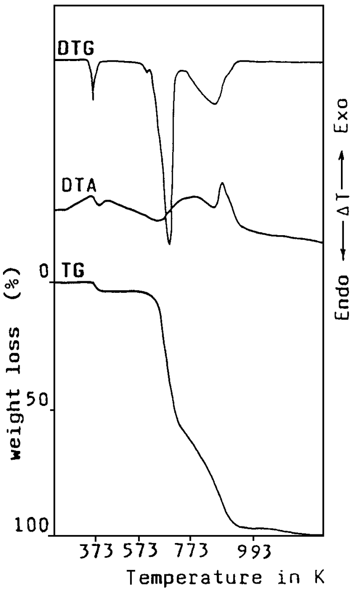

Figure 1. TG, DTG, and DTA curves of $[Zn_2(C_7H_3Cl_2O_2)_2\cdot(H_2O)_6]\cdot(C_7H_3Cl_2O_2)_2$ (heating rate of 10 K min^{-1}).

The magnetic susceptibility was measured by Faraday's method from room and up to liquid nitrogen temperatures at different magnetic field intensities. The $Hg[Co(NCS)_4]$ complex was used as reference. The investigated Zn(II) complex with dichlorobenzoic acid is diamagnetic within the studied temperature range (LNT-RT) as it was expected. The mean gram-susceptibility is 0.50×10^6 cm^3 g^{-1} and the mean molar susceptibility is 248×10^6 cm^3 mol^{-1}.

The approximate unit-cell dimensions were determined from the rotation and Weisenberg photographs. The diffraction data for $[Zn_2(C_7H_3Cl_2O_2)_2\cdot(H_2O)_6]\cdot(C_7H_3Cl_2O_2)_2$ were collected with MoK_α radiation on a Kuma KM-4 four-circle diffractometer with a graphite monochromator. The crystallographic data and details of the refinement procedure are given in Table 2. The intensities were corrected for the Lorentz and polarization effects, but not for extinction or absorption. The structure was solved and refined using the SHELXS-97 [12] and SHELXL-97 [13] programs. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of water molecules were found on a difference map; the others were generated at the calculated positions. Fractional atomic coordinates for nonhydrogen atoms and equivalent isotropic displacement parameters are given in Table 3. Selected interatomic distances and valence angles are in Table 4.

Figure 2 presents the crystal structure of dimeric complex $[Zn_2(C_7H_3Cl_2O_2)_2\cdot(H_2O)_6]\cdot(C_7H_3Cl_2O_2)_2$ and numbering of the atoms.

The complex obtained has a dimeric structure, where two zinc(II) ions are connected by two bidentate-bridging carboxylate groups of organic ligands and by two bridging water molecules. Each metal ion bonds additionally two water molecules

O(2) and O(3) achieving the coordination number 6. The charge of complex ion is compensated by 2,5-dichlorobenzoate ions, hydrogen bonded with the coordinate water molecules O(1) and O(2) (Table 5).

Table 2. Crystal data, data collection details and refinement.

Formula	$C_{28}H_{24}Cl_8O_{14}Zn_2$
a (Å)	7.380(2)
b (Å)	7.464(2)
c (Å)	16.816(3)
α (deg)	80.15(3)
β (deg)	80.54(3)
γ (deg)	71.19(3)
V ($Å^3$)	858.0(3)
Space group	$P\bar{1}$
Z	1
F(000)	500
T (K)	295(2)
25 refl. to determine cell const. Range (2θ)	25.3–44.2
D_m flotation (Mg/m^3)	1.94
D_c (Mg/m^3)	1.933
λ (Å)	0.71069
Monochromator	graphite
Cristal size (mm)	0.25 × 0.25 × 0.30
Linear absorption coefficient (cm^{-1})	20.91
Data collection method	ω /2θ scan
2θ limit (deg)	60
Number of standard reflections and interval	3 (100 ref.)
Number of unique reflections with $I \geq 2\sigma(I)$	3123
Variable parameters	245
GOF	1.065
R1	0.0303
wR	0.0833
Largest diff. peak and hole ($eÅ^{-3}$)	0.631, –0.354

Table 3. Fractional atomic coordinates for non-hydrogen atoms and equivalent isotropic displacement parameters ($Å^2$).

Atom	x	y	z	U_{eq}
Zn(1)*	0.19834(5)	–0.13096(5)	–0.02626(2)	0.0242 (1)
Zn(2)*	0.1973(13)	0.3671(19)	–0.0273(7)	0.108(4)
Cl(11)	–0.4770(1)	0.2418(1)	–0.2133(5)	0.0430(2)
Cl(12)	0.2906(1)	0.2630(1)	–0.4239(1)	0.0456(2)
Cl(21)	0.4693(1)	0.2672(1)	0.2257(1)	0.0420(2)
Cl(22)	–0.3045(1)	0.2406(1)	0.4274(1)	0.0476(2)
O(11)	0.0916(3)	–0.0403(1)	–0.1328(1)	0.0284(4)

O(12)	–0.1983(3)	0.1570(3)	–0.0946(1)	0.0310(4)
O(21)	0.1989(3)	0.3500(3)	0.1000(1)	0.0360(5)
O(22)	–0.0883(3)	0.5435(3)	0.1382(1)	0.0396(5)
O(1)	0.0970(3)	0.1859(3)	–0.0142(1)	0.0335(4)
O(3)	0.4644(3)	–0.0971(3)	–0.0579(1)	0.0392(5)
O(2)	0.3039(3)	–0.4168(3)	–0.0375(1)	0.0411(5)
C(11)	–0.0838(4)	0.1652(3)	–0.2345(1)	0.0229(5)
C(12)	–0.2570(4)	0.2435 (4)	–0.2673(2)	0.0267(5)
C(13)	–0.2615(4)	0.3263(4)	–0.3476(1)	0.0339(6)
C(14)	–0.0947(5)	0.3342(4)	–0.3958((2)	0.0340(6)
C(15)	0.0782(4)	0.2540(4)	–0.3638((2)	0.0289((5)
C(16)	0.0857(4)	0.1684(4)	–0.2847(2)	0.0273(5)
C(17)	–0.0639(4)	0.0860(4)	–0.1467(1)	0.0214(5)
C(21)	0.0791(4)	0.3337(3)	0.2410(1)	0.0239(5)
C(22)	0.2495(4)	0.2571(4)	0.2765(2)	0.0262(5)
C(23)	0.2496(4)	0.1739(4)	0.3566(2)	0.0348(6)
C(24)	0.0796(5)	0.1666(4)	0.4030(2)	0.0356(6)
C(25)	–0.0898(4)	0.2461(4)	0.3688(2)	0.0297(5)
C(26)	–0.0922(4)	0.3298(4)	0.2896(2)	0.0286(5)
C(27)	0.0641(4)	0.4169(4)	0.1533(2)	0.0276(5)

* Factor occupation Zn(1) 0.93 and Zn(2) 0.07.

Table 4. Selected bond distances (Å) and angles (deg).

Zn(1)–Zn(1)$^{\mathrm{i}}$	3.037(1)
Zn(2)–Zn(2)$^{\mathrm{iii}}$	3.05(2)
Zn(1)–O(11)	1.999(2)
Zn(1)–O(12)$^{\mathrm{i}}$	2.009(2)
Zn(1)–O(3)	2.033(2)
Zn(1)–O(2)	2.052(2)
Zn(1)–O(1)	2.273(2)
Zn(1)–O(1)$^{\mathrm{i}}$	2.318(2)
Zn(2)–O(21)	2.124(12)
Zn(2)–O (22)$^{\mathrm{iii}}$	2.072(12)
Cl(11)–C(12)	1.729(3)
Cl(12)–C(15)	1.734(3)
Cl(21)–C(22)	1.726(3)
Cl(22)–C (25)	1.732(3)
O(11)–C (17)	1.255(3)
O(12)–C(17)	1.252(3)
O(21)–C(27)	1.257(3)
O(22)–C (27)	1.244(3)
O(11)–Zn(1)–O(3)	100.01(9)
O(12)$^{\mathrm{i}}$–Zn(1)–O(3)	96.93(9)

Table 4 (continuation)

O(11)–Zn(1)–O(2)	98.18(9)
O(12)^{i}–Zn(1)–O(2)	96.87(9)
O(3)–Zn(1)–O(2)	91.90(9)
O(11)–Zn(1)–O(1)	82.94(8)
O(12)^{i}–Zn(1)–O(1)	82.89(8)
O(3)–Zn(1)–O(1)	85.27(9)
O(2)–Zn(1)–O(1)	177.10(9)
O(11)–Zn(1)–O(1)^{i}	82.49(8)
O(12)^{i}–Zn(1)–O(1)^{i}	81.26(8)
O(3)–Zn(1)–O(1)^{i}	176.71(8)
O(2)–Zn(1)–O(1)^{i}	85.61(9)
O(1)–Zn(1)–O (1)^{i}	97.20(7)
Zn(1)–O(1)–Zn(1)^{i}	82.80(7)

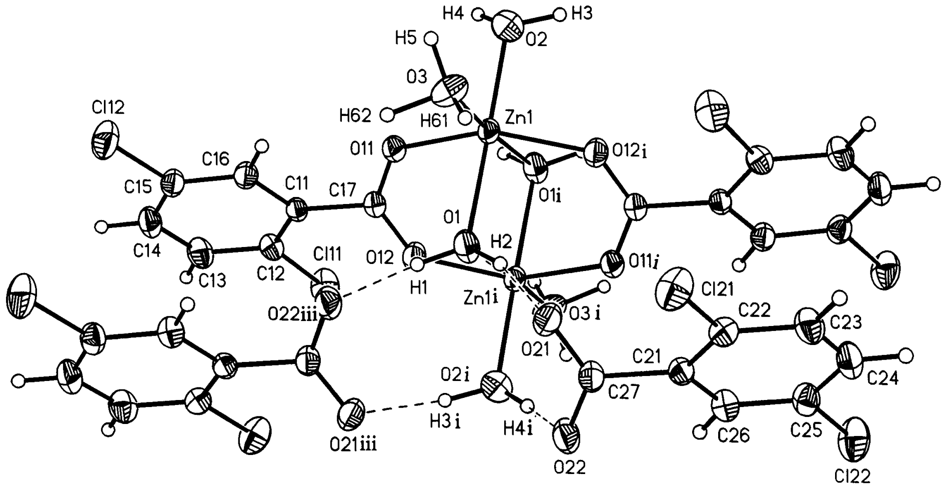

Figure 2. Molecular structure of $[Zn_2(C_7H_3Cl_2O_2)_2\cdot(H_2O)_6]\cdot(C_7H_3Cl_2O_2)_2$.

During the structure solution investigation in the standard way in the difference Fourier map appears a maximum 2.83 $e^-/Å^3$, assigned to Zn atom with occupancy of 0.07. By those values of occupancy of Zn(1) and Zn(2) factor wR1 decreases about 1% and the maximal electron density is 0.61 $e^-/Å^3$. In this model of structure the Zn(1) –Zn(1)^{i} and Zn(2)–Zn(2)^{iii} distances are almost the same (3.037(1) and 3.05(2) Å) (Table 4). The bond distances between Zn(1) ion and bridging water molecules, forming the caves, are much longer (2.273(2) and 2.318(2) Å) and those between Zn(1) and monodentate coordinated water molecules O(2) and O(3): 2.033(2) and 2.052(2) Å. The coordination of each metal nucleus is completed by two water molecules, each of them acting as a bridge through an oxygen atom. This bridging mode is rather uncommon in metal carboxylate chemistry. The bridging arrangement is asymmetric: O(1)–Zn (1) and O(1)–Zn(1)^{i} bond distances with different lengths, 273(2) and 2.318(2) Å, are involved. Moreover, two zinc ions are joined by two water molecules, acting as a monodentate donor. The Zn–O(water) bond distances are 2.052(2) Å for Zn(1)–O(2) and 2.033(2) Å for Zn(1)–O(3). In the third water molecule O(3) the hydrogen atom H(6) has disordered position H(61) and H(62) with half-occupancy 0.5. Both half-occupancy hydrogen atoms take part in hydrogen bonds O(3)– H(62)$\cdots$Cl(11) and O(3)–H(61)$\cdots$O(3) formation.

Table 5. Hydrogen bond lengths (Å) and bond angles (°) with esd's in parentheses.

D - H$\cdots$A	D - H	H$\cdots$A	D$\cdots$A	D - H$\cdots$A
O(1)–H (2)$\cdots$O(21)	0.92	1.86	2.762(3)	163.9
O(1)–H(1)$\cdots$O(22)^{iii}	0.93	1.71	2.637(3)	170.9
O(2)–H(3)$\cdots$O(21)^{iv}	0.99	1.84	2.807(3)	164.1
O(2)–H(4)$\cdots$O(22)^{i}	0.99	1.99	2.950(3)	162.7
O(3)–H(5)$\cdots$O(21)^{v}	0.94	1.81	2.664(3)	149.5
O(3)^{v}–H(61)$\cdots$O(3)^{vi}	0.91	1.94	2.822(4)	164.3
O(3)–H(62)$\cdots$Cl(11)^{vi}	1.17	2.23	3.390(4)	169.9

i: –x, –y, –z; ii: x, y + 1, z; iii –x, –y + 1, –z; iv: x, y – 1, z; v: –x + 1, –y, –z; vi: x + 1, y, z.

The overall geometry around the zinc atom is distorted octahedron. All the Zn–O distances, including of 1.999–2.009 Å for the bridging carboxylate groups and 2.033–2.052 Å for the water molecule, are normal for octahedral Zn(II). Also the Zn–O (bridging water) distances, 2.273 and 2.318 Å, which are longer than all the Zn–O distances, are in the usual range. Two 2,5-dichlorobenzoate ligands are in the outer coordination sphere of the complex. Two of these carboxylate groups of outer sphere are bonded with hydrogen atoms with inner sphere water molecules. The geometry of hydrogen bonds is given in Table 5.

The 2,5-dichlorobenzoate ligands exhibit the same geometry of phenyl ring as in the structure of free acid and in other complexes [14–16], but carboxylate group in each ligand is rotated from phenyl ring plane above 31.05°. The angles O–C–O in carboxylate bridging is 126.2(2)° and in uncoordinated carboxylate group equals 124.2(2)°. In the structure of this complex, the zinc(II) cations are not located in the carboxylate group planes. The distance of the zinc(II) ion from the carboxylate group is –0.44287 Å.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC 142057.

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