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Preparation, Structure, and Thermal Decomposition of Cu(II) 3,5-Dichlorobenzoate Trihydrate

W. Wołodkiewicz[1], **W. Brzyska**[1], and **T. Głowiak**[2]

[1] Faculty of Chemistry, Maria Curie-Skłodowska University, PL-20031 Lublin, Poland
[2] Faculty of Chemistry, University of Wrocław, PL-50383 Wrocław, Poland

Summary. The title compound was studied. Its solubility in water at 293 K was determined ($4 \cdot 10^{-4}$ mol $\cdot$ dm^{-3}). The IR spectrum of the prepared complex was recorded, and its thermal decomposition in air was investigated. The trihydrated complex starts to lose its crystallization water at 343 K; it then decomposes either to CuO (5 K min heating rate) or to gaseous products (10 K min heating rate). $[Cu(C_7H_3Cl_2O_2)_2 \cdot (H_2O)_3]$ crystallizes in the monoclinic system (space group $P2_1n$ (No. 14)); cell parameters: $a = 16.854(3)$ Å, $b = 8.330(2)$ Å, $c = 13.655(3)$ Å, $\beta = 104.20(3)°$, $V = 1858(5)$ Å^3, $Z = 4$, $D_C = 1.778$ g/cm^3, $D_m = 1.78$ g/cm^3.

Keywords. Copper; 3,5-Dichlorobenzoic acid; Complexes; X-Ray analysis; Thermal analysis.

Herstellung, Struktur und thermische Zersetzung von Cu(II)-3,5-Dichlorobenzoat-trihydrat

Zusammenfassung. Die Titelverbindung wurde untersucht. Ihre Löslichkeit in Wasser wurde bestimmt (4×10^{-4} mol $\cdot$ dm^{-3}). Das IR-Spektrum des Komplexes wurde aufgenommen, und die thermische Zersetzung der Verbindung an der Luft wurde verfolgt. Der dreifach hydratisierte Komplex beginnt bei 343 K sein Kristallwasser zu verlieren. Anschließend zersetzt er sich zu CuO (Aufheizgeschwindigkeit 5 K/min) oder zu gasförmigen Produkten (10 K/min). $[Cu(C_7H_3Cl_2O_2) \cdot 2H_2O)]$ kristallisiert im monoklinen System (Raumgruppe $P2_1n$ (Nr. 14)) mit den Zellparametern $a = 16.854(3)$ Å $b = 8.330(2)$ Å, $c = 13.655(3)$ Å, $\beta = 104.20(3)°$, $V = 1858(5)$ Å^3, $Z = 4$, $D_c = 1.778$ g/cm^3, $D_m = 1.78$ g/cm^3.

Introduction

Chlorobenzoic and dichlorobenzoic acids form complexes with Cu(II) ions with different structures and different properties [1–8]. In these complexes, the carboxylate groups act as monodentate [5], bidentate bridging [2, 6–8], or bidentate chelating ligands [1, 3, 4]. Copper(II) complexes with monochlorobenzoic acids decompose to CuO when heated, whereas those with isomers of 2,4- [9], 2,5- [10], 2,6- [11], and 3,4-dichlorobenzoic acids [12] afford gaseous products. All complexes mentioned are sparingly soluble in water.

This work is a continuation of our study on the structure and physico-chemical properties of metal complexes with dichlorobenzoic acids. Its aim was to prepare solid Cu(II) 3,5-dichlorobenzoate and to examine its structure, its thermal decomposition, and some of its physico-chemical properties.

Results and Discussion

The 3,5-dichlorobenzoate of Cu(II) with the formula $\mathrm{Cu(C_7H_3Cl_2O_2)_2 \cdot 3H_2O}$ was prepared as a green crystalline solid. The complex is sparingly soluble in water; its solubility is $4.1 \cdot 10^{-4}\,\mathrm{mol \cdot dm^{-3}}$.

Infrared spectra

The IR spectra of free dichlorobenzoic acid as well as of the Cu(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 $1707\,\mathrm{cm^{-1}}$ (COOH group). In the IR spectrum of the Cu(II) complex, this absorption band disappears, and a split band of asymmetrical OCO vibrations (ν_{as}) appears at 1616 and $1559\,\mathrm{cm^{-1}}$ as well as a band of symmetrical vibrations (ν_{s}) at $1384\,\mathrm{cm^{-1}}$. The broad absorption bands of ν(OH) can be found at $3320\,\mathrm{cm^{-1}}$, and a narrow band of $\delta(\mathrm{H_2O})$ at $1620\,\mathrm{cm^{-1}}$ confirms the presence of crystal water. The bands of ν(C-Cl) appear at 780 and $804\,\mathrm{cm^{-1}}$ and are insignficantly displaced compared to ν(C-Cl) of the free acid

Table 1. Frequencies for characteristic absorption bands in the IR spectra of 3, 5-dichlorobenzoic acid and its Cu(II) and Na(I) complexes ($\mathrm{cm^{-1}}$; $L = \mathrm{C_7H_3Cl_2O_2}^-$; s: strong, m: medium, w: weak, v: very)

H*L*	Na*L*	Cu*L*$_2$	Assignment
480_{w}	483_{w}	486_{w}	ϕ(CC)
577_{w}	554_{w}	595_{w}	ϕ(CC)
660_{m}	663_{m}	664_{m}	ϕ(CC)
710_{m}	738_{m}	736_{m}	γ(CC)
770_{s}	781_{s}	780_{s}	ν(C–Cl)
809_{s}	804_{s}	804_{s}	ν(C–Cl)
876_{m}	870_{m}	875_{m}	β_{s}(OCO)
909_{s}	905_{s}	906_{s}	β(CH)
1100_{w}	1097_{w}	1096_{w}	β(CH)
1165_{w}	1173_{w}	1172_{w}	β(CH)
1289_{w}	1293_{w}	1293_{w}	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
–	1381_{vs}	1384_{vs}	ν_{s}(OCO)
1403_{s}	1402_{s}	1403_{s}	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1426_{s}	1422_{s}	1422_{s}	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1448_{vs}	1435_{vs}	1431_{vs}	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
–	1556_{vs}	1559_{vs}	
		1616_{vs}	ν_{as}(OCO)
–	1642_{s}	1620_{s}	$\delta(\mathrm{H_2O})$
1707_{vs}	–	–	COOH
	3371_{s}	3320_{s}	ν(OH)

(770 and 809 cm^{-1}), suggesting that the Cl atoms do not participate in the metal ligand bonding. The split band of ν_{as}(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 175 and 232 cm^{-1}, respectively, suggesting that the carboxylate groups act as bidentate asymmetric ($\Delta\nu_{Cu} = \Delta\nu_{Na}$) and monodentate ($\Delta\nu_{Cu} > \Delta\nu_{Na}$) ligands. The C$\overset{\cdots}{-}$C and C-H vibrational bands of the Cu(II) complex change their frequencies only insignificantly compared to the corresponding bands of the sodium salt and the free acid. This means that the Cu(II) ion in the complex does not deform the aromatic ring, an assumption which was confirmed by the crystal structure determination.

Crystal structure

The 3,5-dichlorobenzoate of Cu(II) cristallizes in the monoclinic system (space group $P2_1n$; Fig. 1). Tables 2 and 3 list selected bond lengths and bond angles. The final atomic parameters are listed in Tables 4 and 5. In the title compound, the

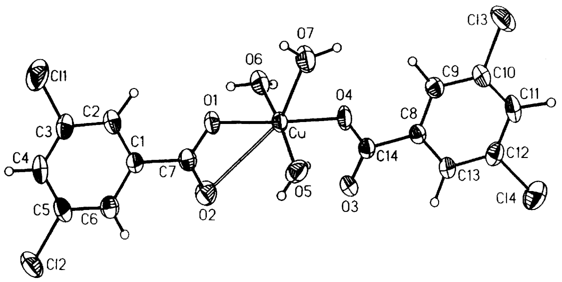

Fig. 1. Molecular structure of $[Cu(C_7H_3Cl_2O_2)_2 \cdot (H_2O)_3]$

Table 2. Selected bond distances (Å) and angles (°) with *esd*s in parentheses

Cu–O(1)	1.945(2)	O(3)–Cu–O(5)	91.53(1)
Cu–O(3)	1.904(2)	O(1)–Cu–O(5)	90.48(1)
Cu–O(5)	1.968(3)	O(3)–Cu–O(6)	89.27(1)
Cu–O(6)	1.970(3)	O(1)–Cu–O(6)	89.11(1)
Cu–O(7)	2.309(3)	O(3)–Cu–O(1)	177.16(1)
Cu–O(2)	2.795(3)	O(5)–Cu–O(6)	169.42(1)
Cl(1)–C(3)	1.734(4)	O(2)–Cu–O(7)	145.3(1)
Cl(2)–C(5)	1.732(4)	O(2)–C(7)–O(1)	122.9(3)
Cl(3)–C(10)	1.732(4)	O(4)–C(14)–O(3)	125.2(3)
Cl(4)–C(12)	1.730(4)		
O(1)–C(7)	1.280(4)		
O(2)–C(7)	1.243(4)		
O(4)–C(14)	1.279(4)		
O(3)–C(14)	1.233(4)		
C(1)–C(7)	1.498(4)		
C(8)–C(14)	1.502(4)		

Table 3. Hydrogen bond distances (Å) and angles (°) with *esd*s in parentheses

D–H···A	D–H	H···A	D···A	Angle
O(5)–H(1)···O(4)i	0.72(6)	2.05(6)	2.740(5)	160(3)
O(5)–H(2)···O(1)ii	0.70(6)	2.08(6)	2.754(5)	161(3)
O(6)–H(1)···O(2)iii	0.81(5)	2.03(5)	2.806(5)	161(3)
O(6)–H(2)···O(4)iii	0.81(5)	1.93(5)	2.727(5)	169(3)
O(7)–H(1)···O(2)i	0.84(7)	2.22(6)	3.051(5)	153(4)
O(7)–H(2)	0.85(7)			

Table 4. Fractional coordinates ($\times 10^4$) for non-H atoms and equivalent isotropic thermal parameters ($\times 10^3$, Å^2) with *esd* values in parentheses

	x	y	z	U_{eq}
Cu	374(3)	1418(5)	1557(4)	31.3(2)
Cl(1)	−2672(1)	7581(1)	72(1)	70.0(4)
Cl(2)	−4394(1)	2076(2)	−386(1)	59.6(1)
Cl(3)	4491(1)	−131(1)	3056(10)	63.3(3)
Cl(4)	3414(1)	−6202(1)	2607(1)	61.8(3)
O(1)	−580(1)	2814(2)	1251(2)	32.7(5)
O(2)	−1258(1)	563(3)	745(2)	42.5(6)
O(3)	1340(1)	137(3)	1839(2)	40.5(6)
O(4)	838(1)	−2291(3)	1349(2)	40.4(6)
O(5)	98(2)	701(4)	2806(2)	49.2(7)
O(6)	518(2)	1812(4)	188(2)	41.3(6)
O(7)	1243(2)	3311(4)	2488(3)	52.5(7)
C(1)	−2009(2)	3002(4)	518(2)	30.6(6)
C(2)	−1985(2)	4669(4)	461(3)	35.4(7)
C(3)	−2711(2)	5505(4)	153(3)	41.6(8)
C(4)	−3456(2)	4731(5)	−106(3)	43.5(8)
C(5)	−3463(2)	3072(5)	−58(3)	39.8(8)
C(6)	−2752(2)	2198(4)	251(3)	35.7(7)
C(7)	−1238(2)	2045(4)	857(2)	30.7(6)
C(8)	2269(2)	−1990(4)	2067(2)	29.4(6)
C(9)	2909(2)	−914(4)	2344(3)	34.1(7)
C(10)	3695(2)	−1489(4)	2691(3)	38.1(7)
C(11)	3858(2)	−3114(5)	2769(3)	40.2(8)
C(12)	3213(2)	−4165(4)	2490(3)	38.0(7)
C(13)	2412(2)	−3641(4)	2124(3)	34.1(7)
C(14)	1409(2)	−1373(4)	1712(3)	32.0(7)

Cu(II) ion coordinates two 3,5-dichlorobenzoate ions and three water molecules forming a pseudomolecular complex with the composition $[\mathrm{Cu}L_2 \cdot (\mathrm{H_2O})_3]$. One of the carboxylate groups acts as a monodentate and the second one as a bidentate (asymmetric) chelating ligand. In the complex described, the Cu(II) ion occupies the symmetry centre, and six oxygen atoms (three from the carboxylate groups and three from the water molecules) form a distorted octahedron. The Cu-O (water)

Table 5. Hydrogen atom coordinates ($\times 10^3$) and isotropic displacement parameters ($\times 10^3$, Å^2) with *esd* values in parentheses

	x	y	z	U_{eq}
H(1)	−23(2)	107(5)	299(3)	21(9)
H(2)	29(3)	9(7)	312(5)	70(2)
H(3)	82(3)	115(7)	4(4)	60(2)
H(4)	8(3)	192(5)	−22(3)	37(11)
H(5)	174(5)	302(5)	269(5)	100(2)
H(6)	119(4)	389(8)	297(5)	90(2)
H(7)	−145(3)	534(5)	63(3)	49(12)
H(8)	−389(3)	531(6)	−40(4)	57(13)
H(9)	−280(3)	111(5)	24(3)	47(12)
H(10)	281(2)	13(5)	232(3)	40(11)
H(11)	433(3)	−352(6)	310(4)	61(14)
H(12)	200(3)	−429(5)	193(3)	27(9)

bond distances are in the range of 1.968(3)–2.309(3) Å, the Cu-O (carboxylate chelating) bond distances amount to 1.945(2) and 2.795(3) Å, and the Cu-O (carboxylate monodentate) bond distance is 1.904(2) Å. Four oxygen atoms (two water molecules, two carboxylate groups) are located in a plane, and two more distant oxygen atoms (one from water and one from the OCO chelating group) occupy apical positions. The in-plane O-Cu-O angles have values in the range of 89.11(1) to 91.53(1) Å which are very close to the theoretical value. The angle O(2)-Cu-O(7) is rather small (145.3(1)°) compare to 180° for a regular octahedron. Therefore, copper has a (4+2) coordination typical for cupric compounds. The coordination of two carboxylate groups influences the O-C-O angle values. The angle O(3)-C(14)-O(4) of the monodentate carboxylate group has a value of 125.2(3)°, whereas the angle O(2)-C(7)-O(1) of the bidentate chelating carboxylate group is 122.9(3)°.

The molecules of the complex are linked by hydrogen bonds (Table 3). The water molecules act as proton donors to the carboxylate oxygen atoms of neighbouring complex molecules. The C-Cl bond lengths are 1.734(4) and 1.730(4) Å. C(phenyl)-C(carboxyl) bond distances are the same as in the free carboxylic acid [17], and the C-O distances in the carboxylate groups are in the range of 1.233(4)–1.280(4) Å, a typical distance in carboxylate complexes [18]. The distances C-C and the angles C-C-C in the benzene ring (Table 2) do not show any deformation of the aromatic ring.

Thermochemical properties

Cu(II) 3,5-dichlorobenzoate is stable in air at room temperature. During heating, it decomposes in different ways dependent on the heating rate (Table 6, Figs. 2 and 3). With a heating rate of 10 K min, the trihydrated complex is stable up to 343 K and then loses three crystal water molecules. Heated above 503 K, the

Table 6. Thermal decomposition of Cu(II), 3, 5-dichlorobenzoates (T_1: – endothermic peaks on DTA; [a]heating rate of 10 K min; [b]heating rate of 5 K min)

	Range of dehydration (K)	T_1 (K)	Loss of weight (%)		Temp. of decomp. (K)	Temp of oxide formation (K)	Residue (%)	
			Calcd.	Found			Calcd.	Found
$CuL_2 \cdot 3H_2O^a$	343–433	393	10.86	10.5	503	–	–	–
$CuL_2 \cdot 3H_2O^b$	343–403	393	10.86	10.7	533	793	15.99	16.0

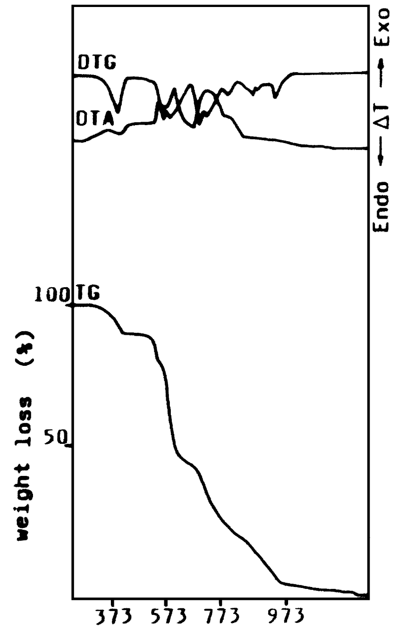

Fig. 2. TG, DTG, and DTA curves of $[Cu(C_7H_3Cl_2O_2)_2 \cdot (H_2O)_3]$ (heating rate: 10 K min)

anhydrous complex decomposes to gaseous products (similarly behave Cu(II) complexes with 2,4- [19], 2,5- [10], 2,6- [11], and 3,4- [12] dichlorobenzoic acids).

The thermochemical behaviour of the dehydrated complex is different using a heating rate of 5 K min: the anhydrous compound decomposes to the oxide CuO at 797 K. These results indicate that the thermal decomposition of the prepared complex can be presented as

$$CuL_2 \cdot 3H_2O \rightarrow CuL \rightarrow \text{gaseous products} \ (10\,\text{K min})$$

$$CuL_2 \cdot 3H_2O \rightarrow CuL \rightarrow CuO \ (5\,\text{K min})$$

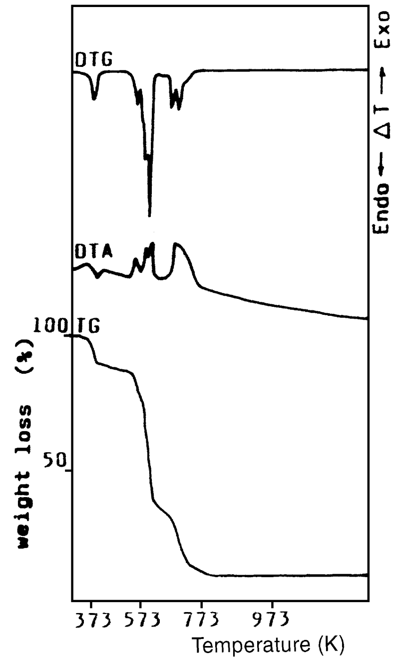

Fig. 3. TG, DTG, and DTA curves of $[Cu(C_7H_3Cl_2O_2)_2 \cdot (H_2O)_3]$ (heating rate: of 5 K min)

Experimental

The dichlorobenzoate of Cu(II) was obtained by adding hot 0.1 *M* ammonium 3,5-dichlorobenzoate solution (p*H* = 5.5) to a 0.2 M solution of Cu(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 carbon and hydrogen content in the complex were determined by elemental analysis using a Perkin Elmer CAN 2000 analyzer. The chlorine content was measured by the Schöniger method. The Cu(II) content was determined by AAS using an Atomic Absorption Spectrophotometer AAS-3 (Carl Zeiss-Jena). The crystal water content was determined from TG curves and by heating the complex isothermally to 433 K. The experimental results are concordant with the calculated data (Cu 12.77 (12.7)%, C 33.76 (33.7)%, H 2.40 (2.3)%, Cl 28.54 (28.54)%). IR spectra were recorded over the range of 4000–400 cm^{-1} using a FT-IR 1725X Perkin Elmer spectrophotometer. The thermal stability of the Cu(II) complex was determined using a Paulik-Paulik-Erdey Q 1500 D derivatograph with a *Derill* converter; TG, DTG, and DTA curves were recorded. Measurements were made at a sensitivity of 100 mg (TG). The sensitivities of DTG and DTA were regulated by the *Derill* computer programme. Samples (100 mg) were heated in platinum crucibles to 1273 K in static air at a heating rate of 10 K min^{-1}. The solubility of the complex in water was determined at 295 K. The saturated solution was prepared under isothermal conditions. The content of Cu(II) ions was determined by the AAS method.

From saturated solution, monocrystals of the Cu(II) complex appear after several days at room temperature. D_m was measured by the flotation method in $CCl_4/C_2H_4Br_2$. Oscillation and *Weissenberg* photographs showed that the crystals are monoclinic. The diffraction data were collected with CuK_α radiation on a KUMA-4 diffractometer with a graphite monochromator. 3945 reflections were measured under the conditions listed in Table 7, where crystallographic data and refinement procedures are also given. The intensities were corrected for *Lorentzian* and polarization effects. The structure determination was based on 3945 reflections with $I \geq 36(I)$. It was solved by the heavy atom method using SHELXS-86 [13] and refined by the full-matrix least square method using the SYNTEX XL93 structure determination program [14]. The position of all hydrogen atoms were

Table 7. Crystal data and structure refinement

Formula	$C_{14}H_{12}O_7Cl_4Cu$
Molecular weight	497.58
a (Å)	16.854(3)
b (Å)	8.330(2)
c (Å)	13.655(3)
β(°)	104.20(3)
V(Å^3)	1858.5(7)
Space group	$P2_1n$ (No. 14)
Z	4
F (100)	996
T (K)	297(2)
25 refl. 2θ range:	22.4–48.6
D_m (g/cm^3)	1.78
D_c (g/cm^3)	1.778
λ (Å) (CuK$_\alpha$)	1.5418
Monochromator	graphite
Crystal size (mm)	0.15 × 0.15 × 0.20
Linear absorption coefficient (mm^{-1})	7.280
Data collection method	$\omega/2\Theta$ Scan
2Θ limit(°)	2.70–80.18
Number of standard reflections	3 (100 references)
Variation standard reflections (%)	3
Number of unique reflections collected	3945
Number of unique reflections with $I \geq 3\sigma$ (I)	3823
Variable parameters	283
Final R indices [$I > 3.5\sigma(I)$]	$R_1 = 0.0399$, $wR_2 = 0.1113$
Goodness-of-fit on F^2	1.030
Largest diff. pcak and hole	0.532 and $-0.377\,\mathrm{c} \cdot \text{Å}^{-3}$

determined by difference *Fourier* synthesis. The lattice constants as well as the data collection parameters and some physical constants of the Cu(II) complex are given in Table 7.

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