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Properties and thermal decomposition in air atmosphere of complexes of Co(II), Ni(II) and Cu(II) with 2,6-dichlorobenzoic acid

W. Brzyska *, W. Wołodkiewicz

Department of Inorganic and General Chemistry, Faculty of Chemistry, Marie Curie Skłodowska University, 20-031 Lublin, Poland

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Abstract

The conditions for the formation of Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates were studied and their quantitative compositions and solubilities in water at 293 K were determined. The IR spectra of the prepared complexes were recorded and their thermal decompositions in air were investigated. During heating, the hydrated complexes $M(C_7H_3O_2Cl_2) \cdot nH_2O$ lose the molecules of water of crystallization in two steps, before decomposing to the oxides (Co, Ni) or gaseous products (Cu).

Keywords: Cobalt compound; Copper compound; Decomposition; Dehydration; Dichlorobenzoate; DTA; DTG; IRS; Nickel compound; TG

1. Introduction

2,6-Dichlorobenzoic acid $C_6H_3Cl_2COOH$ is a crystalline solid, soluble in water and ethanol [1]. Its compounds with metal ions are almost unknown. There are some data [1] on the preparation and properties of the 2,6-dichlorobenzoate of Ba(II), which was prepared as 3.5 hydrate and is soluble in water and ethanol.

This work is a continuation of our study on the physico-chemical properties of metal complexes with chlorobenzoic acids [2–5].

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* Corresponding author.

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The aim of this work was to prepare Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates in the solid state and to examine their physico-chemical properties and thermal decomposition in air atmosphere.

2. Experimental

2,6-Dichlorobenzoates of Co(II), Ni(II) and Cu(II) were prepared by dissolving Co(II), Ni(II) and Cu(II) carbonates in a hot solution of 2,6-dichlorobenzoic acid and then crystallizing at room temperature. The precipitates formed were filtered, washed with water and dried in room air at 303 K to a constant mass.

The carbon and hydrogen contents in the prepared complexes were determined by elemental analysis. The chlorine content was measured by the Schoniger method. The Co(II), Ni(II) and Cu(II) contents were determined by a polarographic method using an OH-102 Radelkis polarograph. The water of crystallization content was determined from the TG curves and by isothermal heating of the complexes at a suitable temperature.

IR spectra of the prepared complexes were recorded using an EF-IR 1725X Perkin-Elmer spectrophotometer within the range 4000–400 cm^{-1}. The samples were prepared as KBr discs.

The solubilities of the prepared 2,6-dichlorobenzoate complexes in water were determined at 293 K. The saturated solutions were prepared under isothermal conditions. The concentrations of Co(II), Ni(II) and Cu(II) were determined using polarography.

The thermal stability of the obtained complexes was studied. The TG, DTG and DTA curves were recorded. Measurements were made with a Q 1500 D derivatograph at a heating rate of 10 K min^{-1} for full scale with the sensitivity: TG, 100 mg; DTG, 500 μV; DTA, 500 μV, using α-Al_2O_3 as the standard.

The paper speed was 2.5 mm min^{-1}. The samples (100 mg) were heated in platinum crucibles in air to 1273 K. The final products of decomposition were identified by X-ray diffractometry.

3. Results and discussion

2,6-Dichlorobenzoate complexes of Co(II), Ni(II) and Cu(II) were prepared as crystalline solids, with a molar ratio of metal to organic ligand (calculated from the quantitative composition) of 1.0:2.0 and general formula $M(C_7H_3O_2Cl_2)_2 \cdot nH_2O$, where $n = 6$ for Co(II) and Ni(II), $n = 1$ for Cu(II), see Table 1. The complexes of Ni(II) and Cu(II) are green, whereas that of Co(II) is pink.

The complexes of Co(II), Ni(II) and Cu(II) are soluble in water (Table 1). The solubilities of the Co(II) and Ni(II) complexes are of the order of 10^{-3} mol dm^{-3}, whereas that of the Cu(II) complex is 10^{-1} mol dm^{-3} and increases in the order $Co < Ni \ll Cu$. The difference in the solubility of the Cu(II) complex in comparison to those of the Co(II) and Ni(II) complexes suggests that the Cu(II) complex has a different structure to that of the Co(II) and Ni(II) complexes.

Table 1
Analytical data and solubilities of Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates

Complex[a]	M/%		C/%		H/%		Cl/%		Solubility/(mol dm^{-3})[b]
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$CoL_2 \cdot 6H_2O$	10.77	10.8	30.25	30.4	3.76	4.1	23.38	23.8	5.2×10^{-3}
$NiL_2 \cdot 6H_2O$	10.74	10.8	30.76	30.7	3.32	3.6	25.97	25.7	6.8×10^{-3}
$(CuL_2 \cdot H_2O)_2$	13.77	13.8	36.40	36.2	1.73	2.0	36.40	37.0	1.5×10^{-1}

[a] L is $C_7H_3O_2Cl_2^-$. [b] Solubility in water at 293 K.

Table 2
Frequencies for characteristic absorption bands in IR spectra in cm^{-1} of Co(II), Ni(II) and Cu(II) and Na(I) 2,6-dichlorobenzoates

Complex	ν(OH)	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$ [a]	$\Delta\nu_{as}$ [b]	$\Delta\nu_s$ [c]	ν(C–Cl)
$CoL_2 \cdot 6H_2O$	3163	1563	1385	178	−44	−6	781, 766
$NiL_2 \cdot 6H_2O$	3172	1563	1386	177	−44	−5	781, 766
$(CuL_2 \cdot H_2O)_2$	3485	1601	1395	206	−6	+4	788, 766
NaL	–	1607	1391	216			792, 765

[a] $\Delta\nu = \nu_{as}(OCO) - \nu_s(OCO)$. [b] $\Delta\nu_{as} = \nu_{as(M)}(OCO) - \nu_{as(Na)}(OCO)$. [c] $\Delta\nu_s = \nu_{s(M)}(OCO) - \nu_{s(Na)}(OCO)$.

All the complexes prepared show similar solid-state IR spectra (Table 2) but they differ from the spectrum of the free acid. When the acid is converted into the complexes, the absorption band of the COOH group at 1720 cm^{-1} disappears and the asymmetric ν_{as} and symmetric ν_s bands of OCO^- appear at 1601–1563 cm^{-1} and at 1390–1385 cm^{-1}, respectively. The splitting of the absorption bands arising from the vibrations ν_{as}(OCO) and ν_s(OCO) ($\Delta\nu = \nu_{as} - \nu_s$) are smaller than that for sodium salt, suggesting a smaller degree of ionic bond character in these complexes compared to the sodium salt. The $\Delta\nu$ values for the Cu(II) complex (206 cm^{-1}) is greater than those for the Co(II) (178 cm^{-1}) and Ni(II) (177 cm^{-1}) complexes. The very similar $\Delta\nu$ values for the Co(II) and Ni(II) 2,6-dichlorobenzoate complexes indicate a similar character of the bond in the two complexes. Moreover, the values of the shifts in the IR frequencies of ν_{as}(OCO) and ν_s(OCO) for the Co(II) and Ni(II) complexes are practically the same, differing from that of the Cu(II) complex. From spectroscopic criteria [6–8], the carboxylate group in the Co(II) and Ni(II) complexes is bidentate chelating, whereas in the Cu(II) complex it is bidentate bridging. The IR spectra of the prepared complexes show broad absorption bands with maxima at 3163 and 3172 cm^{-1} for the Co(II) and Ni(II) complexes respectively, and at 3485 cm^{-1} for the Cu(II) complex. This suggests that the water molecules are bonded differently in the Cu(II) complex compared with the Co(II) and Ni(II) complexes.

The bands of ν(Cl) at 788–781 cm^{-1} and 766 cm^{-1} are in the same position in the IR spectra of the prepared complexes as in the spectrum of the acid, suggesting that the Cl atoms do not take part in metal–ligand bonding.

2,6-Dichlorobenzoate complexes of Co(II), Ni(II) and Cu(II) are stable in air and can be stored for several months without change. The complexes decompose in different ways during heating (Tables 3 and 4, Figs. 1–3). They are stable up to 348–395 K and then lose the water molecules of crystallization in two steps forming anhydrous complexes at 413–513 K. Comparing the final temperatures of the first and second dehydration steps, it is possible to suggest that the water of crystallization in Cu(II) 2,6-dichlorobenzoate is more strongly bonded with the cation than the water molecules in the Co(II) and Ni(II) complexes. All water molecules are in the inner sphere of the complexes.

Table 3
Data on dehydration of Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates

Complex [a]	Temp. range/K of dehyd. I	Loss/% of weight		Loss/mol of H_2O	Temp. range/K of dehyd. II	Loss/% of weight		Loss/mol of H_2O	T_{endo}/K (DTA)	Residue/ % of weight		Compound
		Calc.	Found			Calc.	Found			Calc.	Found	
$CoL_2 \cdot 6H_2O$	348-383	9.87	10.0	3	383-443	19.75	19.5	3	378, 413	89.25	80.5	CoL_2
$NiL_2 \cdot 6H_2O$	368-413	9.88	10.0	3	413-513	19.75	20.0	3	393, 453	80.25	80.0	NiL_2
$(CuL_2 \cdot H_2O)_2$	395-420	1.95	2.0	1	440-465	3.90	4.2	1	403, 453	96.10	95.8	$(CuL_2)_2$

[a] L is $C_7H_3Cl_2O_2^-$.

Table 4
Data for decomposition of Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates

Complex	Temp. range/K of stability	Temp. range/K of decomposition	Temp./K of decomp. peaks (DTG)	Temp./K of oxide formation	Residue/% of weight	
					Calc.	Found
CoL_2	443-593	593-893	633, 758	893 [a]	14.62	14.0
				1163 [b]	13.67	13.0
NiL_2	513-563	563-833	623, 793	833	13.66	13.5
$(CuL_2)_2$	465-513	513-933	523, 653	–	0	0

[a] Co_3O_4. [b] CoO.

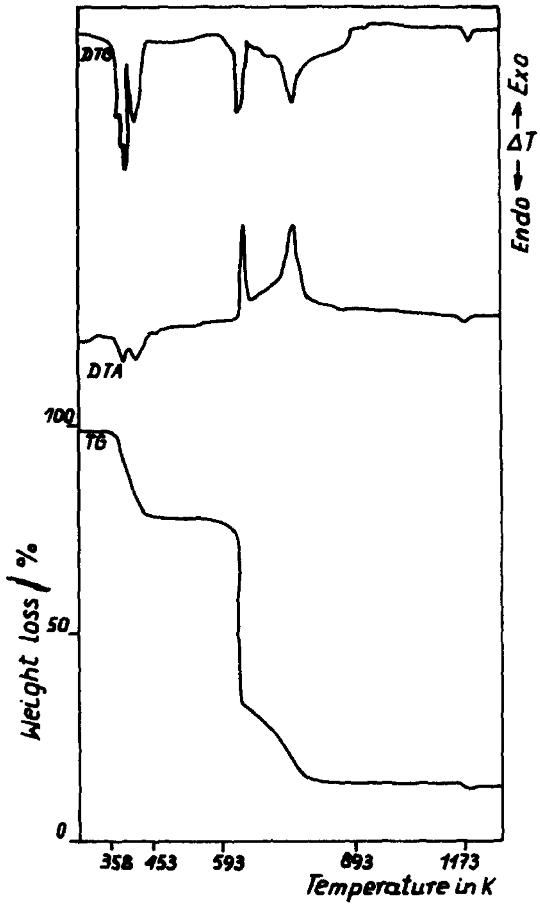

Fig. 1. TG, DTG and DTA curves of $Co(C_7H_3O_2Cl_2)_2 \cdot 6H_2O$.

From the nature of the dehydration of the Cu(II) complex and the results of the spectroscopic study, it is possible to suggest that the Cu(II) complex of 2,6-dichlorobenzoate forms a dimer, $(CuL_2(H_2O))_2$ (L is $C_7H_3O_2Cl_2^-$), whereas the complexes of Co(II) and Ni(II) are monomers. This suggestion was confirmed by XRD studies of the monocrystals [9], which showed that Co(II) and Ni(II) 2,6-dichlorobenzoates form complexes of $[M(H_2O)_6]L_2$, whereas that of copper(II) is $[CuL_2(H_2O)]_2$ (Figs. 4 and 5). In the Co(II) and Ni(II) complexes, the organic ligand is in the outer sphere, whereas in the Cu(II) complex it is in inner sphere. The water molecules in the prepared complexes are in the inner sphere.

Anhydrous complexes heated above 513–593 K decompose in various ways. On the DTG curves, there are two peaks for the Cu(II) and Ni(II) complexes, and three peaks for the Co(II) complex. This process is accompanied by strong exothermic effects, which are observed on the DTA curves and are connected with the ignition of the decomposition products. The endothermic effect observed on the

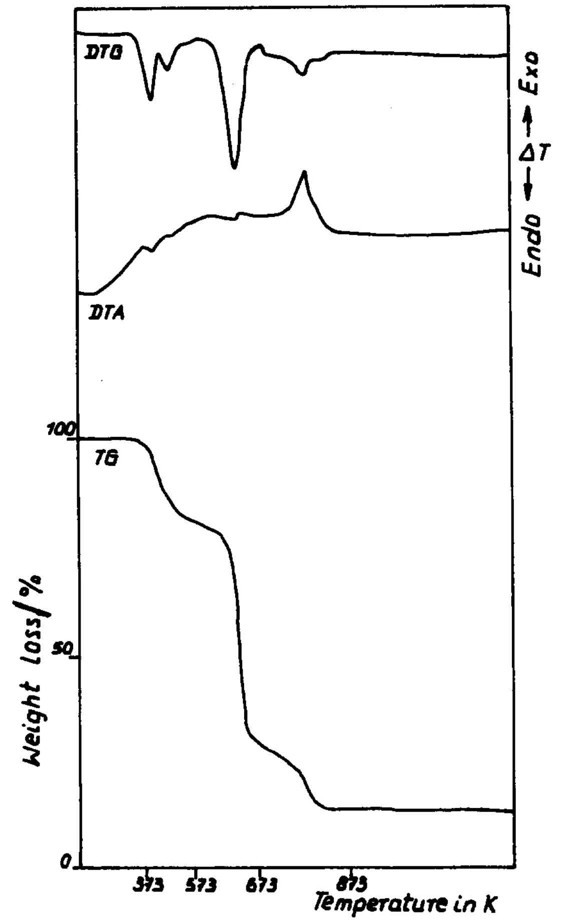

Fig. 2. TG, DTG and DTA curves of $Ni(C_7H_3O_2Cl_2)_2 \cdot 6H_2O$.

DTA curve for the Co(II) complex is connected with decomposition of Co_3O_4 to CoO. The intermediate products of the decomposition were not identified. During heating, the complexes of Co(II) and Ni(II) decompose directly to the oxides (Co_3O_4, CoO, NiO), whereas that of Cu(II) decompose to gaseous products. (Volatile chloroorganic compounds of copper are probably formed; a solid residue was not observed (Table 4).) This observation again suggests the different character of the bond between the organic ligand and the Cu(II) ion and that between the ligand and the Co(II) and Ni(II) ions.

The temperature of CoO formation is higher than that of NiO, reflecting the decrease in atomic number of the metal.

The results indicate that the thermal decomposition of hydrated Co(II), Ni(II) and Cu(II) 2,6-dichlorobenzoates can be presented as

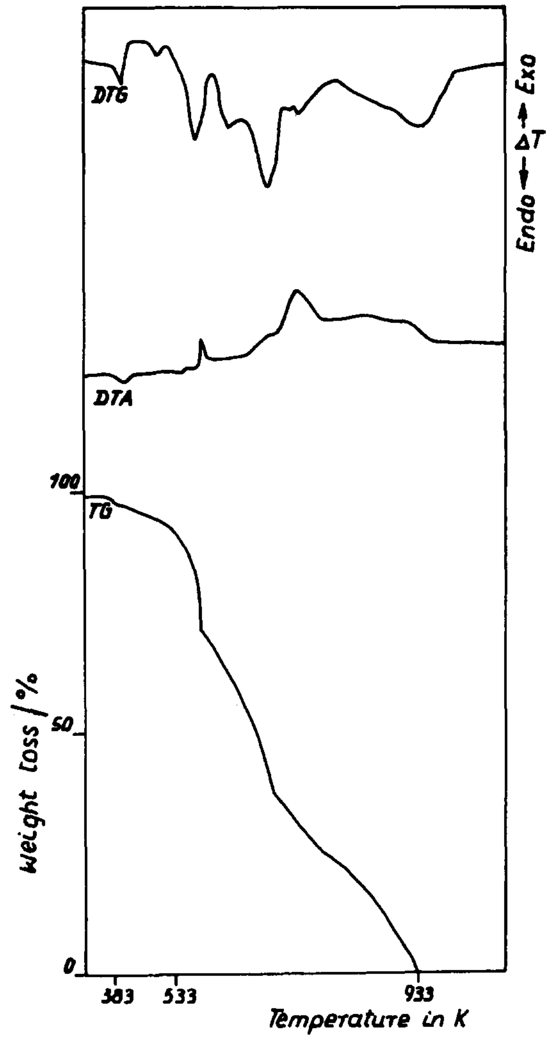

Fig. 3. TG, DTG and DTA curves of $[Cu(C_7H_3O_2Cl_2)_2 \cdot H_2O]_2$.

$CoL_2 \cdot 6H_2O \rightarrow CoL_2 \cdot 3H_2O \rightarrow CoL_2 \rightarrow Co_3O_4 \rightarrow CoO$

$NiL_2 \cdot 6H_2O \rightarrow NiL_2 \cdot 3H_2O \rightarrow NiL_2 \rightarrow NiO$

$(CuL_2 \cdot H_2O)_2 \rightarrow Cu_2L_4 \cdot H_2O \rightarrow Cu_2L_2 \rightarrow$ gaseous products

4. Conclusions

In summary, it can be suggested that when the hydrated complexes of 2,6-dichlorobenzoates of Co(II), Ni(II) and Cu(II) are heated in air, they are dehy-

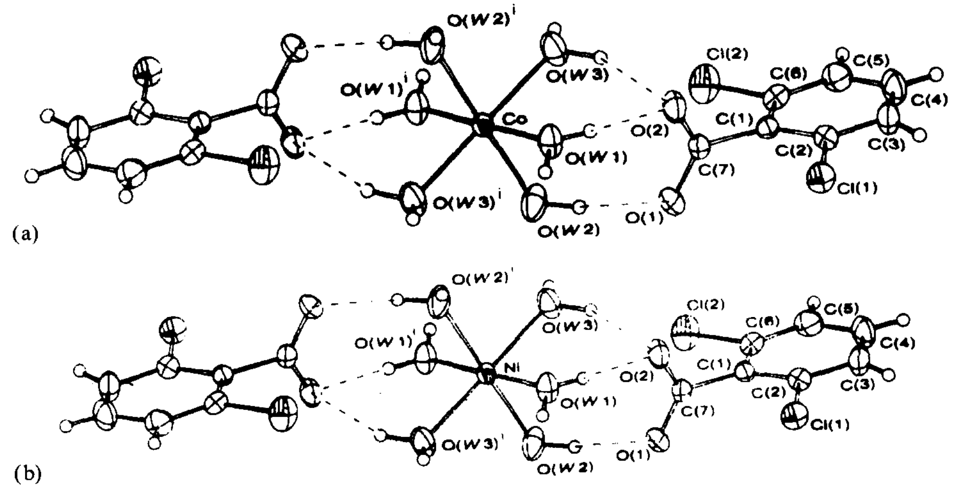

Fig. 4. Perspective view of the coordination sphere of (a) $[Co(H_2O)_6]L_2$ and (b) $[Ni(H_2O)_6]L_2$.

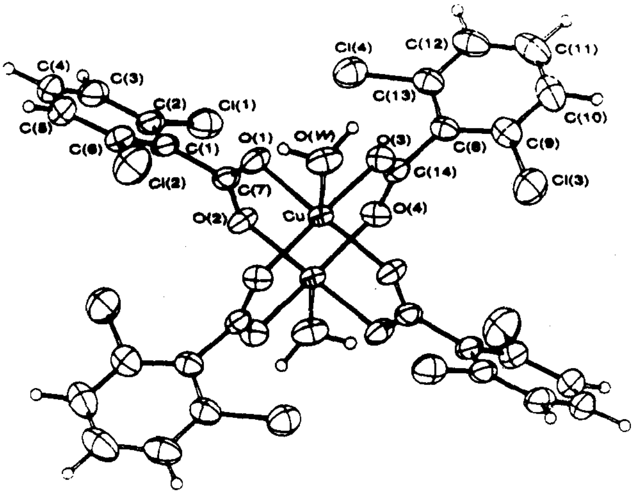

Fig. 5. Perspective view of the coordination sphere of $[CuL_2(H_2O)]_2$.

drated in two steps losing their water molecules of crystallization to give anhydrous complexes which decompose directly to the oxides (Co, Ni) or the gaseous products (Cu).

Comparing the values of the temperatures of the dehydration peaks from the DTG curves, it was found that the thermal stabilities of the studied hydrated complexes increase in the order Co < Ni < Cu, with increasing atomic number Z of the metal, and the temperatures of the decomposition of the anhydrous complexes increase in the order Cu < Ni < Co, with decreasing atomic number Z of the metal.

From the results obtained, it is possible to confirm that the structure, the manner of the coordination of the organic ligand and the properties of the Co(II) and Ni(II) 2,6-dichlorobenzoates are similar to each other and that they differ from the structure and properties of the Cu(II) complex.

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