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PREPARATION, PROPERTIES AND THERMAL DECOMPOSITIONS OF Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) COMPLEXES OF 2,5-DICHLOROBENZOIC ACID

W. Wołodkiewicz and W. Brzyska

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

Abstract

Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates were prepared and their compositions and solubilities in water at 295 K were determined. The IR spectra and X-ray diffractograms of the obtained complexes were recorded. The complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were obtained as solids with a 1:2 molar ratio of metal to organic ligand and different degrees of hydration. When heated at a heating rate of 10 K min^{-1}, the hydrated complexes lose some (Co, Zn) or all (Ni, Cu, Cd) of the crystallization water molecules and then decompose to oxide MO (Co, Ni) or gaseous products (Cu, Zn, Cd). When heated at a heating rate of 5 K min^{-1}, the complexes of Ni(II) and Cu(II) lose some (Ni) or all (Cu) of the crystallization water molecules and then decompose directly to MO.

Keywords: 2,5-dichlorobenzoic acid, complexes, IR spectra

Introduction

2,5-Dichlorobenzoic acid (HL) is a crystalline solid sparingly soluble in water, but soluble in ethanol [1]. Its complexes with metal ions are not well known.

2,5-Dichlorobenzoates of Na(I) [2], K(I), NH_4^+, Ca(II) and Ba(II) [1] have been prepared as crystalline solids soluble in water, and the complexes of Pb(II), Ag(I), Fe(II) [1] and Cu(II) [1, 3] as compounds sparingly soluble in water. The complexes of Y(III) and lanthanides (III) [4] have been prepared as crystalline solids with a molar ratio of metal to organic ligand of 1:3 and different degrees of hydration, sparingly soluble in water. Their IR spectra have been recorded and their thermal decompositions have been studied. When heated in air, the complexes undergo dehydration and then decompose to oxides, either directly or with the intermediate formation of LnOCl.

This work is a continuation of our studies on the physico-chemical properties of *d*-electron metal complexes with dichlorobenzoic acids [5–11]. Its aims were

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to prepare Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates in the solid state and to examine their physico-chemical properties and thermal decompositions in air.

Experimental

2,5-Dichlorobenzoates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by dissolving the metal(II) carbonates in a hot (~343 K) saturated solution of 2,5-dichlorobenzoic acid and then crystallizing at room temperature after filtration to remove the excess of reagents. The precipitates formed were filtered off, washed with water and dried at 303 K to constant mass. The carbon and hydrogen contents of the prepared complexes were determined by elemental analysis (Perkin Elmer CHN 2400 analyser). The chlorine contents were measured by the Schoniger method. The Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) contents were determined by the AAS method with an AAS-3 atomic absorption spectrophotometer (Carl Zeiss, Jena). The crystallization water contents were determined from the TG curves and by isothermal heating of the complexes at a suitable temperature. The experimental results are in accordance with the calculated data. The IR spectra of the complexes, of 2,5-dichlorobenzoic acid and of its sodium salt were recorded on KBr discs on an FT-IR 1725X Perkin-Elmer spectrophotometer (range 4000–400 cm^{-1}). The solubilities in water were determined at 295 K, the saturated solutions being prepared isothermally.

The thermal stabilities of the prepared 2,5-dichlorobenzoates were determined with a Paulik-Paulik-Erdey Q 1500 D Derivatograph, with recording of the TG, DTG and DTA curves. The measurements were made at sensitivities of 100 mg (TG), 500 μ V(DTG) and 500 μ V(DTA). Samples (100 mg) were heated in platinum crucibles to 1273 K at a heating rate of θ_{heat}=10 or 5 K min^{-1}. The hydrated complexes were heated isothermally at a set temperature to constant mass. The products of decomposition were calculated for the TG curves and were confirmed by recordering their X-ray patterns via the powder Debye-Scherrer method (DRON-2 diffractometer).

Results and discussion

2,5-Dichlorobenzoates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared as crystalline solids with different structures (Fig. 1) and with colours characteristic of the hydrated M(II) ions, and with a molar ratio of metal to organic ligand (calculated from the quantitative composition) of 1:2 and general formula $M(C_7H_3O_2Cl_2)_2 \cdot nH_2O$, where n=5 for Co(II), n=4 for Ni(II), n=3 for Zn(II) and n=2 for Cu(II) and Cd(II) (Table 1). The complex of Ni(II) is soluble in water. Its solubility is of the order of 10^{-2} mol dm^{-3}. The complexes of Cd(II), Zn(II), Co(II) and Cu(II) are sparingly soluble in water. Their solubilities are of

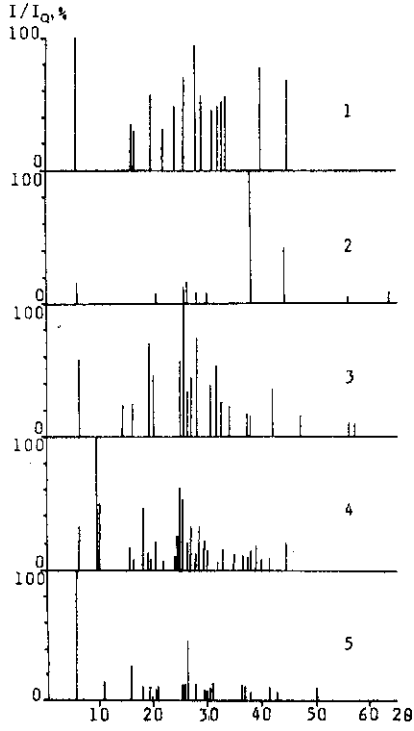

Fig. 1 Radiogram sheets of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates

the order of 10^{-3}–10^{-4} mol dm^{-3}. The solubilities of the prepared complexes decrease in the sequence Ni(II)>Cd(II)>Zn(II)=Co(II)>Cu(II).

The IR spectra of 2,5-dichlorobenzoic acid, its sodium salt and its rare earth element complexes are presented in Table 2. In the IR spectra of the studied complexes, there are broad absorption bands of valency vibrations of the OH group in H_2O with maxima at 3420–3376 cm^{-1} and a narrow band $\delta(H_2O)$ at 1599–1604 cm^{-1}, confirming the presence of crystallization water molecules. When the acid is converted to the complex, the absorption band of the COOH group at 1704 cm^{-1} disappears, and the split bands of the asymmetric valency vibrations $\nu_{as}(OCO^-)$ at 1572 cm^{-1} and 1544–1557 cm^{-1}, and the bands of the symmetric valency vibrations $\nu_s(OCO^-)$ at 1404 –1412 cm^{-1} appear.

The split absorption bands of the asymmetric vibrations of OCO^- group show [12, 13] that the carboxylate groups coordinate to the metal ion in different ways. In the IR spectra of the Co(II) and Ni(II) complexes, the splitting of the absorption bands arising from the vibrations $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ ($\Delta\nu=\nu_{as}-\nu_s$) is equal to 172–168 cm^{-1} and 140 cm^{-1}, respectively, a little smaller than for the sodium salt, suggesting a similar degree of ionic bond character in these complexes as in the sodium salt. The spectroscopic criterion [12, 13] and our previous work [7, 9] suggest that the carboxylate group in these complexes is probably both bi-

Table 1 Analytical data and solubilites of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates

Empirical formula	Formula mass	%M		%H		%C		%Cl		Solubility/ mol dm^{-3}
		calcd.	found	calcd.	found	calcd.	found	calcd.	found	
$(C_7H_3Cl_2O_2)_2Co{\cdot}5H_2O$	529.03	11.14	10.9	3.05	3.0	31.78	32.0	26.80	26.9	$1.3{\cdot}10^{-3}$
$(C_7H_3Cl_2O_2)_2Ni{\cdot}4H_2O$	510.77	11.49	11.1	2.77	2.8	32.92	32.8	27.76	27.8	$1.2{\cdot}10^{-2}$
$(C_7H_3Cl_2O_2)_2Cu{\cdot}2H_2O$	479.59	13.25	13.2	2.11	2.1	35.06	35.1	29.57	29.7	$8.0{\cdot}10^{-4}$
$(C_7H_3Cl_2O_2)_2Zn{\cdot}3H_2O$	499.45	13.09	13.0	2.43	2.3	33.67	33.5	28.39	28.4	$1.3{\cdot}10^{-3}$
$(C_7H_3Cl_2O_2)_2Cd{\cdot}2H_2O$	528.45	21.27	21.1	1.91	1.8	31.82	31.8	26.83	26.7	$5.0{\cdot}10^{-3}$

*Solubility in water at 293 K

Table 2 Frequencies of characteristic absorption bands in IR spectra (in cm^{-1}) of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Na(I) 2,5-dichlorobenzoates

Complex	ν(OH)	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu^*$	ν(C – Cl)
$(C_7H_3Cl_2O_2)_2Co{\cdot}5H_2O$	3420	1584, 1552	1412	172, 140	816, 756
$(C_7H_3Cl_2O_2)_2Ni{\cdot}4H_2O$	3376	1580, 1552	1412	168, 140	812, 760
$(C_7H_3Cl_2O_2)_2Cu{\cdot}2H_2O$	3416	1568, 1548	1404	164, 144	812, 766
$(C_7H_3Cl_2O_2)_2Zn{\cdot}3H_2O$	3424	1592, 1548	1408	184, 140	816, 760
$(C_7H_3Cl_2O_2)_2Cd{\cdot}2H_2O$	3392	1572, 1544	1408	160, 136	812, 760
$(C_7H_3Cl_2O_2)_2Na$	3459	1595, 1554	1408	187, 146	813, 763

Table 3 Data on dehydration of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates at a heating rate of 10 K min^{-1}

Complex	$[T_1 - T_1']$/K	Mass loss/%		Loss of H_2O/mol	T_2/K	Compound
		calcd.	found			
$(C_7H_3Cl_2O_2)_2Co{\cdot}5H_2O$	353–433	10.22	10.0	3	408	$(C_7H_3Cl_2O_2)_2Co{\cdot}2H_2O$
$(C_7H_3Cl_2O_2)_2Ni{\cdot}4H_2O$	353–483	14.11	14.4	4	403	$(C_7H_3Cl_2O_2)_2Ni$
$(C_7H_3Cl_2O_2)_2Cu{\cdot}2H_2O$	393–473	7.51	7.5	2	453	$(C_7H_3Cl_2O_2)_2Cu$
$(C_7H_3Cl_2O_2)_2Zn{\cdot}3H_2O$	393–453	3.61	3.5	1	393	$(C_7H_3Cl_2O_2)_2Zn{\cdot}2H_2O$
$(C_7H_3Cl_2O_2)_2Cd{\cdot}2H_2O$	373–483	6.82	6.5	2	423	$(C_7H_3Cl_2O_2)_2Cd$

$[T_1 - T_1']$ – temperature range of dehydration

T_2 – endothermic peaks on DTA

Table 4 Data on decomposition of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates at a heating rate of 10 K min^{-1}

Complex	T_1/	$[T_2 - T_2']$/	T_3/	Mass of residue/%	
	K			calcd.	found
$(C_7H_3Cl_2O_2)_2Co \cdot 2H_2O$	563	753–913, 1198–1213	993[a] 1213[b]	15.17 14.16	15.5 14.0
$(C_7H_3Cl_2O_2)_2Ni$	573	773–983	1033	14.62	14.9
$(C_7H_3Cl_2O_2)_2Cu$	533	533–633, 673–933	–	–	–
$(C_7H_3Cl_2O_2)_2Zn \cdot 2H_2O$	613	693–973	–	–	–
$(C_7H_3Cl_2O_2)_2Cd$	543	593–973	–	–	–

T_1 – temperature of decomposition
$[T_2 - T_2']$ – temperature range of exothermic peaks on DTA
T_3 – temperature of oxide formation
[a] Co_3O_4
[b] CoO

dentate and monodentate. When these results are compared with the data obtained for Co(II) and Ni(II) 3,4-dichlorobenzoates, the crystallographic structures of which have been determined [11], it is possible to suggest for Co(II) and Ni(II) 2,5-dichlorobenzoates the formula $[ML_2(H_2O)][ML_2(H_2O)_4 \cdot nH_2O$, where n=4 for Co(II) and n=2 for Ni(II).

The 2,5-dichlorobenzoates of Co(II) and Ni(II) have different structures (Fig. 1), whereas Co(II) and Ni(II) 2,4-, 2,6-, 3,4- and 3,5-dichlorobenzoates are isostructural [8 –11]. In the IR spectra of Cu(II), Zn(II) and Cd(II) 2,5-dichlo-

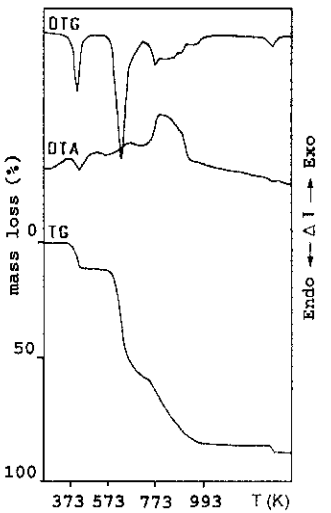

Fig. 2 TG, DTG and DTA curves of $CoL_2 \cdot 5H_2O$ (θ_{heat}=10 K min^{-1})

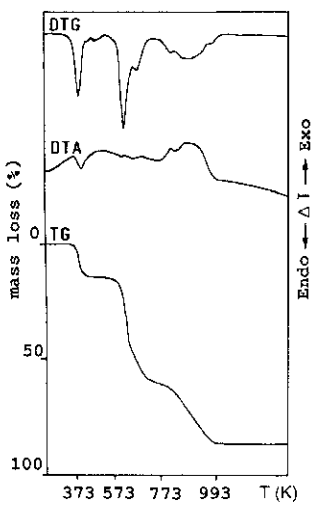

Fig. 3 TG, DTG and DTA curves of $NiL_2 \cdot 4H_2O$ (θ_{heat}=10 K min^{-1})

robenzoates, the bands $\nu_{as}(OCO^-)$ are also split and occur at 1568–1592 cm^{-1} and 1544–1458 cm^{-1}, respectively, with $\nu_s(OCO^-)$ at 1404–1408 cm^{-1}. The bands $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ in these complexes are shifted to lower frequencies or are practically the same as for the sodium salt.

On this basis, it is possible to suggest that the carboxylate groups act as both dibentate chelating and bridging groups. The two bands of ν(C–Cl) at 812–816 cm^{-1} and 756–760 cm^{-1} in the IR spectra of the complexes are insignificantly displaced as compared to ν(C–Cl) in the spectrum of the sodium salt (813

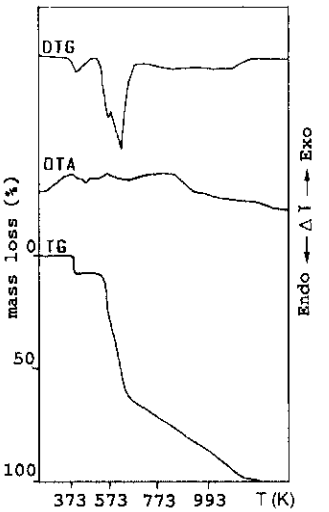

Fig. 4 TG, DTG and DTA curves of $CuL_2 \cdot 2H_2O$ (θ_{heat}=10 K min^{-1})

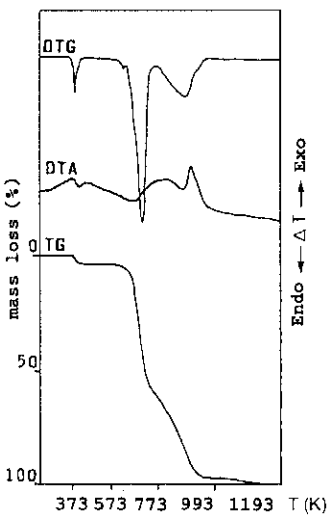

Fig. 5 TG, DTG and DTA curves of $ZnL_2 \cdot 3H_2O$ (θ_{heat}=10 K min^{-1})

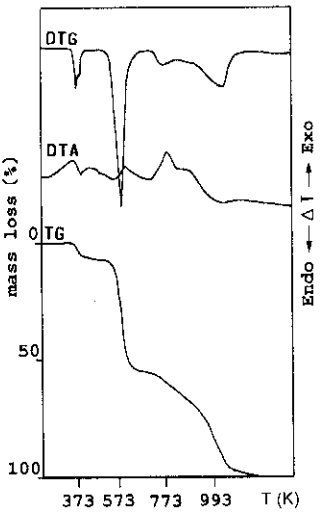

Fig. 6 TG, DTG and DTA curves of $CdL_2 \cdot 2H_2O$ (θ_{heat}=10 K min^{-1})

and 763 cm^{-1}), which suggests that the Cl atoms do not participate in the metal – ligand bonding. In general, it is possible to state that only the oxygen atoms of the carboxylate groups take part in the metal – organic ligand coordination.

The 2,5-dichlorobenzoates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are stable in air and can be stored for several months without change. During heating, they decompose in different ways (Tables 3 and 4, Figs 2–6). When heated at a heating rate of 10 K min^{-1}, the complexes are stable p to 353–393 K and next lose all (Ni, Cu, Cd) or some (Co, Zn) of their crystallization water molecules in the temperature range 353–483 K, affording anhydrous complexes or less hydrated ones, which decompose in different ways. The dihydrate Co(II) complex decomposes to CoO with the intermediate formation of Co_3O_4, whereas the anhydrous complex of Ni(II) decomposes directly to NiO. The complexes of Co(II) and Ni(II) with other isomers of dichlorobenzoic acid decompose in a similar way [5, 7–9]. The anhydrous complexes of Cu(II) and Cd(II) and the dihydrated complex of Zn(II) decompose to gaseous products (volatile chloroorganic compounds of Cu(II), Cd(II) and Zn(II) are probably formed: a solid residue was not observed) (Table 3, Figs 4–6). The results indicate that the thermal decompositions of hydrated Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) 2,5-dichlorobenzoates at 10 K min^{-1} can be presented as

$$CoL_2 \cdot 5H_2O \rightarrow CoL_2 \cdot 2H_2O \rightarrow Co_3O_4 \rightarrow CoO$$

$$NiL_2 \cdot 4H_2O \rightarrow NiL_2 \rightarrow NiO$$

$$CuL_2 \cdot 2H_2O \rightarrow CuL_2 \rightarrow \text{gaseous products}$$

$$ZnL_2 \cdot 3H_2O \rightarrow ZnL_2 2H_2O \rightarrow \text{gaseous products}$$

$$CdL_2 \cdot 2H_2O \rightarrow CdL_2 \rightarrow \text{gaseous products.}$$

Table 5 Data on dehydration and decomposition of Ni(II) and Cu(II) 2,5-dichlorobenzoates at a heating rate of 5 K min^{-1}

Complex	$[T_1 - T_1']$/K	Mass loss/%		Loss of H_2O/ mol	T_2/	T_3/	Mass of residue/%		T_4/K
		calcd.	found		K		calcd.	found	
$(C_7H_3Cl_2O_2)_2Ni{\cdot}4H_2O$	333–423	7.05	7.0	2	393	573	15.17	15.0	873
$(C_7H_3Cl_2O_2)_2Cu{\cdot}2H_2O$	363–423	7.51	7.5	2	413	533	16.59	15.0	913

$[T_1 - T_1']$ – temperature range of dehydration
T_2 – endothermic peak on DTA
T_3 – temperature of decomposition
T_4 – temperature of oxide formation

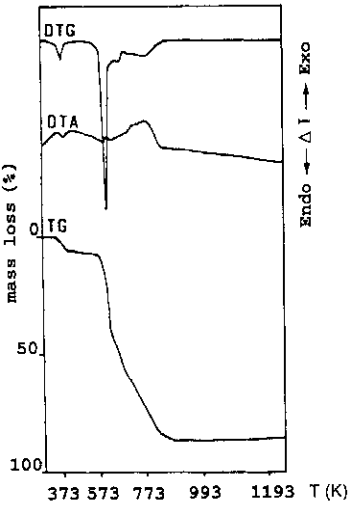

Fig. 7 TG, DTG and DTA curves of $NiL_2 \cdot 4H_2O$ (θ_{heat}=5 K min^{-1})

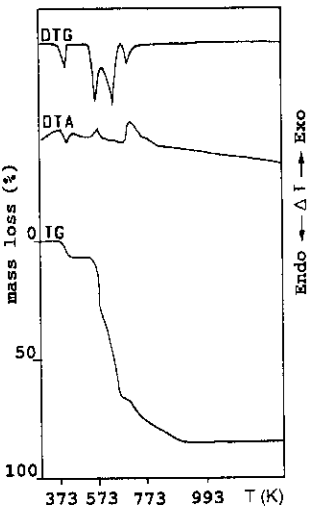

Fig. 8 TG, DTG and DTA curves of $CuL_2 \cdot 2H_2O$ (θ_{heat}=5 K min^{-1})

The prepared complexes were also heated at a heating rate of 5 K min^{-1}. The 2,5-dichlorobenzoates of Co(II), Zn(II) and Cd(II) decompose in a similar way as during heating at a heating rate of 10 K min^{-1}, whereas the complexes of Ni(II) and Cu(II) decompose in a different way (Table 5, Figs 7 and 8). On heating, the tetrahydrated complex of Ni(II) loses 2 crystallization water molecules, and the resulting dihydrate decomposes directly to NiO. The oxide NiO is formed at 873 K, whereas at a heating rate of 10 K min^{-1} it is formed at 1033 K. The dihy-

drated 2,5-dichlorobenzoate of Cu(II) undergoes dehydration at 363–423 K, and the anhydrous complex decomposes to CuO, which is formed at 913 K.

The thermal decompositions of Ni(II) and Cu(II) 2,5-dichlorobenzoates at 5 K min^{-1} can be presented as

$$NiL_2 \cdot 4H_2O \rightarrow NiL_2 \cdot 2H_2O \rightarrow NiO$$

$$CuL_2 \cdot 2H_2O \rightarrow CuL_2 \rightarrow CuO.$$

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