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*Thermal decomposition of rare earth element complexes
with 2,3-dichlorobenzoic acid*

Termiczny rozkład kompleksów pierwiastków ziem rzadkich
z kwasem 2,3-dichlorobenzoesowym

INTRODUCTION

A survey of literature shows that the complexes of dichlorobenzoic acids with metal ions are not well known. The study is not complete and concerns only complexes of some metal ions. The salts of 2,4-dichlorobenzoic acid with Ba [1], Cu (II) [2], Na [3–5], K [6], Sc (III) [7], a double salt with Fe (III) and Na [8], the salts of 2,5-dichlorobenzoic acid with Na [4], K, NH₄, Ca, Ba, Ag (I), Cu (II), and Fe (III) [9], the salts of 2,6-dichlorobenzoic acid with Ba [1], Cu (II) [10], Co (II) and Ni (II) [11], the salts of 3,4-dichlorobenzoic acid with Ca, Ba [1], Cu (II), Co (II), Ni (II) and Zn (II) [12], and the salts of 2,3-dichlorobenzoic acid with Ca and Ba [1] are known. 2,3-Dichlorobenzoates of Ca and Ba have been prepared as crystalline solids with formula: Ca(C₇H₃O₂Cl₂)₂·2H₂O and Ba(C₇H₃O₂Cl₂)·3H₂O, respectively [11]. In our previous work [12], we described the preparation of Y and lanthanide (from La (III) to Lu (III), without Pm) 2,3-dichlorobenzoates with the molar ratio of metal to organic ligand of 1:3 and crystallizing with two water molecules. The hydrated complexes are stable in air at room temperature and can be stored for several months without

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changes. The IR spectra and diffractograms were recorded [13]. The solubilities of the complexes are of the order $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and change from $2.33 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ for the Eu complex to $4.96 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ for the Y one.

The aim of this work was to examine thermal decomposition of Y (III) and lanthanide (III) 2,3-dichlorobenzoates in air atmosphere and to determine the influence of the metal and its ionic potential on thermal decomposition of the complexes in the lanthanide series.

The studies of thermal decomposition of Y and lanthanide 2,3-dichlorobenzoates are the continuation of our work on the thermal decomposition of rare earth complexes with 2,4- [14,15], 2,5- [16-18] and 2,6-dichlorobenzoic [19,20] acids.

The systematic studying of the lanthanide complexes with isomers of dichlorobenzoic acids permits to determine the influence of the twochlorine atom position in benzene ring on the properties and thermal decomposition of the complexes, which is connected with the change of the type of the metal-ligand coordination and the energy bonding.

EXPERIMENTAL

The thermal stabilities of Y(III) and lanthanide (III) (La—Lu) 2,3-dichlorobenzoates $\text{Ln}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3 \cdot 2\text{H}_2\text{O}$ (Tab. 1) were studied in static air atmosphere. The complexes of light lanthanides from La (III) to Gd (III) were heated to 1773K, whereas those of Y (III) and heavy lanthanides from Tb (III) to Lu (III) to 1273K. The TG, DTG and DTA curves were recorded. The measurements were made using a Paulik-Paulik-Erdey Q-1500D derivatograph at a heating rate $7.5 \text{ K} \cdot \text{min}^{-1}$ for the complexes of light lanthanides and $10 \text{ K} \cdot \text{min}^{-1}$ for the complexes of Y and heavy lanthanides. The samples of 100mg were heated in platinum crucibles with the following sensibilities: TG 100mg, DTG 500 μV , DTA 500 μV . Al_2O_3 was used as a standard. The samples of the lanthanide complexes were also heated isothermally at 410K and the thermal curves were recorded [Fig. 1b]. The products of thermal decomposition were calculated from TG curves and their IR spectra and X-ray patterns were recorded.

RESULTS AND DISCUSSION

The thermal analysis results presented in Figures 1, 2 and in Tables 1 and 2 indicate that 2,3-dichlorobenzoates of Y (III) and lanthanides (III) decompose in various ways when heated. Dihydrated complexes of lanthanides from La (III) to Ho (III) are stable up to 323–353 K, and then dehydrate at 403–413 K losing both molecules of water of crystallization and go to anhydrous ones. The process of dehydration is connected with endothermic effect at 383–398 K. The similar temperatures of dehydration permit to suggest that the water molecules in these complexes are bonded in the similar ways. During dehydration the structure of the complexes are changed (Fig. 3).

Anhydrous complexes of La (III) to Ho (III) are stable up to 548–661 K (TBD, Tab. 2) and then during heating decompose to the oxides Ln_2O_3 , Pr_6O_{11} , Tb_4O_7 with intermediate formation LnOCl (except Ce (III) complex which decomposes directly to CeO_2 at 548–778 K).

Dihydrated complexes of Y (III) and lanthanides from Er (III) to Lu (III) are stable up to 655–678 K and then decompose to oxides with intermediate formation LnOCl . Dehydration takes place simultaneously with decomposition of the organic ligand, which indicates that the energy of bonding water molecules and organic ligand are similar to each other.

The hydrated complexes of Y (III) and heavy lanthanides (with smaller ionic radius) are more stable than those of light lanthanides (with greater ionic radius), which is connected with the lanthanide contraction effect. Comparing the thermal stability of the complexes in the lanthanide series one can observe clearly a division into two groups (the complexes of light and heavy lanthanides). The complex of Y (III), which has the ionic radius similar to the ionic radius of heavy lanthanides, has thermal stability similar to their stability. On this basis it is possible to state that the energy bond of water molecules and the thermal stability of the complexes increases with decreasing ionic radius in the lanthanide series.

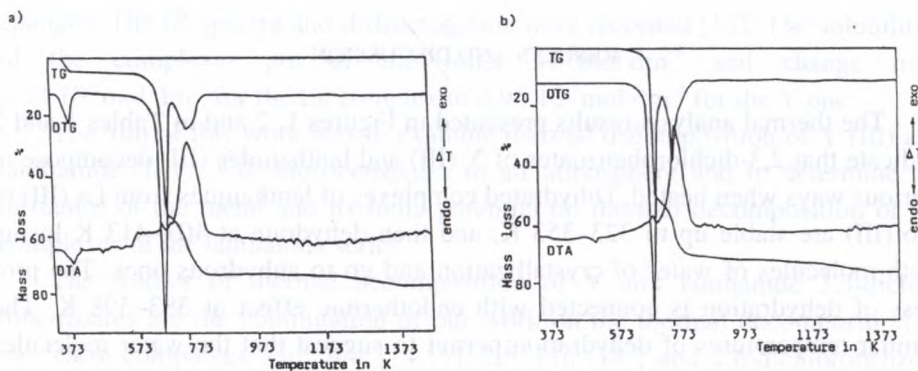


Fig. 1. TG, DTA and DTG curves for: a) $\text{Sm}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3 \cdot 2\text{H}_2\text{O}$; b) $\text{Sm}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3$

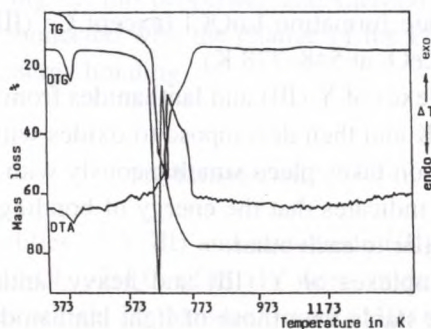


Fig. 2. TG, DTA and DTG curves for $\text{Ce}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3 \cdot 2\text{H}_2\text{O}$

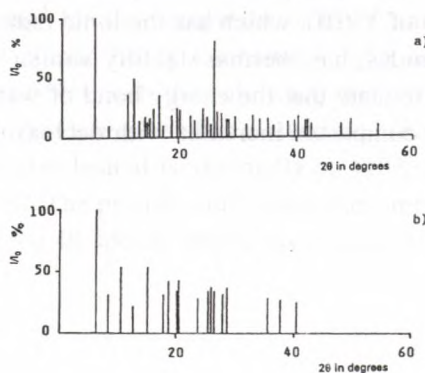


Fig. 3. Comparison of XRD patterns:
a) hydrated $\text{Sm}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3 \cdot 2\text{H}_2\text{O}$; b) anhydrous $\text{Sm}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2)_3$

Table 1. Data for dehydration of Y and lanthanide 2,3-dichlorobenzoates

Complex	$\Delta T_1/K^a$	Loss of mass [%]		Moles of H_2O lost	Endothermic peak on DTA/K	$\Delta T_1/K^b$	Endothermic peak on DTA/K ^c	Compound formed
		Calcd.	Found					
$LaL_3 \cdot 2H_2O$	353–408	4.84	5.0	2	393	408–603	498	LaL_3
$CeL_3 \cdot 2H_2O$	323–403	4.83	5.2	2	388	403–548	488	CeL_3
$PrL_3 \cdot 2H_2O$	333–408	4.82	5.0	2	388	408–628	483	PrL_3
$NdL_3 \cdot 2H_2O$	338–413	4.80	5.0	2	398	413–618	483	NdL_3
$SmL_3 \cdot 2H_2O$	348–405	4.76	5.0	2	383	403–573	473	SmL_3
$EuL_3 \cdot 2H_2O$	348–403	4.75	4.8	2	383	403–608	478	EuL_3
$GdL_3 \cdot 2H_2O$	323–403	4.73	5.0	2	383	403–588	483	GdL_3
$TbL_3 \cdot 2H_2O$	348–408	4.71	4.4	2	391	408–653	515	TbL_3
$DyL_3 \cdot 2H_2O$	343–403	4.69	4.6	2	391	403–653	513	DyL_3
$HoL_3 \cdot 2H_2O$	343–403	4.67	4.4	2	388	403–661	553	HoL_3
$ErL_3 \cdot 2H_2O$	—	—	—	—	—	—	573	$ErL_3 \cdot 2H_2O$
$TmL_3 \cdot 2H_2O$	—	—	—	—	—	—	588	$TmL_3 \cdot 2H_2O$
$YbL_3 \cdot 2H_2O$	—	—	—	—	—	—	601	$YbL_3 \cdot 2H_2O$
$LuL_3 \cdot 2H_2O$	—	—	—	—	—	—	601	$LuL_3 \cdot 2H_2O$
$YL_3 \cdot 2H_2O$	—	—	—	—	—	—	561	$YL_3 \cdot 2H_2O$

^a ΔT_1 – temperature range of dehydration; ^b ΔT_2 – temperature range of complex stability after dehydration; ^c connected with polymorphic change; L is $C_7H_3Cl_2O_2$

Table 2. Data for the decomposition of Y and lanthanide 2,3-dichlorobenzoates

Compound	$\Delta T_3/K^a$	Loss of mass [%]		$\Delta T_4/K^b$	Loss of mass [%]		Break down temp. (TBD)/K	Exothermic peak on DTA/K	Temp. of oxide formation T_K/K
		Calcd.	Found		Calcd.	Found			
LaL ₃	603–768	74.45	74.8	768–1578	78.13	78.4	603	743	1578
CeL ₃	—	—	—	548–778	76.93	77.2	548	723	778
PrL ₃	623–813	74.25	74.4	813–1513	77.21	77.6	623	778	1513
NdL ₃	618–803	73.92	74.4	803–1453	77.58	78.0	618	783	1453
SmL ₃	573–828	73.32	73.6	828–1373	76.98	77.2	573	783	1373
EuL ₃	608–843	73.16	73.4	843–1328	76.78	76.8	608	803	1328
GdL ₃	588–818	72.59	73.0	818–1283	76.19	76.6	588	798	1283
TbL ₃	653–1028	72.50	72.8	1028–1233	75.57	76.0	653	811	1233
DyL ₃	653–908	72.16	72.4	908–1218	75.73	76.0	653	813	1218
HoL ₃	661–1033	71.93	72.0	1033–1198	75.50	75.6	661	823	1198
ErL ₃ ·2H ₂ O	655–953	71.72	72.0	953–1148	75.27	75.2	655	823	1148
TmL ₃ ·2H ₂ O	676–928	71.56	71.2	928–1128	75.30	75.0	678	863	1128
YbL ₃ ·2H ₂ O	678–933	71.18	71.4	933–1123	74.71	74.8	668	888	1123
LuL ₃ ·2H ₂ O	668–941	71.01	71.2	941–1108	74.42	74.4	668	851	1108
YL ₃ ·2H ₂ O	668–1103	79.74	79.6	1103–1185	83.75	83.4	668	798	1185

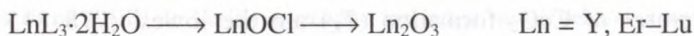
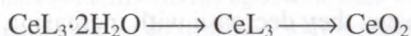
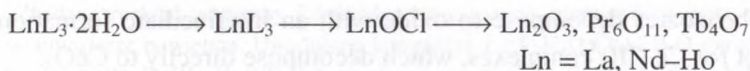
^a ΔT_3 – temperature range of decomposition to LnOCl; ^b ΔT_4 – temperature range of decomposition to oxides

During heating the prepared complexes change their crystal structure at 473–601 K (endothermic peaks on DTA) (Figs 1 and 2, Tab. 1).

The intermediate products of decomposition are formed at 768–1103 K (Tab. 2) and are stable. Only the Ce (III) complex decomposes directly to CeO_2 and does not form oxychloride. The other complexes of Ce (III) with organic ligand behave similarly [14,18,20]. The decomposition of organic ligand is connected with a strong exothermic effect (DTA) with a maximum at 723–888 K (Tab. 2).

The final products of decomposition of Y(III) and lanthanide (III) 2,3-dichlorobenzoates are the oxides: Ln_2O_3 , CeO_2 , Pr_6O_{11} and Tb_4O_7 , which are formed at 778–1578 K (T_K , Table 2). Comparing the final temperatures of oxide formation (T_K) it is possible to suggest that they change with increasing the atomic number in the lanthanide series from 1578K for La_2O_3 to 1108K for Lu_2O_3 (Tab. 2), except for CeO_2 which is formed at 778K (the lowest temperature in all series of the lanthanides). This change is connected with the lanthanide contraction and increasing polarization effect. The temperature of Y_2O_3 formation (1185K) is similar to the temperature of Ho_2O_3 formation (1198K), which is connected with the similarity of the ionic radii of Y (III) and Ho (III).

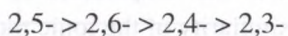
The thermal decomposition of rare earth element 2,3-dichlorobenzoates can be presented in the following manner:



In general, it can be suggested, that the complexes of Y(III) and lanthanides (III) with 2,3-dichlorobenzoic acid during heating decompose in three steps (La, Pr–Ho) or in two steps (Y, Ce, Er–Lu). The complexes of the lanthanides from La to Ho heated are dehydrated and next they decompose to oxides with an intermediate formation of LnOCl , without anhydrous Ce (III) complex, which decomposes directly to CeO_2 . The hydrated complexes of Y and Er–Lu heated do not form anhydrous complexes, but they decompose to oxides with an intermediate formation of LnOCl . The yttrium (III) complex has properties similar to the complexes of heavy lanthanides.

Comparing the thermal properties of the lanthanide complexes with isomers of dichlorobenzoic acids it is possible to suggest that they change with changing the position of chlorine atoms in the benzene ring [14,16,18,20], which influences the electron cloud density on the carbon atom of carboxylate group as well as the way and the energy of the bonding metal–ligand. The nature of metal–ligand bonding can be explained in detail following the determination of the crystal and molecular structure of monocrystals, but they have not been prepared up to now, except for 2,6-dichlorobenzoates of light lanthanides [21]. In these complexes carboxylate groups are mono- and terdentate. The chlorine atoms do not take part in coordination metal–ligand.

2,6-Dichlorobenzoates of all lanthanides (III), 2,3-dichlorobenzoates of light lanthanides (III) and 2,4- and 2,5-dichlorobenzoates of Y (III) and Gd (III) heated are dehydrated forming anhydrous compounds. The remaining hydrated complexes heated lose some crystallization water molecules and do not form anhydrous compounds. The temperatures of decomposition of dichlorobenzoates of the most lanthanides change in the order



with the change of the position of chlorine atoms. The Ce (III) dichlorobenzoates decompose at the lowest temperature in the lanthanide series. All lanthanide dichlorobenzoates decompose to oxide with an intermediate formation of LnOCl , except for Ce (III) complexes, which decompose directly to CeO_2 .

Comparing the temperatures of oxide formation it is possible to suggest that for 2,4-, 2,5-, 2,6- as for 2,3-dichlorobenzoates they decrease with increasing the atomic number Z of the metal in the lanthanide series. In all the discussed complexes the temperatures of CeO_2 formation (T_K) are the lowest (778–813 K) [16,18,20].

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STRESZCZENIE

Zbadano rozkład termiczny 2,3-dichlorobenzoesanów pierwiastków ziem rzadkich (Y, La–Lu) w atmosferze powietrza. Uwodnione kompleksy $\text{Ln}(\text{C}_7\text{H}_3\text{O}_2\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ ogrzewane rozkładają się dwu- (La(III), Pr(III)–Ho(III)) lub trójstopniowo (Ce(III), Er(III)–Lu(III), Y(III)). Uwodnione kompleksy La(III)–Ho(III) ogrzewane tracą wszystkie cząsteczki wody krystalizacyjnej, a następnie rozkładają się do tlenków z wytworzeniem związków pośrednich LnOCl , z wyjątkiem kompleksu Ce(III), który rozkłada się bezpośrednio do CeO_2 . Dwuwodne kompleksy Y i lantanowców ciężkich od Er(III) do Lu(III) ogrzewane rozkładają się do tlenków z wytworzeniem związków pośrednich LnOCl . W czasie ogrzewania otrzymane kompleksy ulegają przemianie polimorficznej.

