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Thermal decomposition of rare earth element complexes with 2,6-dichlorobenzoic acid

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Abstract

The thermal decomposition in air of 2,6-dichlorobenzoates of rare earth elements (Y, La-Lu, except Pm) was studied. During heating, the hydrated complexes Ln($C_7H_3Cl_2O_2)_3 \cdot nH_2O$ ($n = 1, 2, 4, 6$) decompose in three steps, with the exception of cerium, which decomposes in two steps. When heated, the hydrated complexes lose all their molecules of water of crystallization and then decompose to the oxides with intermediate formation of LnOCl, except the Ce(III) complex which decomposes directly to CeO_2.

Keywords: Dichlorobenzene; DTA; DTG; Lanthanon compound; Solubility; TG

1. Introduction

2,6-Dichlorobenzoic acid is a crystalline solid, soluble in hot water. Complexes of 2,6-dichlorobenzoic acid are little known. Its salt with Ba [1] was prepared as a solid soluble in water. The complexes of Y and lanthanides [2] were prepared by dissolving freshly precipitated metal hydroxides in hot solution of 2,6-dichlorobenzoic acid followed by crystallization. Cerium(III) complex was prepared by dissolving cerium(III) carbonate in a solution of 2,6-dichlorobenzoic acid. Rare earth element 2,6-dichlorobenzoates were prepared as complexes with 1 : 3 molar ratio of metal to organic ligand, having the general formula $Ln(C_7H_3Cl_2O_2)_3 \cdot nH_2O$ where

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$n = 6$ for La, $n = 4$ for Ce–Gd, $n = 2$ for Tb and Dy, and $n = 1$ for Ho–Lu and Y. Their IR spectra and X-ray diffractograms were recorded and their solubilities in water were determined [2].

Table 1
Data for dehydration of Y and lanthanide 2,6-dichlorobenzoates

Complex	$\Delta T_1/K$[a]	Loss of mass/%		Moles of H_2O lost	Endothermic peak on DTA/K	$\Delta T_2/K$[b]	Compounds formed
		Calcd.	Found				
$LaL_3 \cdot 6H_2O$	363–483	13.24	12.6	6	413	483–638	LaL_3
$CeL_3 \cdot 4H_2O$	353–433	9.22	9.6	4	388	433–603	CeL_3
$PrL_3 \cdot 4H_2O$	343–453	9.21	9.4	4	403	453–618	PrL_3
$NdL_3 \cdot 4H_2O$	353–443	9.17	8.8	4	393	443–633	NdL_3
$SmL_3 \cdot 4H_2O$	353–433	9.09	8.8	4	398	433–623	SmL_3
$EuL_3 \cdot 4H_2O$	343–433	9.08	9.4	4	393	433–618	EuL_3
$GdL_3 \cdot 4H_2O$	353–433	9.02	9.0	4	398	433–643	GdL_3
$TbL_3 \cdot 2H_2O$	343–433	4.71	4.2	2	403	433–623	TbL_3
$DyL_3 \cdot 2H_2O$	333–433	4.69	4.2	2	408	433–613	DyL_3
$HoL_3 \cdot H_2O$	343–428	2.39	2.4	1	398	428–643	HoL_3
$ErL_3 \cdot H_2O$	343–423	2.38	2.2	1	398	423–648	ErL_3
$TmL_3 \cdot H_2O$	333–428	2.38	2.4	1	393	428–673	TmL_3
$YbL_3 \cdot H_2O$	343–423	2.37	2.2	1	393	423–673	YbL_3
$LuL_3 \cdot H_2O$	333–428	2.36	2.2	1	383	428–673	LuL_3
$YL_3 \cdot H_2O$	353–433	2.66	3.2	1	413	433–643	YL_3

[a] ΔT_1, temperature range of dehydration. [b] ΔT^2, temperature range of complex stability after dehydration. L is $C_7H_3Cl_2O_2$.

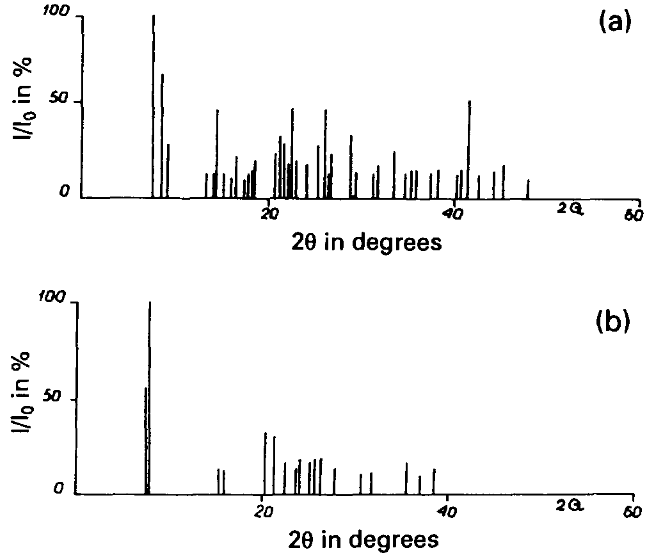
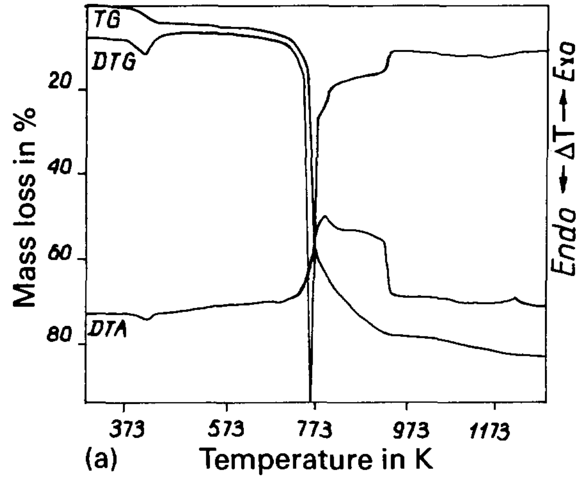


Fig. 1. Comparison of XRD patterns: (a) hydrated $La(C_7H_3O_2Cl_2)_3$; (b) anhydrous $La(C_7H_3O_2Cl_2)_3$.



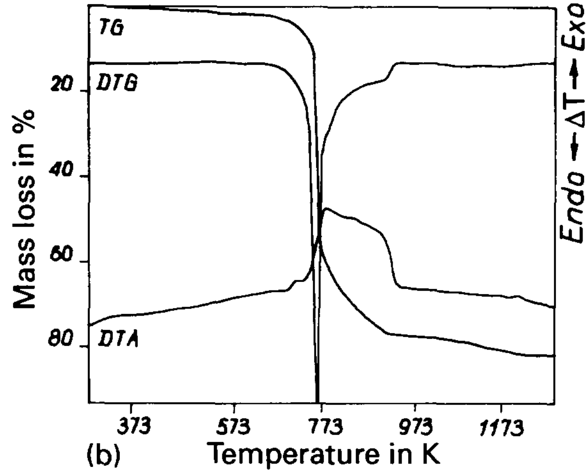


Fig. 2. TG, DTG and DTA curves for: (a) $Y(C_7H_3O_2Cl_2)_3 \cdot H_2O$; (b) $Y(C_7H_3O_2Cl_2)_3$.

The aim of this work was to examine the thermal decomposition of rare earth element 2,6-dichlorobenzoates. This work is a continuation of our study on the thermal decomposition of rare earth element complexes with 2,4- [3,4] and 2,5-dichlorobenzoic acids [5].

2. Experimental

The thermal solubilities of rare earth element (Y, La–Lu, except Pm) 2,6-dichlorobenzoates, $Ln(C_7H_3Cl_2O_2)_3 \cdot nH_2O$ (Table 1) were studied in air. The

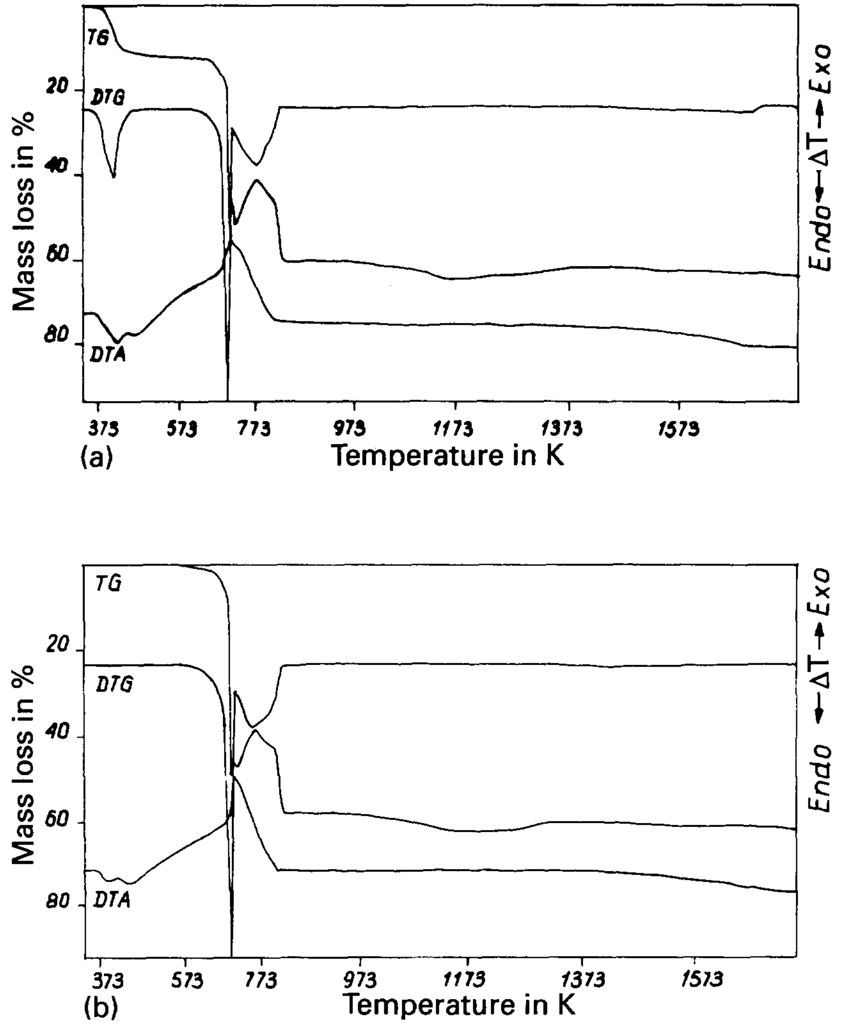


Fig. 3. TG, DTG and DTA curves for: (a) $La(C_7H_3O_2Cl_2)_3 \cdot 6H_2O$; (b) $La(C_7H_3O_2Cl_2)_3$.

complexes of light lanthanides (La(III)–Gd(III)) were heated to 1773 K, whereas those of Y and heavy lanthanides (Tb(III)–Lu(III)) were heated to 1273 K. The TG, DTG and DTA curves were recorded with Q-1500D derivatograph at a heating rate of 7.5 K min^{-1} for the light lanthanide complexes and 10 K min^{-1} for Y and the heavy lanthanide complexes. The samples of (100 mg) were heated in platinum crucibles with the following sensitivities: TG, 100 mg; DTG, 500 μV; DTA, 500 μV. Al_2O_3 was used as a standard. To confirm the results the samples were heated isothermally at 423–483 K and the thermal curves were recorded. The intermediate

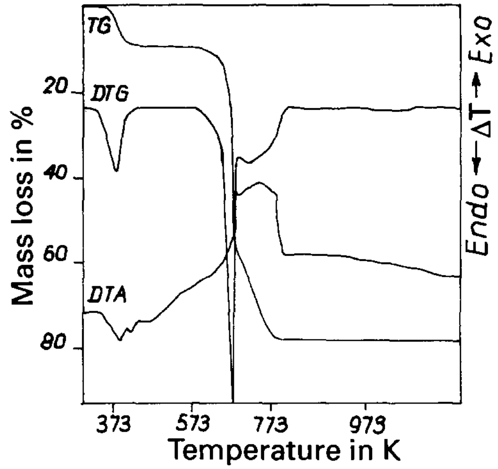


Fig. 4. TG, DTG and DTA curves for $Ce(C_7H_3O_2Cl_2)_3 . 4H_2O$.

products were calculated from TG curves and were confirmed by IR spectra and X-ray patterns.

3. Results and discussion

The results presented in Figs. 1–8 and Tables 1 and 2 indicate that rare earth element 2,6-dichlorobenzoates decompose in a similar way when heated. The hydrated complexes of Y and lanthanides (La–Lu) are stable up to 333–363 K and

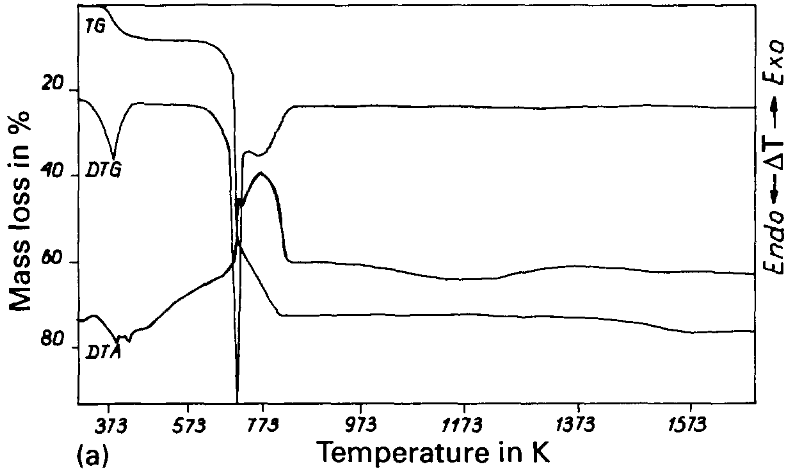


Fig. 5(a)

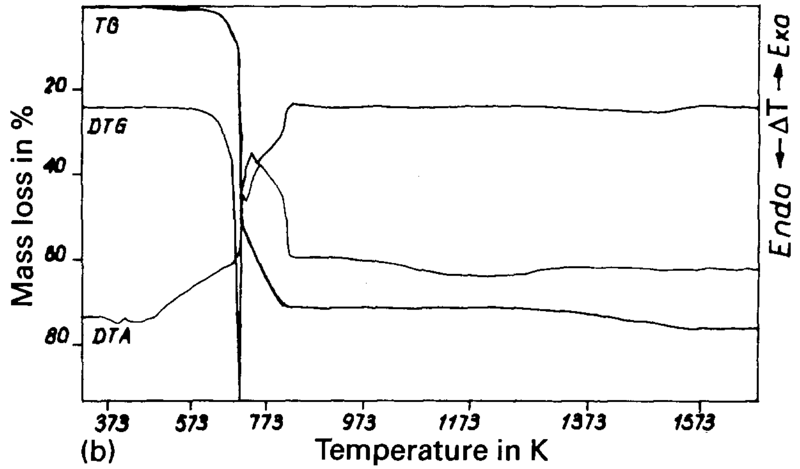


Fig. 5. TG, DTG and DTA curves for: (a) $Nd(C_7H_3O_2Cl_2)_3 \cdot 4H_2O$; (b) $Nd(C_7H_3O_2Cl_2)_3$.

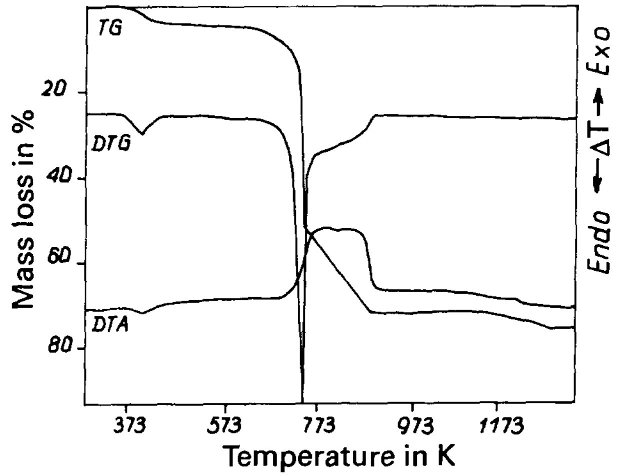


Fig. 6. TG, DTG and DTA curves for $Tb(C_7H_3O_2Cl_2)_3 \cdot 2H_2O$.

then dehydrate at 423–483 K losing all molecules of water of crystallization, forming the anhydrous complexes (Table 1). From these results, it is possible to suggest that all the molecules of water of crystallization in one complex are bonded with the same energy. The molecules of water are probably bonded by hydrogen bonds with an anion in the space lattice. During dehydration a change in the structure of the prepared complexes takes place (Fig. 1). The dehydration process is connected with a strong endothermic effect at 383–413 K (minimum on the DTA curves).

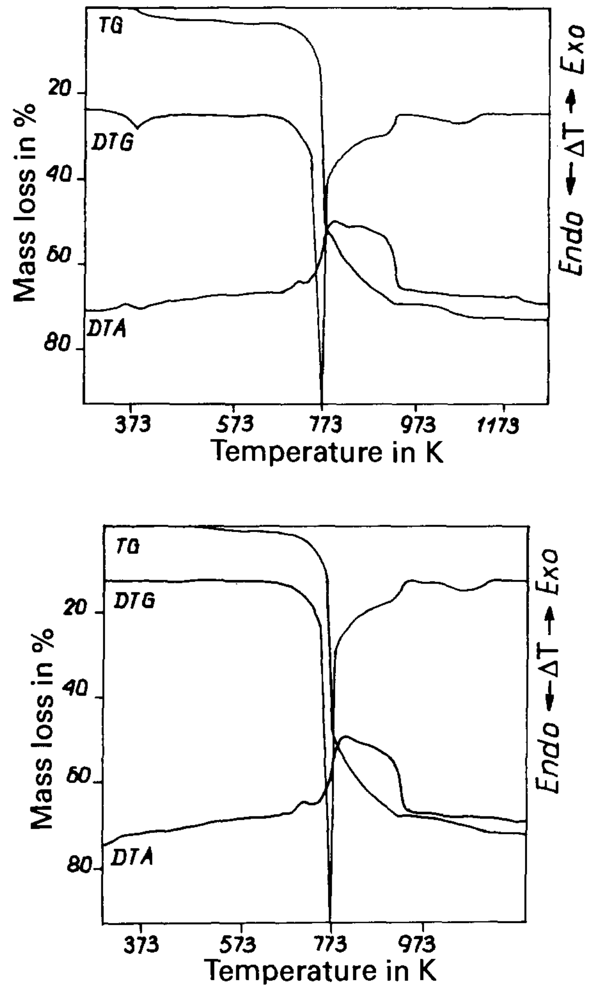


Fig. 7. TG, DTG and DTA curves for: (a) $Yb(C_7H_3O_2Cl_2)_3 \cdot H_2O$; (b) $Yb(C_7H_3O_2Cl_2)_3$.

Comparing the final temperatures of dehydration of the various complexes, it is possible to suggest that molecules of crystallization water are most strongly bonded in the La(III) and Pr(III) complexes (483 and 453 K, respectively) and least strongly in the Ho(III)-Lu(III) complexes (423-428 K). For the full interpretation of the nature of the bonding of water molecules, it is necessary to define the coordination and molecular structure of the complexes on the basis of an X-ray crystallographic study of the monocrystals.

Anhydrous complexes are stable at 603-673 K (TBD, Table 2) and then decompose to oxides with intermediate formation of LnOCl compounds, which are formed at 803-933 K (Table 2). Only the anhydrous complex of cerium(III)

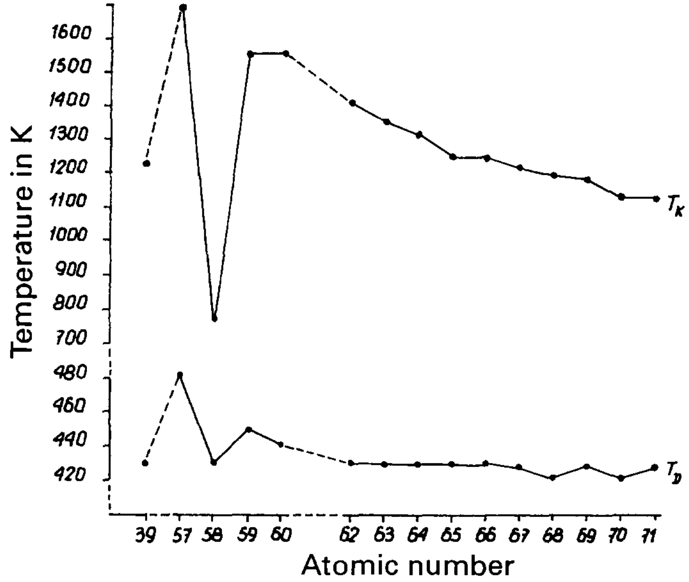


Fig. 8. Relationship between the final temperatures of dehydration T_D and of the oxide formation T_K, and the atomic number Z of the metal.

decomposes directly to CeO_2 when heated in the range 603–783 K. The complexes of Ce(III) with other organic acids [3,5] also decompose directly to CeO_2.

The process of organic ligand decomposition is accompanied by a strong exothermic effect (DTA) with a maximum at 753–803 K (Table 2). The final products of decomposition of rare earth 2,6-dichlorobenzoates are the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7, which are formed at 783–1693 K (Table 2). Comparing the temperatures of oxide formation (T_K), it is possible to suggest that they change regularly with increasing atomic number (Z) of the metal (Fig. 8) from 1693 K for La_2O_3 to 1133 K for Yb_2O_3 and Lu_2O_3, except for CeO_2. The temperature of CeO_2 formation is the lowest (783 K) (Fig. 8), as has been observed during the thermal decomposition of many series of lanthanide complexes [3,5].

The results indicate that the thermal decomposition of rare earth element 2,6-dichlorobenzoates can be presented in the following manner:

$$LnL_3 \cdot H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3$$

Ln = Y, Ho–Lu

$$LaL_3 \cdot 4H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3, \quad Pr_6O_{11}$$

Ln = Pr–Gd

$$LnL_3 \cdot 2H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3, \quad Tb_4O_7$$

Ln = Tb, Dy

$$CeL_3 \cdot 4H_2O \rightarrow CeL_3 \rightarrow CeO_2$$

Table 2
Data for the decomposition of Y and lanthanide 2,6-dichlorobenzoates

Complex	ΔT_3/K[a]	Loss of mass/%		ΔT_4/K[b]	Loss of mass/%		Break down temperature (TBD)/K	Exothermic peak on DTA/K	Temp. of oxide formation T_K/K
		Calcd.	Found		Calcd.	Found			
LaL_3	638–803	76.69	76.0	803–1693	80.05	80.4	638	773	1693
CeL_3	–	–	–	603–783	77.98	78.4	603	753	783
PrL_3	618–803	75.42	75.2	803–1563	78.25	78.4	618	773	1563
NdL_3	633–808	75.10	75.2	808–1563	78.59	78.4	633	768	1563
SmL_3	623–818	74.46	74.0	818–1413	77.94	78.0	623	773	1413
EuL_3	618–803	74.37	73.6	803–1368	77.83	77.6	618	763	1368
GdL_3	643–823	73.88	73.2	823–1323	77.31	77.2	643	773	1423
TbL_3	623–883	72.48	72.2	883–1253	75.49	75.6	623	783	1253
DyL_3	613–883	73.13	72.6	883–1253	75.70	75.6	613	783	1253
HoL_3	643–913	71.26	71.2	913–1223	74.91	75.0	643	791	1223
ErL_3	648–918	71.05	70.5	918–1198	74.68	74.5	648	793	1198
TmL_3	673–925	70.90	70.2	925–1188	74.41	74.2	677	793	1188
TbL_3	673–923	70.50	70.0	923–1133	74.11	74.0	673	798	1133
LuL_3	673–933	70.33	70.0	933–1133	73.92	73.6	673	803	1133
YL_3	643–928	79.29	78.4	928–1233	83.31	83.2	643	793	1233

[a] ΔT_3, temperature range of decomposition to LnOCl. [b] ΔT_4, temperature range of decomposition to oxides.

In general, it can be suggested that rare earth 2,6-dichlorobenzoates when heated in air decompose in three steps (except Ce(III) complex). The hydrated complexes lose all water molecules during heating and then decompose to oxides Ln_2O_3, Pr_6O_{11} and Tb_4O_7 with intermediate formation of LnOCl, except for the Ce(III) complex which decomposes directly to CeO_2. The yttrium(III) 2,6-dichlorobenzoate decomposition is similar to those of the heavy lanthanides, which is connected with the similarity in their ionic radius.

Comparing the dehydration processes of 2,4-, 2,5- and 2,6-dichlorobenzoates of rare earth elements, it was found that in 2,4- and 2,5-dichlorobenzoates the molecules of crystallization water are bonded as outer and inner sphere water [3,5], whereas in 2,6-dichlorobenzoates, they are bonded only as outer sphere water. The dehydration of 2,4- and 2,5-dichlorobenzoates proceeds in two steps, whereas the dehydration of 2,6-dichlorobenzoates proceeds in one step.

Comparing the temperatures of oxide formation it is possible to suggest, for 2,4- and 2,5-dichlorobenzoates as for 2,6-dichlorobenzoates, that they decrease regularly with increasing atomic number of the metal and have similar values. In all the discussed complexes, the temperatures of CeO_2 formation (T_K) are the lowest values [3,5].

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