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Thermal decomposition of rare earth element complexes with 2,5-dichlorobenzoic acid

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Abstract

The thermal decomposition in air of 2,5-dichloribenzoates of rare earth elements (Y, La–Lu, without Pm) has been studied. During heating, the hydrated complexes $Lu(C_7H_3Cl_2O_3) \cdot nH_2O$ ($n = 2, 4, 8$) decompose in three steps, with the exception of cerium, which decomposes in two steps. The hydrated complexes heated lose all (Y, Gd) or some molecules of water of crystallization (La, Pr–Eu, Tb–Tm) and next decompose to the oxides with intermediate formation of LnOCl, except Ce(III) complex which decomposes directly to CeO_2. The anhydrous complexes of Yb and Lu decompose in two steps to the oxides with intermediate formation LnOCl.

INTRODUCTION

Complexes of 2,5-dichlorobenzoic acid are little known. In the previous work [1], we described the preparation of Y and lanthanide (from La(III) to Lu(III), without Pm) 2,5-dichlorobenzoates with the molar ratio of metal to organic ligand of 1:3 and different degrees of hydration, their IR spectra, X-ray patterns [2] and solubilities in water.

The studies of the thermal decomposition of Y and lanthanide 2,5-dichlorobenzoates are the continuation of our work on the thermal decomposition of rare earths with *o*- [3], *m*- [4], *p*-chlorobenzoic acid [5] and 2,4-dichlorobenzoic acid [6].

EXPERIMENTAL

The thermal stabilities of rare earth (Y, La–Lu) 2,5-dichlorobenzoates, $Ln(C_7H_3Cl_2O_2)_3 \cdot nH_2O$ (Table 1) were studied in air atmosphere. The complexes of light lanthanides (La–Gd) were heated to 1773 K, whereas those of Y and heavy lanthanides (Tb–Lu) were heated to 1273 K. The TG,

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TABLE 1

Data for dehydration of Y and lanthanide 2,5-dichlorobenzoates

Complex	ΔT_1 [a] in K	Loss of mass in %		Moles of H_2O lost	Endothermic peak on DTA in K	ΔT_2 [b] in K	Endothermic peak on DTA [c] in K	Compounds formed
		Calc.	Found					
$LaL_3 \cdot 8H_2O$	313–418	4.2	4.2	2	408	418–633	473	$LaL_3 \cdot 6H_2O$
$CeL_3 \cdot 4H_2O$	323–408	4.6	4.2	2	403	408–463	458	$CeL_3 \cdot 2H_2O$
$PrL_3 \cdot 8H_2O$	348–418	4.2	4.2	2	408	418–633	473	$PrL_3 \cdot 6H_2O$
$NdL_3 \cdot 4H_2O$	333–403	4.6	3.6	2	393	403–618	463	$NdL_3 \cdot 2H_2O$
$SmL_3 \cdot 4H_2O$	333–403	4.5	4.2	2	383	403–613	463	$SmL_3 \cdot 2H_2O$
$EuL_3 \cdot 4H_2O$	328–411	4.5	4.0	2	393	411–623	468	$EuL_3 \cdot 2H_2O$
$GdL_3 \cdot 2H_2O$	343–413	4.7	4.0	2	403	413–663	493	GdL_3
$TbL_3 \cdot 4H_2O$	338–408	4.5	4.0	2	393	408–663	478	$TbL_3 \cdot 2H_2O$
$DyL_3 \cdot 4H_2O$	348–393	4.5	4.2	2	373	393–653	483	$DyL_3 \cdot 2H_2O$
$HoL_3 \cdot 4H_2O$	348–388	4.5	4.2	2	373	388–653	481	$HoL_3 \cdot 2H_2O$
$ErL_3 \cdot 4H_2O$	343–393	4.4	4.4	2	373	393–663	493	$ErL_3 \cdot 2H_2O$
$TmL_3 \cdot 4H_2O$	328–378	4.4	4.0	2	363	378–661	503	$TmL_3 \cdot 2H_2O$
YbL_3							513	YbL_3
LuL_3							521	LuL_3
$YL_3 \cdot 2H_2O$	333–385	5.2	4.8	2	373	385–681	493	YL_3

[a] ΔT_1, Temperature range of dehydration. [b] ΔT_2, Temperature range of complex stability after dehydration. [c] Connected with polymorphic change.

DTG and DTA curves were recorded with a Q-1500 D 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 also heated isothermally at 378–418 K and the thermal curves were recorded. The intermediate products were confirmed by IR spectra and X-ray patterns.

RESULTS AND DISCUSSION

The results presented in Figs. 1–6 and Tables 1 and 2 indicate that rare earth 2,5-dichlorobenzoates decompose in various ways when heated. The hydrated complexes of Y and lanthanides from La(III) to Tm(III) are stable up to 313–348 K, and then dehydrate at 378–418 K. Dihydrated complexes of Y and Gd lose both molecules of water of crystallization and go to anhydrous ones. The complexes of the remaining rare earth elements (La–Eu, Tb–Tm) lose only two water molecules, forming less hydrated compounds (Table 1). From these results, it is possible to suggest that molecules of water of crystallization in the complexes of La–Eu and Tb–Tm are bonded in different ways: with an anion in the space lattice bonded by hydrogen bond (lost during dehydration) and as coordination water which is strongly bonded with metal ion (lost simultaneously with decomposition of the organic ligand). The dehydration process is connected with a strong endothermic effect at 363–408 K.

Comparing the final temperatures of dehydration of the various complexes, it is possible to suggest that molecules of water of crystallization are most strongly bonded in La(III) and Pr(III) complexes (418 K), and

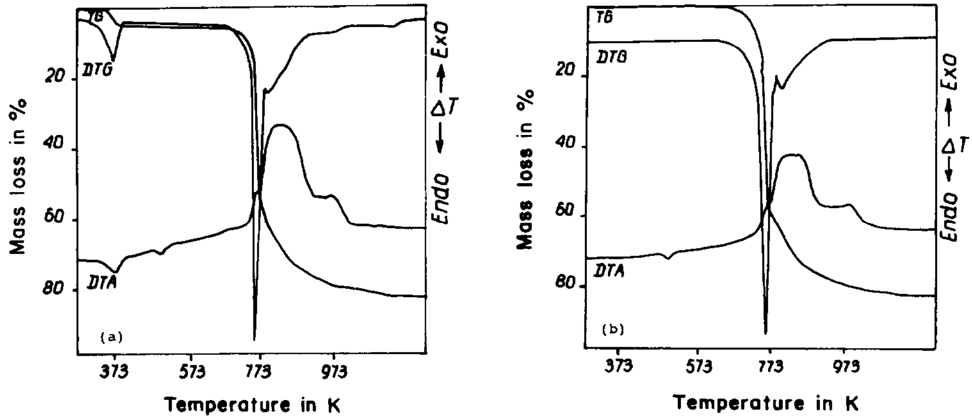

Fig. 1. TG, DTG and DTA curves for (a) $Y(C_7H_3O_2Cl_2)_3 \cdot 2H_2O$ and (b) $Y(C_7H_3O_2Cl_2)_3$.

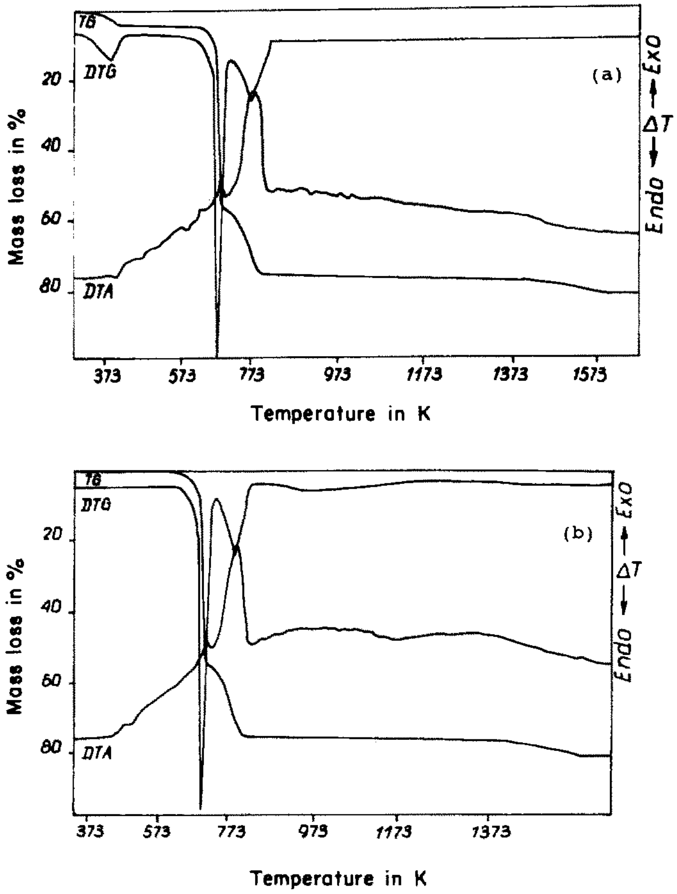

Fig. 2. TG, DTG and DTA curves for (a) $La(C_7H_3O_2Cl_2)_3 \cdot 8H_2O$ and (b) $La(C_7H_3O_2Cl_2)_3 \cdot 6H_2O$.

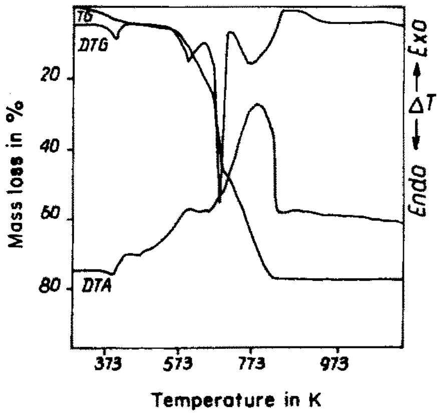

Fig. 3. TG, DTG and DTA curves for $Ce(C_7H_3O_2Cl_2)_3 \cdot 4H_2O$.

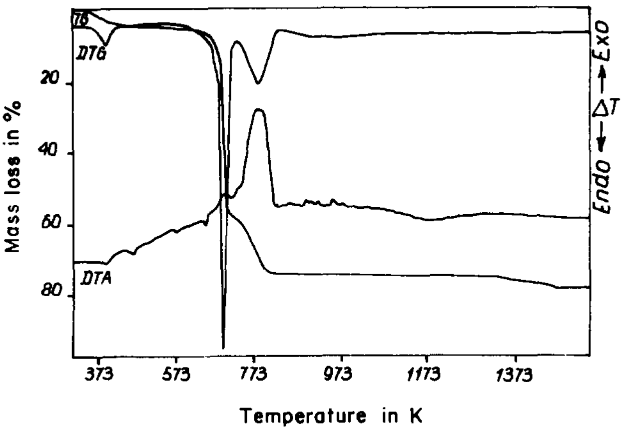

Fig. 4. TG, DTG and DTA curves for $Nd(C_7H_3O_2Cl_2)_3 \cdot 4H_2O$.

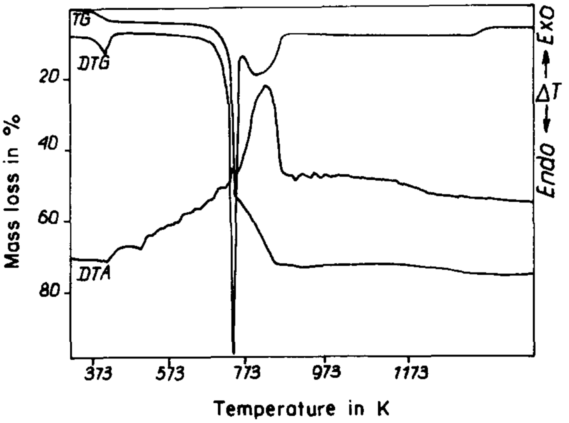

Fig. 5. TG, DTG and DTA curves for $Gd(C_7H_3O_2Cl_2)_3 \cdot 2H_2O$.

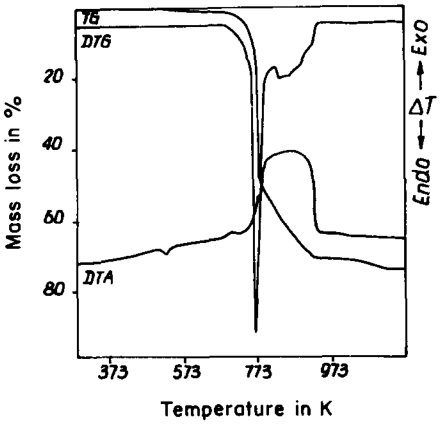

Fig. 6. TG, DTG and DTA curves for $Lu(C_7H_3O_2Cl_2)_3$.

TABLE 2

Data of decomposition of Y and lanthanide 2,5-dichlorobenzoates

Complex	ΔT_3 [a] in K	Loss of mass in %		ΔT_4 [b] in K	Loss of mass in %		Breakdown temperature (TBD) in K	Exothermic peak on DTA in K	Temperature of oxide formation T_K in K
		Calc.	Found		Calc.	Found			
$LaL_3 \cdot 6H_2O$	633–793	77.7	77.0	793–1593	80.9	81.0	633	783	1593
$CeL_3 \cdot 2H_2O$		–	–	463–813	78.0	78.0	463	793	813
$PrL_3 \cdot 6H_2O$	633–823	77.5	76.6	823–1548	80.2	80.0	633	813	1548
$NdL_3 \cdot 2H_2O$	618–801	75.1	74.6	801–1483	78.6	78.6	618	785	1483
$SmL_3 \cdot 2H_2O$	613–813	74.6	74.6	813–1378	78.0	78.0	613	793	1378
$EuL_3 \cdot 2H_2O$	623–838	74.4	74.3	838–1323	77.8	78.0	623	793	1323
GdL_3	663–858	72.6	72.6	858–1323	76.2	76.4	663	838	1323
$TbL_3 \cdot 2H_2O$	663–913	73.7	73.5	913–1238	76.6	77.0	663	843	1238
$DyL_3 \cdot 2H_2O$	653–908	73.4	73.2	908–1213	76.8	76.8	653	843	1213
$HoL_3 \cdot 2H_2O$	653–893	73.2	74.0	893–1183	76.6	77.0	653	843	1183
$ErL_3 \cdot 2H_2O$	663–883	72.9	73.2	883–1138	76.4	76.6	663	813	1138
$TmL_3 \cdot 2H_2O$	661–901	72.8	73.0	901–1123	76.2	76.4	661	840	1123
YbL_3	678–913	69.8	70.2	913–1118	73.5	73.6	678	845	1118
LuL_3	683–923	69.6	70.4	923–1118	73.3	73.8	683	855	1118
YL_3	681–983	79.8	80.0	983–1138	83.7	83.6	681	843	1138

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

least strongly in Dy(III)–Tm(III) and Y(III) complexes (378–393 K). The DTA curve data also confirm these results. For a 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 X-ray crystallographic study of single crystals.

Fully or partially dehydrated complexes when heated undergo polymorphic change (the endothermic peak on the DTA curve at 463–521 K) and then decompose to the oxides with intermediate formation of very stable LnOCl. The anhydrous complexes of Yb(III) and Lu(III) also decompose oxides with intermediate formation of YbOCl and LuOCl. The oxychlorides form in the temperature range 613–983 K. Partially dehydrated complexes of Ce(III) when heated decompose directly to CeO_2 in the range 463–813 K. The other complexes of Ce(III) [3–6] also decompose directly to CeO_2.

The process of organic ligand decomposition is accompanied by a strong exothermic effect (DTA) with maximum at 783–855 K (Table 2). The final products of decomposition of the rare earth 2,5-dichlorobenzoates are the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7, which are formed at 813–1593 K. Comparing the temperatures of oxide formation (T_K) it is possible to suggest that they change regularly with increasing atomic number (Z) of metal (Fig. 7) from 1593 K for La_2O_3 to 1118 K for Yb_2O_3 and Lu_2O_3, with the exception of CeO_2, which is formed at 811 K. The temperature of CeO_2 formation is the lowest, as observed during the thermal decomposition of many series of lanthanide complexes [3–6].

The results indicate that the thermal decomposition of rare earth element 2,5-dichlorobenzoates can be presented in the following manner:

$$LnL_3 \cdot nH_2O \rightarrow LnL_3 \cdot mH_2O \rightarrow LnOCl \rightarrow Ln_2O_3, \quad Pr_6O_{11}, \quad Tb_4O_7$$

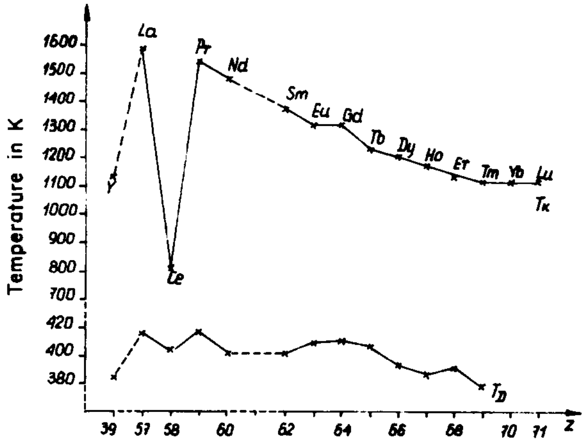

Fig. 7. Relationship between the final temperatures of dehydration T_D and of the oxide formation T_K, and the atomic number Z of the metal.

where Ln is La, Pr–Eu, Tb–Tm and $n > m$;

$LnL_3 \cdot 2H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3$

where Ln is Y, Gd;

$LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3$

where Ln is Yb, Lu;

$CeL_3 \cdot 4H_2O \rightarrow CeL_3 \cdot 2H_2O \rightarrow CeO_2$

In general, it can be suggested that 2,5-dichlorobenzoates decompose in two or three steps. The hydrated complexes lose during heating all or some water molecules, undergo polymorphic change, and then decompose to oxides Lu_2O_3, Pr_6O_{11} and Tb_4O_7 with intermediate formation LnOCl, except for the Ce(III) complex which decomposes directly to CeO_2. The anhydrous complexes of Yb and Lu decompose to Yb_2O_3 and Lu_2O_3 with intermediate formation of LnOCl. Yttrium(III) 2,5-dichlorobenzoate decomposition is similar to those of heavy lanthanides.

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