

Thermal decomposition of rare earth element 2,4-dihydroxybenzoates in air

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Abstract

The conditions of the formation of rare earth 2,4-dihydroxybenzoates were studied, and their quantitative composition and solubilities in water at 293 K were determined. The IR spectra and X-ray diffraction patterns of the hydrated complexes were recorded and their thermal decompositions in air were investigated. During heating, the hydrated complexes $\text{Ln}(\text{C}_7\text{H}_5\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ ($n = 2, 4$) lose water of crystallization in one step, then decompose to the oxides, with intermediate formation of very unstable $\text{Ln}_2(\text{C}_7\text{H}_5\text{O}_4)_3$ and $\text{Ln}_2\text{O}(\text{C}_7\text{H}_4\text{O}_4)_2$ compounds, with the exception of cerium which forms only $\text{Ce}_2(\text{C}_7\text{H}_5\text{O}_4)_3$.

INTRODUCTION

Rare-earth element complexes with 2,4-dihydroxybenzoic acid, $\text{C}_6\text{H}_3(\text{OH})_2\text{COOH}$, are not very well known. 2,4-Dihydroxybenzoates of La, Pr, Nd, Sm and Gd have been prepared as anhydrous salts of formulae $\text{Ln}(\text{C}_7\text{H}_5\text{O}_4)_3$ [1] by the method described earlier for the antranilates [2, 3], and their IR and UV spectra have been recorded. The solubilities of Y, La, Nd, Sm, Gd, Ho and Yb complexes as a function of temperature [4], the luminescent spectra of Tb complex in methanol [5] and the transfer energy from 2,4-dihydroxybenzoic acid to several lanthanide ions ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}$) in methanol [6] have been determined.

As a continuation of our work on the properties and the thermal decomposition of rare earth 2- [7], 3- [8–10] and 4-hydroxybenzoates [11], we now report the properties and the thermal decomposition of rare earth 2,4-dihydroxybenzoate hydrates during heating in air.

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EXPERIMENTAL

Complexes of 2,4-dihydroxybenzoic acid with Y(III) and lanthanides from La(III) to Lu(III) (without Pm) were prepared by the addition of equivalent quantities of ammonium 2,4-dihydroxybenzoate (pH 5.0) to a hot solution containing the rare earth chloride (Ce was used as its nitrate). The precipitate formed was filtered off, washed with methanol and dried at 303 K to a constant mass.

The quantitative compositions of the prepared complexes were determined by elemental analysis, by ignition of the complexes to form the oxides and from the TG curves. The crystallization water was determined from the TG curves.

The IR spectra for the complexes, and the spectra for 2,4-dihydroxybenzoic acid and its sodium salt, were recorded as KBr discs on a UR-2 spectrophotometer (range 4000–400 cm^{-1}). The X-ray diffraction patterns of the prepared 2,4-dihydroxybenzoates were taken on a DRON-2 diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. The measurements were made within the range $2\theta = 5\text{--}60^\circ$ by means of the Debye–Scherrer method. The solubilities of the rare-earth 2,4-dihydroxybenzoates in water at 293 K were determined by measuring the concentration of Ln^{3+} ions in saturated solutions by the oxalate method.

The thermal stabilities of yttrium and lanthanide 2,4-dihydroxybenzoates were studied in air. The TG, DTG and DTA curves were recorded with a Q-1500 D derivatograph at a heating rate of 10 K min^{-1} with the sensitivities: TG, 100 mg; DTG, 500 μV ; DTA, 500 μV . The samples (100 mg) were heated to 1273 K in platinum crucibles. The paper speed was 2.5 mm min^{-1} and Al_2O_3 was used a standard.

RESULTS AND DISCUSSION

2,4-Dihydroxybenzoates of yttrium(III) and lanthanides(III) were obtained as solids with the colour characteristic for Ln(III) ions, a molar ratio of metal to ligand of 1:3, and general formula $\text{Ln}[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]_3 \cdot n\text{H}_2\text{O}$. The complexes of light lanthanides from La(III) to Gd(III) were prepared as dihydrates and those of Y(III) and heavy lanthanides from Tb(III) to Lu(III) as tetrahydrates. The hydrated 2,4-dihydroxybenzoates of Pr(III), Nd(III), Sm(III) and Eu(III) are amorphous solids whereas the hydrated complexes of the remaining lanthanides are crystalline, being isostructural in the groups; La and Ce; Tb, Dy, Ho and Er; and Tm, Yb and Lu.

2,4-Dihydroxybenzoates of rare-earth elements are soluble in water. Their solubilities are in the order of 10^{-3} to $10^{-2} \text{ mol l}^{-1}$ (Table 1) and change in the lanthanide series with increasing atomic number. The

TABLE 1

Frequencies (cm^{-1}) of the absorption bands of COO^- and OH groups of 2,4-dihydroxybenzoic acid and its compounds and their solubility ($\text{mol l}^{-1} \times 10^{-2}$) in water at 293 K

Complex ^a	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu_{\text{as}} - \nu_{\text{s}}$	$\delta(\text{OH})$	$\nu(\text{OH})$	$\nu(\text{M-O})$	Solubility
HL	–	–	–	1440	870, 1280	–	–
NaL	1645	1410	235	1445	860, 1300	430	–
$\text{YL}_3 \cdot 4\text{H}_2\text{O}$	1630	1400	230	1455	860, 1285	455	3.98
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	1630	1400	230	1455	865, 1285	455	0.67
$\text{CeL}_3 \cdot 2\text{H}_2\text{O}$	1630	1400	230	1455	855, 1285	455	0.56
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	1635	1400	235	1455	860, 1290	455	0.58
$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$	1635	1410	225	1455	865, 1290	455	0.62
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	1635	1405	230	1455	860, 1290	455	0.82
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	1635	1400	235	1455	860, 1290	455	1.16
$\text{GdL}_3 \cdot 2\text{H}_2\text{O}$	1630	1400	230	1445	870, 1290	455	1.51
$\text{TbL}_3 \cdot 4\text{H}_2\text{O}$	1635	1405	230	1455	860, 1290	455	2.82
$\text{DyL}_3 \cdot 4\text{H}_2\text{O}$	1635	1405	230	1450	860, 1285	455	3.94
$\text{HoL}_3 \cdot 4\text{H}_2\text{O}$	1635	1405	230	1460	855, 1290	450	3.85
$\text{ErL}_3 \cdot 4\text{H}_2\text{O}$	1640	1405	235	1465	860, 1290	450	4.81
$\text{TmL}_3 \cdot 4\text{H}_2\text{O}$	1640	1400	240	1465	850, 1305	450	9.84
$\text{YbL}_3 \cdot 4\text{H}_2\text{O}$	1640	1400	240	1465	850, 1305	450	18.17
$\text{LuL}_3 \cdot 4\text{H}_2\text{O}$	1640	1400	240	1465	850, 1305	450	16.12

^a L = $[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]^-$.

solubilities of the light lanthanide complexes change insignificantly and those of the heavy lanthanides increase very rapidly from Tb to Lu.

All rare-earth 2,4-dihydroxybenzoates show similar solid-state IR spectra (Table 1). However the characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salt. In the IR spectrum of 2,4-dihydroxybenzoic acid, there is an absorption band at 3370 cm^{-1} due to the valency vibration of the OH group, the band of the COOH group at 1640 cm^{-1} , and the bands of $\delta(\text{OH})$ and $\nu(\text{OH})$ at 1440, 870 and 1270 cm^{-1} respectively. In the IR spectra of the prepared complexes, there are bands at $1640\text{--}1630 \text{ cm}^{-1}$ and $1405\text{--}1400 \text{ cm}^{-1}$ of the asymmetric and symmetric vibrations of the COO^- group, respectively, broad absorption bands with a maximum at $3380\text{--}3310 \text{ cm}^{-1}$ and narrow bands at $1620\text{--}1605 \text{ cm}^{-1}$, confirming the presence of lattice water, and bands of the metal–oxygen bond at $455\text{--}450 \text{ cm}^{-1}$ (Table 1). The absorption bands due to the free OH group in the IR spectra of the complexes are obscured by the broad absorption band of the lattice water molecules. The absorption bands of the C–OH group at $1305\text{--}1285 \text{ cm}^{-1}$, and the bands of $\delta(\text{OH})$ at $1465\text{--}1445 \text{ cm}^{-1}$ and $870\text{--}850 \text{ cm}^{-1}$, are shifted insignificantly relative to the absorption bands in the spectrum of the acid, which suggests that the OH groups do not play any direct part in the coordination of the metal ion. The absorption bands of the asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_{\text{s}}(\text{COO}^-)$ vibrations in the prepared com-

plexes have values that are similar to each other and also similar to the bands in the spectrum of the sodium salt.

The values of the splitting for the absorption bands of the valency vibrations $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ ($\Delta\nu = \nu_{as} - \nu_s$) are very high ($\Delta\nu = 230\text{--}240\text{ cm}^{-1}$) and are close to those found in the sodium salt. On the basis of the interpretation of the IR spectra, the 2,4-dihydroxybenzoate ligand is monodentate, as in the complexes of Mn(II), Co(II) and Ni(II) [12] and coordinates the metal through the oxygen of the carboxylate group. Moreover, the band of the asymmetric vibration $\nu_{as}(\text{COO}^-)$ is very strong and is not split, which suggests that all the ligands are coordinated in the same manner.

2,4-Dihydroxybenzoate hydrates of rare earth elements are stable in air and can be stored for several months without changes. When heated the complexes decompose in the same steps (Tables 2 and 3, Figs. 1–3). Their stabilities increase insignificantly with increasing atomic number Z of the metal. The hydrated 2,4-dihydroxybenzoates of light lanthanides from La to Gd are stable up to 335–353 K, whereas those of heavy lanthanides from Tb to Lu and Y are stable up to 343–358 K (Table 2, Fig. 4) and then all the complexes dehydrate in one step to form the anhydrous compounds. The anhydrous 2,4-dihydroxybenzoates are unstable and their stabilities decrease with increasing atomic number Z in the lanthanide series. The most stable are the complexes of the light lanthanides from La to Gd, and the least stable are those of the heaviest lanthanides of Tm, Yb and Lu (Table 2, Fig. 4). The anhydrous 2,4-dihydroxybenzoates decompose on heating to the oxides Ln_2O_3 , CeO_2 , Pr_6O_{11} and

TABLE 2

Data of the decomposition of yttrium and lanthanide 2,4-dihydroxybenzoates in air

Complex ^a	ΔT_1 ^b (K)	Weight loss (%)		$n\text{H}_2\text{O}$	ΔT_2 ^c (K)	Weight loss (%)		T_K ^d
		Calc.	Found			Calc.	Found	
$\text{YL}_3 \cdot 4\text{H}_2\text{O}$	358–443	11.61	11.0	4	455–998	81.79	81.0	998
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	343–423	5.76	5.6	2	453–1048	74.31	74.2	1048
$\text{CeL}_3 \cdot 2\text{H}_2\text{O}$	333–398	5.66	5.6	2	433–788	72.91	72.7	788
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	348–413	5.66	5.6	2	448–888	73.24	73.0	888
$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$	353–408	5.63	5.5	2	448–973	73.69	73.5	973
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	343–418	5.57	5.5	2	453–943	72.99	72.8	943
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	343–423	5.56	5.5	2	443–923	72.81	72.8	923
$\text{GdL}_3 \cdot 2\text{H}_2\text{O}$	343–423	5.36	5.2	2	453–953	72.22	72.2	953
$\text{TbL}_3 \cdot 4\text{H}_2\text{O}$	353–458	10.43	10.3	4	473–948	73.49	73.2	948
$\text{DyL}_3 \cdot 4\text{H}_2\text{O}$	353–453	10.31	10.1	4	473–958	73.13	73.5	958
$\text{HoL}_3 \cdot 4\text{H}_2\text{O}$	353–453	10.33	10.1	4	473–960	72.87	73.0	960
$\text{ErL}_3 \cdot 4\text{H}_2\text{O}$	353–448	10.31	10.1	4	463–1003	72.57	72.5	1003
$\text{TmL}_3 \cdot 4\text{H}_2\text{O}$	353–443	10.28	10.0	4	453–963	72.39	72.1	963
$\text{YbL}_3 \cdot 4\text{H}_2\text{O}$	348–438	10.22	10.1	4	453–998	72.03	72.5	998
$\text{LuL}_3 \cdot 4\text{H}_2\text{O}$	343–438	10.19	10.0	4	448–948	71.83	72.0	948

^a L, $[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]^-$. ^b ΔT_1 , temperature range of dehydration. ^c ΔT_2 , temperature range of decomposition. ^d T_K , temperature of oxide formation.

TABLE 3

The temperature range of formation of the unstable intermediate products of yttrium and lanthanide 2,4-dihydroxybenzoate decomposition

Complex	$\text{Ln}_2[\text{C}_6\text{H}_3(\text{O})(\text{OH})\text{COO}]_3$			$\text{Ln}_2\text{O}[\text{C}_6\text{H}_3(\text{O})(\text{OH})\text{COO}]_2$		
	T (K)	Calc. (%)	Found (%)	T (K)	Calc. (%)	Found (%)
$\text{Y}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	523	51.11	50.0	713	40.14	39.6
$\text{La}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	540	57.87	57.0	628	47.14	46.5
$\text{Ce}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	533	57.95	58.0	—	—	—
$\text{Pr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	548	58.00	58.0	623	47.30	47.0
$\text{Nd}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	563	58.22	57.8	623	47.58	47.7
$\text{Sm}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	555	58.62	58.0	618	48.08	48.5
$\text{Eu}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	551	58.72	58.3	608	48.20	47.9
$\text{Gd}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	568	59.05	58.9	638	48.62	47.8
$\text{Tb}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	558	56.07	56.0	643	46.21	46.0
$\text{Dy}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	548	56.29	57.2	643	46.49	46.2
$\text{Ho}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	548	56.45	56.0	641	46.47	46.0
$\text{Er}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	553	56.59	56.5	643	46.85	47.1
$\text{Tm}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	535	56.70	56.7	693	46.98	47.3
$\text{Yb}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	541	56.95	57.5	718	47.29	47.8
$\text{Lu}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	548	57.07	56.7	718	47.43	48.0

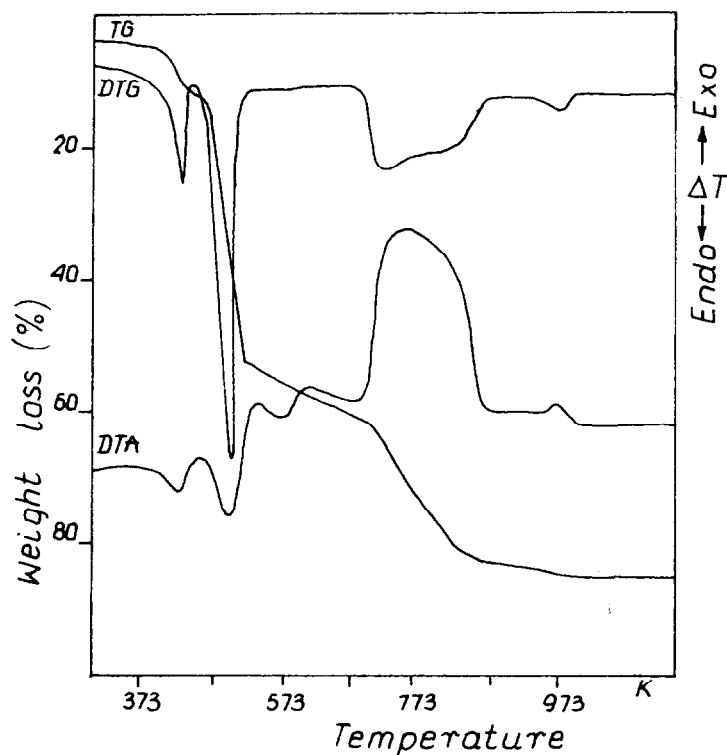


Fig. 1. TG, DTG and DTA curves of $\text{Y}(\text{C}_7\text{H}_5\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$.

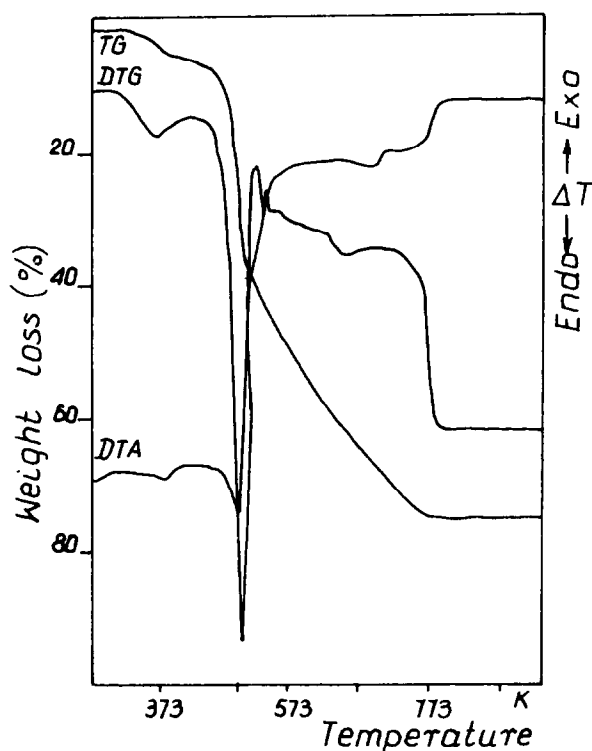
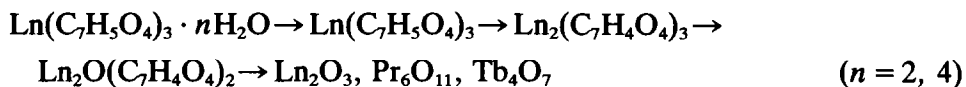


Fig. 2. TG, DTG and DTA curves of $\text{Ce}(\text{C}_7\text{H}_5\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$.

Tb_4O_7 , forming the very unstable intermediates $\text{Ln}_2(\text{C}_7\text{H}_4\text{O}_4)_3$ (with the molar ratio of metal to ligand being 2:3) and $\text{Ln}_2\text{O}(\text{C}_7\text{H}_4\text{O}_3)_2$, with the exception of cerium (Table 3).

The results indicate that the thermal decomposition of hydrated rare earth 2,4-dihydroxybenzoates can be presented as



and



The temperatures of oxide formation (T_x) change insignificantly in the lanthanide series (Fig. 5), with the exceptions of La_2O_3 , which is formed at the highest temperature (1048 K) and CeO_2 , which is formed at the lowest (788 K), as observed during the decomposition of many series of lanthanide complexes. The processes of dehydration and decomposition are connected with strong endothermic effects (Table 4), whereas the processes of combustion of the organic ligand and the products of its decomposition are accompanied by two or three exothermic effects (Table

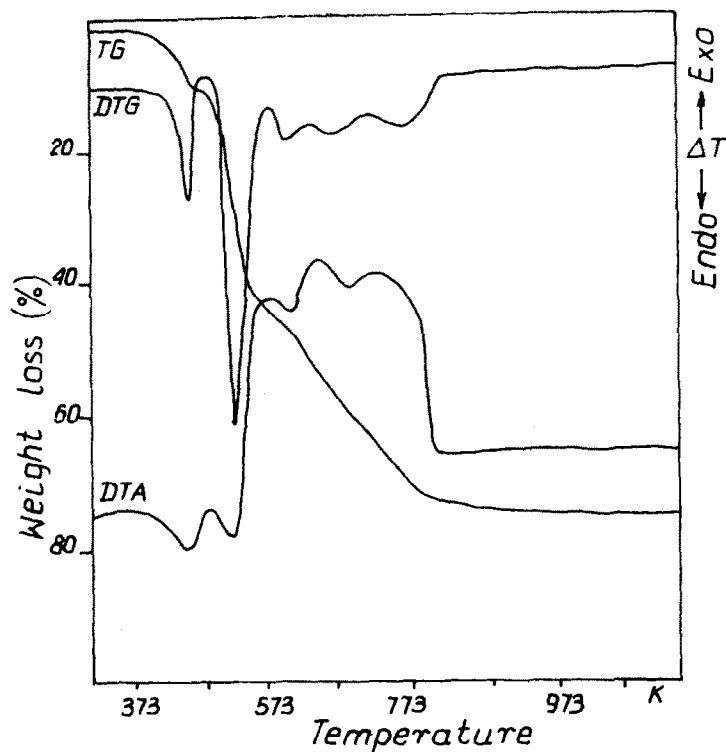


Fig. 3. TG, DTG and DTA curves of $Tb(C_7H_5O_4)_3 \cdot 4H_2O$.

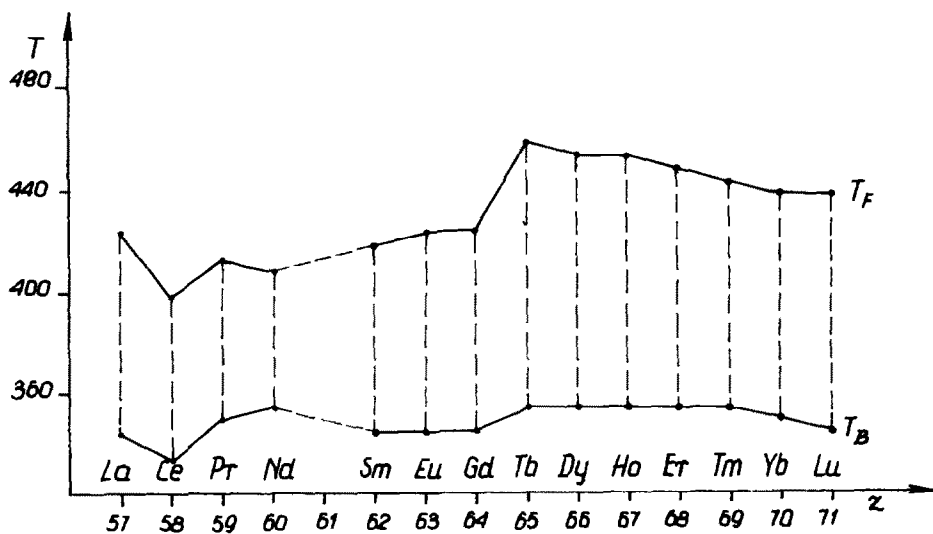


Fig. 4. Relationship between the beginning (T_B) and final (T_F) temperatures of dehydration, and the atomic number (Z) of the metal.

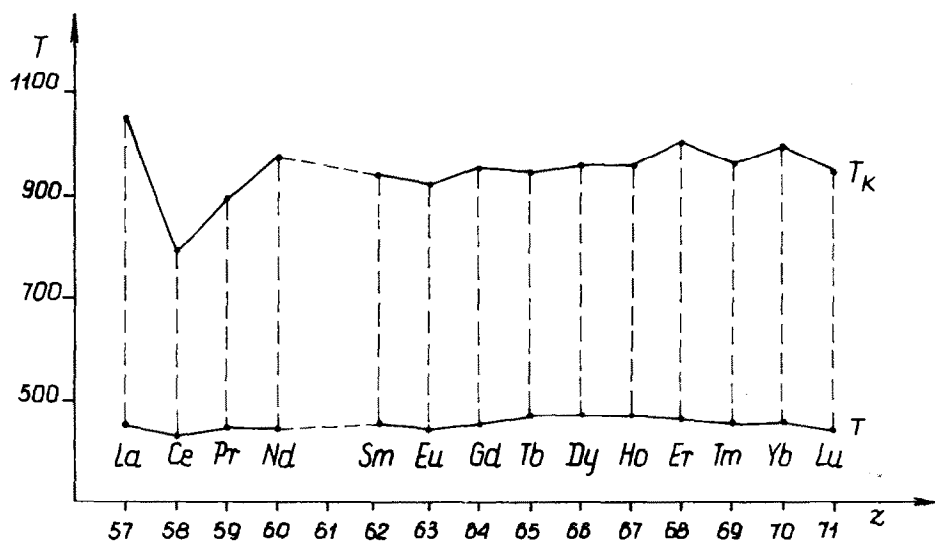


Fig. 5. Relationship between the decomposition temperatures of the anhydrous complexes (T) and of oxide formation T_k , and the atomic number (Z) of the metal.

TABLE 4
DTA studies

Complex	Effects		Complex	Effects	
	Endo (K)	Exo (K)		Endo (K)	Exo (K)
Y	423	533	Tb	458	573
	488	610		503	643
		773			
La	393	558	Dy	446	570
	488	643		503	653
Ce	383	550	Ho	443	578
	478			508	646
Pr	393	558	Er	433	565
	483	640		498	658
					750
Nd	393	560	Tm	428	533
	488	626		493	608
					778
Sm	403	563	Yb	403	541
	488	648		488	603
					753
Eu	398	546	Lu	416	555
	488	613		488	603
					756
Gd	403	560			
	493	650			

4). The decomposition of the Ce(III) complex proceeds with only one exothermic effect at the lowest temperature (550 K).

Comparing the thermal stabilities of rare-earth 2,4-dihydroxybenzoates, and 2- and 4-hydroxybenzoates [7, 11], it is possible to state that the decomposition of anhydrous 2,4-dihydroxybenzoates begins at lower temperatures than those of 2- and 4-hydroxybenzoates, whereas the temperatures of oxide formation are higher than for 2-hydroxybenzoates and similar to those for 4-hydroxybenzoates, which is connected with the presence of the second –OH group in the benzene ring.

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