Thermal decomposition of rare earth element complexes with 3,4-dihydroxybenzoic acid in air

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Abstract

The conditions of the formation of rare earth element 3,4-dihydroxybenzoates have been studied; their quantitative composition and solubilities in water at 293 K have been determined. The IR spectra and X-ray diffraction patterns of the hydrated complexes have been recorded and their thermal decomposition in air determined. During heating the hydrated complexes $Ln(C_7H_5O_4)_3 \cdot nH_2O$ ($n = 2, 3$) lose water of crystallization in one step; then the anhydrous complexes decompose to the oxides with intermediate formation of very unstable $Ln_2(C_7H_4O_4)_3$, with the exception of lanthanum which also forms $La_2O_2CO_3$ as an intermediate.

INTRODUCTION

Rare earth element complexes with 3,4-dihydroxybenzoic acid $(C_6H_3(OH)_2COOH)$ in the solid state are not very well known. The studies are not complete and concern only complexes of some rare earth elements. 3,4-Dihydroxybenzoates of yttrium, lanthanum, praseodymium, neodymium and gadolinium have been prepared as complexes with a molar ratio of metal to organic ligand of 1:3 by the method used for preparation of 3,4-dihydroxybenzaldehyde complexes, and their IR and UV spectra have been recorded [1–3].

The aim of this work has been to obtain complexes of rare earth elements with 3,4-dihydroxybenzoic acid under the same conditions and to examine systematically their physicochemical properties and the thermal decomposition in air, and to compare their properties with those of the complexes of 3- [4–8] and 4-hydroxybenzoic acid [9], and 2,4-dihydroxybenzoic acid [10].

EXPERIMENTAL

3,4-Dihydroxybenzoates of Y(III) and lanthanides from La(III) to Lu(III) (without Pm) were prepared by addition of equivalent quantities of

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ammonium 3,4-dihydroxybenzoate (pH 4.4–4.5) to a solution containing, the rare earth chlorides (Ce(III) was used as its nitrate) at room temperature. The precipitates formed were filtered, washed with ethanol and dried at 303 K to a constant mass.

The quantitative compositions of the prepared 3,4-dihydroxybenzoates were determined by elemental analysis, by ignition of the complexes to form the oxides and from the TG curves. The content of water of crystallization was determined from the TG curve and by isothermal heating of the complexes at specified temperatures.

The IR spectra for the complexes, and the spectra for 3,4-dihydroxybenzoic acid and its sodium salt, were recorded as KBr discs on a Specord M-80 spectrophotometer (4000–400 cm^{-1}). The X-ray diffraction patterns of the prepared complexes were taken on a Dron-2 diffractometer using Ni-filtered Cr Kα radiation. The measurements were made within the range $2\theta = 5–60°$. The solubilities of the rare earth element 3,4-dihydroxybenzoates in water were determined at 293 K. Samples of 1, 2, 5 and 10 cm^3 were removed and concentrations of Ln^{3+} in them were determined spectrophotometrically using arsenazo III. The measurements were made on a Specord M-40 spectrophotometer.

The thermal stabilities of rare earth element 3,4-dihydroxybenzoates were studied in air. The TG, DTG and DTA curves were recorded with Q-1500 D derivatograph at a heating rate of 10 K min^{-1} with the following 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 α-Al$_2$O$_3$ was used as a standard.

RESULTS AND DISCUSSION

3,4-Dihydroxybenzoates of Y(III) and lanthanides(III) from La to Lu(III) were obtained as solids grey-beige in colour, a molar ratio of metal to organic ligand of 1:3, and general formula Ln(C$_6$H$_3$(OH)$_2$COO)$_3$ · nH$_2$O. The complexes of light lanthanides from La(III) to Nd(III) and heavy lanthanides from Ho(III) to Yb(III) were prepared as trihydrates, and those of Y(III), Sm(III) to Dy(III) and Lu(III) as dihydrates. 3,4-Dihydroxybenzoates of rare earth elements during heating in aqueous solution hydrolyze forming hydroxy salts. The hydrated complexes of La(III), Ce(III), Pr(III) and Nd(III) are amorphous solids, whereas the hydrated complexes of the remaining lanthanides (Sm(III) to Lu(III) and Y(III)) are crystalline, being isostructural in the groups Y, Sm to Dy, Lu; and Ho to Yb.

3,4-Dihydroxybenzoates of rare earth elements are sparingly soluble in water. Their solubilities are of the order 10^{-3} to 10^{-4} mol dm^{-3} (Table 1) and change in the lanthanide series with increasing atomic number Z of metal. The solubilities of light lanthanides from La(III) to Nd(III) are

TABLE 1

Frequencies in cm^{-1} of the absorption bands of COO$^-$ and OH groups of 3,4-dihydroxyben-zoic acid and its compounds and their solubilities in mol dm^{-3} × 10^{-4} in water at 293 K

Compound [a]	$\nu_{as}(COO^-)$	$\Delta\nu_{as}$ [b]	$\nu_{s}(COO^-)$	$\Delta\nu_{s}$ [b]	$\nu_{as} - \nu_{s}$	$\delta(OH)$	$\nu(OH)$	$\nu(M-O)$	Solubility
HL	—	—	—	—	—	1440, 1420, 856	1288	—	
NaL	1540		1396		144	872	1292	450	
YL$_3$ · 2H$_2$O	1544	+4	1444	+48	100	888	1288	464	3.41
LaL$_3$ · 3H$_2$O	1508	−32	1400	+4	108	888	1284	452	19.81
CeL$_3$ · 3H$_2$O	1508	−32	1400	+4	108	888	1284	452	9.47
PrL$_3$ · 3H$_2$O	1508	−32	1400	+4	108	888	1284	452	18.65
NdL$_3$ · 3H$_2$O	1508	−32	1400	+4	108	888	1284	452	38.29
SmL$_3$ · 2H$_2$O	1536	−4	1440	+44	96	888	1288	456	0.74
EuL$_3$ · 2H$_2$O	1540	0	1444	+48	96	888	1288	456	5.31
GdL$_3$ · 2H$_2$O	1540	0	1444	+48	96	888	1288	460	1.99
TbL$_3$ · 2H$_2$O	1540	0	1444	+48	96	888	1288	460	1.75
DyL$_3$ · 2H$_2$O	1544	+4	1444	+48	100	888	1288	460	5.81
HoL$_3$ · 3H$_2$O	1544	+4	1444	+48	100	888	1288	464	7.36
ErL$_3$ · 3H$_2$O	1544	+4	1444	+48	100	888	1288	464	8.61
TmL$_3$ · 3H$_2$O	1548	+8	1448	+52	100	888	1288	464	9.28
YbL$_3$ · 3H$_2$O	1548	+8	1448	+52	100	888	1292	464	4.89
LuL$_3$ · 2H$_2$O	1552	+12	1448	+52	104	888	1288	464	0.84

[a] L is [C$_6$H$_3$(OH)$_2$COO]$^-$. [b] Shift of absorption bands $\nu_{as}(COO^-)$ and $\nu_{s}(COO^-)$ compared with bands of sodium 3,4-dihydroxybenzoate.

almost ten times greater than those of yttrium and heavy lanthanides. The solubilities of 3,4-dihydroxybenzoates of heavy lanthanides increase system-atically from Tb(III) to Tm(III) and then decrease from Tm(III) to Lu(III). Dihydrated 3,4-dihydroxybenzoates are more sparingly soluble than tri-hydrated ones.

3,4-Dihydroxybenzoates of light lanthanides show similar solid-state IR spectra, which differ a little from those of the complexes of heavy lan-thanides (Table 1). The characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salt. In the IR spectrum of 3,4-dihydroxycarboxylic acid, there is an absorption band at 3312 cm^{-1} due to the valency vibration of the OH group, the band of the COOH group at 1672 cm^{-1}, and the bands of $\delta(OH)$ and $\nu(OH)$ at 1420, 856 and 1288 cm^{-1}, respectively. In the IR spectra of prepared complexes, there are bands at 1552–1508 cm^{-1} and 1448–1400 cm^{-1} of the asymmetric vibra-tions of the COO$^-$ group, respectively, broad absorption bands with a maximum at 3408–3384 cm^{-1} and narrow bands at 1608–1600 cm^{-1}, confirming the presence of lattice water, and bands of the metal–oxygen bond at 464–452 cm^{-1} (Table 1). The absorption band of $\delta(OH)$ at 1420 cm^{-1} observed in the spectrum of acid, is obscured by the absorption band of the symmetric vibration of COO$^-$ group in the spectra of the complexes. The remaining absorption bands $\delta(OH)$ and $\nu(OH)$ are shifted

insignificantly relative to the absorption bands in the spectrum of acid, which suggests that the OH groups do not take any direct part in the coordination of the metal ion. The absorption bands of the asymmetric $v_{as}(COO^-)$ vibrations in the complexes of light lanthanides (La–Sm) are shifted to lower frequencies ($\Delta v = -32 \text{ cm}^{-1}$), are unchanged in the complexes of Eu–Tb ($\Delta v = 0 \text{ cm}^{-1}$), whereas in the complexes of Y and heavy lanthanides these vibrations are shifted insignificantly to higher frequencies ($\Delta v = 4–12 \text{ cm}^{-1}$) compared to the bands of sodium salt. The bands of symmetric $v_s(COO^-)$ vibrations are shifted to higher frequencies ($\Delta v = 4 \text{ cm}^{-1}$ for La–Nd, $\Delta v = 44–52 \text{ cm}^{-1}$ for remaining metals) in the complexes of all rare earth elements compared to those of sodium salt, and their frequencies increase with the increasing atomic number of Z of metal. The values of splitting for the absorption bands of the valency vibrations $v_{as}(COO^-)$ and $v_s(COO^-)$ ($\Delta v = v_{as} - v_s$) are lower than those found in the sodium salt ($\Delta v = 144 \text{ cm}^{-1}$) (Table 1) and have different values for light ($\Delta v = 108 \text{ cm}^{-1}$), middle ($\Delta v = 96 \text{ cm}^{-1}$), and Y and heavy lanthanides ($\Delta v = 100 \text{ cm}^{-1}$). The values of Δv indicate a lower degree of ionic bond in these complexes as compared to the sodium salt. Based on the spectroscopic criterion of the coordination mode, the carboxylate ion of 3,4-dihydroxy-benzoate ligand is supposed to be a bidentate, chelating one [11], but probably with incomplete equalization of its bonds length. Being higher for light lanthanide 3,4-dihydroxybenzoates than for Y and heavy lanthanide complexes the frequencies due to $v_{as}(COO^-)$ and $v_s(COO^-)$ may indicate a small change in the carboxylate group structure. On the basis of IR spectra interpretation the rare earth element ions were found to coordinate the 3,4-dihydroxybenzoate ligands in hydrated complexes only through oxygen atoms of the carboxylic group. More precisely, interpretation of the coordi-nation mode of metal–3,4-dihydroxybenzoate ligand can be determined on the basis of molecular and crystallographic structure of the monocrystals.

3,4-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 except for the lanthanum complex (Tables 2 and 3, Figs. 1–3). The hydrated 3,4-dihydroxybenzoates of rare earth elements are stable up to 323–333 K and then all the complexes dehydrate in one step to form anhydrous compounds. The anhydrous complexes are unstable and their stabilities decrease with increasing atomic number Z in the lanthanide series. The anhydrous complexes of light lanthanides from La to Nd are a little more stable than the complexes of middle and heavy lanthanides from Sm to Lu (Table 2, Fig. 4).

The stability of anhydrous yttrium complex is similar to those of heavy lanthanide complexes, due to the ionic radius of Y^{3+} and the contraction of lanthanides.

The anhydrous 3,4-dihydroxybenzoates decompose on heating to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7, forming the very unstable intermediates
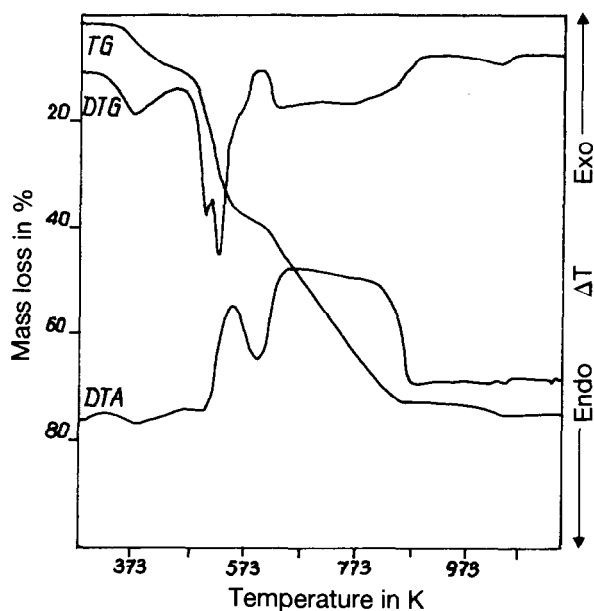
Fig. 1. TG, DTG and DTA curves of $La(C_7H_5O_4)_3 \cdot 3H_2O$.
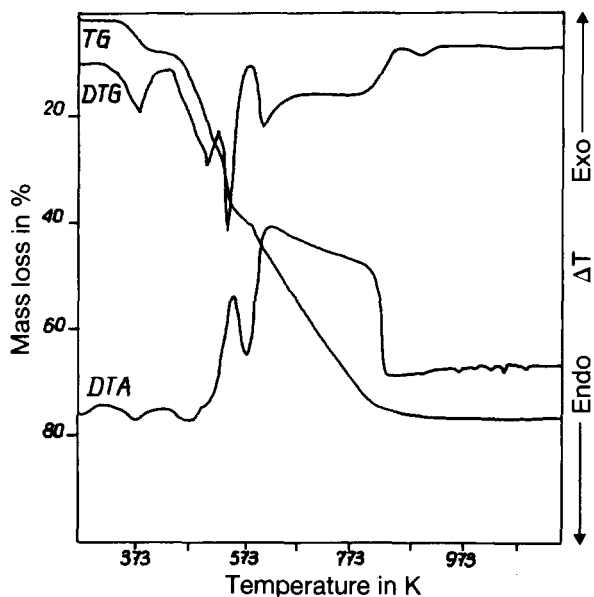
Fig. 2. TG, DTG and DTA curves of $Eu(C_7H_5O_4)_3 \cdot 2H_2O$.

$Ln_2(C_7H_4O_4)_3$ (with the molar ratio of metal to organic ligand of 2:3) (Table 3). Only the lanthanum complex decomposes to oxide La_2O_3 with intermediate formation of $La_2O_2CO_3$, which is stable in the temperature range 866–973 K (Fig. 1).

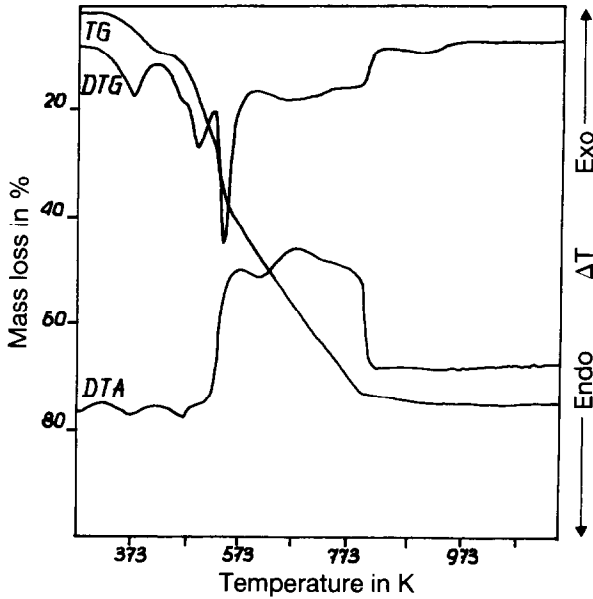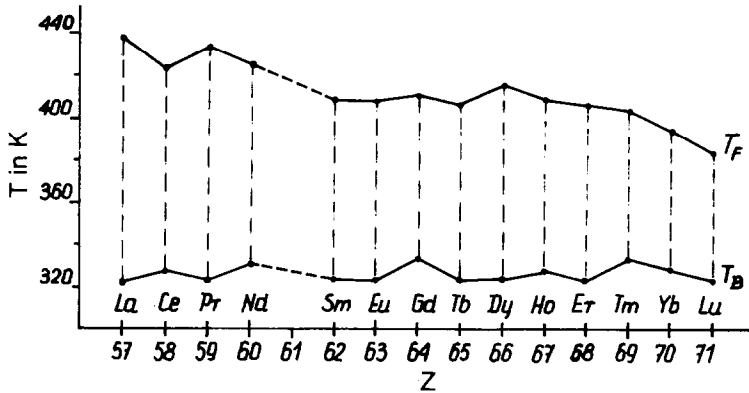Fig. 3. TG, DTG and DTA curves of $Er(C_7H_5O_4)_3 \cdot 3H_2O$.

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

The results indicate that the thermal decomposition of hydrated rare earth element 3,4-dihydroxybenzoates can be presented as

$$Ln(C_7H_5O_4)_3 \cdot nH_2O \rightarrow Ln(C_7H_5O_4)_3 \rightarrow Ln_2(C_7H_4O_4)_3 \rightarrow$$

$$Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7$$

where Ln is Y or Ce–Lu and

$$La(C_7H_5O_4)_3 \cdot 3H_2O \rightarrow La(C_7H_5O_4)_3 \rightarrow$$

$$La_2(C_7H_4O_4)_3 \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$$
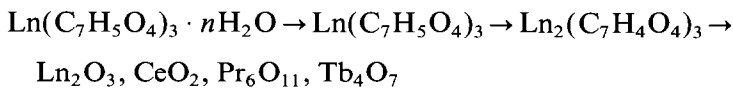
TABLE 2

Data for the decomposition of yttrium and lanthanide 3,4-dihydroxybenzoates in air
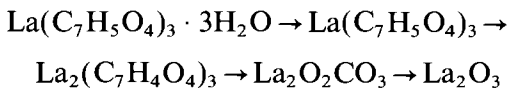
Complex [a]	$\Delta T_1/K$ [b]	Mass loss/%		$n H_2O$	$\Delta T_2/K$ [c]	Mass loss/%		T_K/K [d]
		Calcd.	Found			Calcd.	Found	
$YL_3 \cdot 2H_2O$	328–406	6.16	6.0	2	426–929	80.67	80.0	929
$LaL_3 \cdot 3H_2O$	323–438	8.28	8.0	3	460–1060	75.02	75.0	1060
$CeL_3 \cdot 3H_2O$	328–423	8.26	8.0	3	453–870	73.66	74.0	870
$PrL_3 \cdot 3H_2O$	323–433	8.26	8.3	3	455–878	73.98	74.0	878
$NdL_3 \cdot 3H_2O$	331–425	8.21	8.3	3	456–938	74.41	74.0	938
$SmL_3 \cdot 2H_2O$	323–408	5.57	5.5	2	438–926	72.99	73.0	926
$EuL_3 \cdot 2H_2O$	323–408	5.56	5.5	2	433–903	73.55	74.0	903
$GdL_3 \cdot 2H_2O$	333–410	5.51	5.0	2	443–963	72.22	72.0	963
$TbL_3 \cdot 2H_2O$	323–406	5.50	5.5	2	436–838	72.04	71.8	838
$DyL_3 \cdot 2H_2O$	323–415	5.47	5.5	2	425–921	71.65	72.0	921
$HoL_3 \cdot 3H_2O$	328–408	7.96	7.2	3	428–903	72.14	72.2	903
$ErL_3 \cdot 3H_2O$	323–406	7.94	7.8	3	428–933	71.89	71.8	933
$TmL_3 \cdot 3H_2O$	333–403	7.92	7.8	3	415–915	71.66	71.8	915
$YbL_3 \cdot 3H_2O$	328–393	7.87	7.5	3	418–938	71.29	71.2	938
$LuL_3 \cdot 2H_2O$	323–383	5.37	5.2	2	398–936	70.31	70.0	936

[a] L is $[C_6H_3(OH)_2COO]^-$. [b] ΔT_1 is temperature range of dehydration. [c] ΔT_2 is temperature range of decomposition. [d] T_K is temperature of oxide formation.

The temperatures of oxide formation (T_K) change insignificantly in the lanthanide series (Fig. 5), with the exception of La_2O_3, which is formed at the highest temperature (1060 K) and Tb_4O_7, which is formed at the lowest (838 K). The processes of dehydration and decomposition are connected
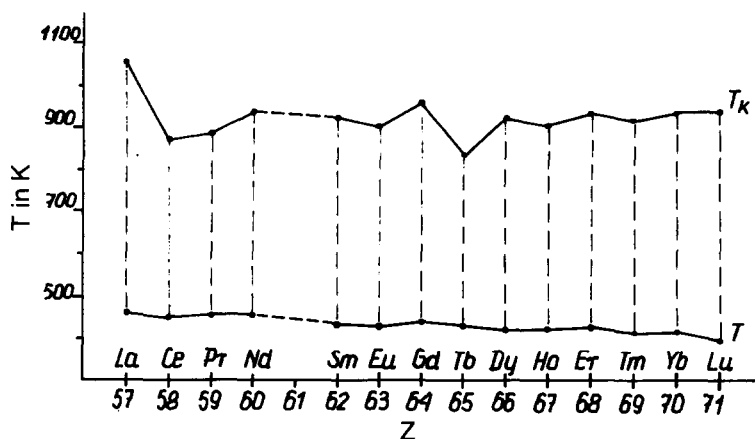

Fig. 5. Relationship between the decomposition temperatures of the anhydrous complexes T and of oxide formation T_K, and the atomic number Z of the metal.

TABLE 3

The temperature range of formation of the unstable intermediate products of yttrium and lanthanide 3,4-dihydroxybenzoates and DTA studies

Complex	$Ln_2[C_6H_3(O)(OH)COO]_3$			Effects	
	T/K	Calcd./%	Found/%	EndoT/K	ExoT/K
$YL_3 \cdot 2H_2O$	628	54.26	54.5	373	560
				468	628
$LaL_3 \cdot 3H_2O$	638	56.27	56.5	378	557
				493	668
$CeL_3 \cdot 3H_2O$	583	56.35	56.5	381	528
				488	611
$PrL_3 \cdot 3H_2O$	663	56.40	56.3	379	547
				491	681
$NdL_3 \cdot 3H_2O$	703	56.62	56.5	383	543
				403	726
$SmL_3 \cdot 2H_2O$	618	58.62	59.0	380	546
				475	623
$EuL_3 \cdot 2H_2O$	591	58.72	58.8	380	551
				465	625
$GdL_3 \cdot 2H_2O$	638	59.05	59.7	388	548
				483	638
$TbL_3 \cdot 2H_2O$	618	59.16	59.3	383	553
				478	623
$DyL_3 \cdot 2H_2O$	623	59.38	59.0	376	547
				463	638
$HoL_3 \cdot 3H_2O$	623	57.94	57.0	383	566
				468	653
$ErL_3 \cdot 3H_2O$	593	58.09	58.0	383	573
				463	681
$TmL_3 \cdot 3H_2O$	583	58.19	58.1	381	573
				463	683
$YbL_3 \cdot 3H_2O$	623	58.44	58.0	380	565
				423	635
$LuL_3 \cdot 2H_2O$	603	60.13	60.2	365	555
				418	628

with strong endothermic effects (Table 3), whereas the processes of combustion of the organic ligand and its decomposition are accompanied by the exothermic effects (Table 3).

Comparing the thermal stabilities of rare earth element 3,4-dihydroxybenzoates, and 3- and 4-hydroxybenzoates [4–9] it is possible to state that the decomposition of anhydrous 3,4-dihydroxybenzoates begins at considerably lower temperatures than those of 3- and 4-hydroxybenzoates (Fig. 6). Similarly, the temperatures of oxide formation for 3,4-dihydroxybenzoates are lower than those for 3- and 4-hydroxybenzoates (Fig. 7). These effects
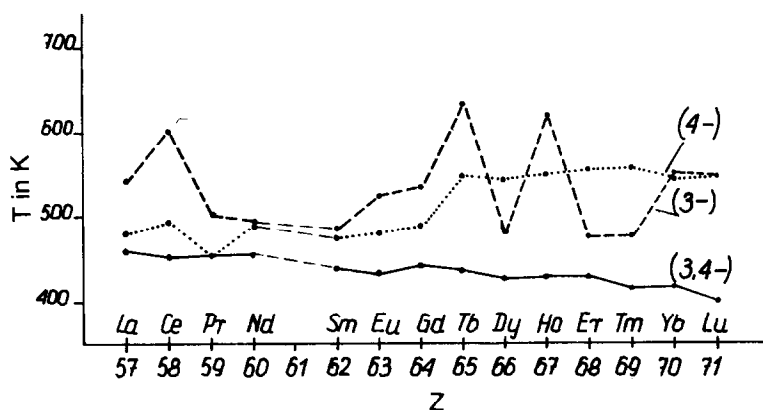
Fig. 6. The decomposition temperatures of the anhydrous 3,4-dihydroxybenzoates (——), 3-hydroxybenzoates (– – –) and 4-hydroxybenzoates (· · ·) of rare earth elements.
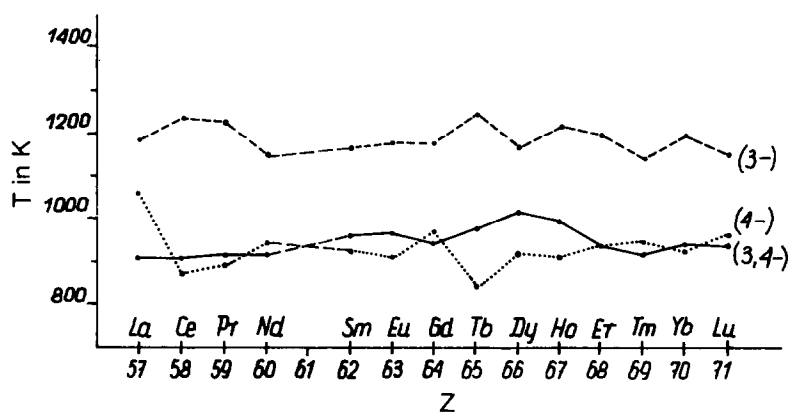

Fig. 7. The temperatures of oxide formation from 3,4-dihydroxybenzoates (——), 3-hydroxybenzoates (– – –) and 4-hydroxybenzoates (· · ·) of rare earth elements.

are connected with the presence of the second OH group in the benzene ring. The temperatures of decomposition of anhydrous 3,4-dihydroxybenzoates and the temperatures of oxide formation for 3,4-dihydroxybenzoates are similar to those temperatures for 2,4-dihydroxybenzoates [10].

On this basis it is possible to confirm that the presence of two OH groups in the benzene ring in the 3,4 and 2,4 positions influences the electron cloud density on the carbon atom in the COO^- group and causes the decreasing thermal stability of rare earth complexes compared to the thermal stability of the complexes of these elements with monohydroxybenzoic acids.

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