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Preparation, properties and thermal decomposition of rare earth element complexes with 3, 5-dihydroxybenzoic acid

Wanda Brzyska*, Alina Kula

Marie Curie Sklodowska University, Faculty of Chemistry, Department of Inorganic and General Chemistry, 20-031 Lublin, Poland

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Abstract

The conditions of the formation of rare earth element 3, 5-dihydroxybenzoates have been studied; their quantitative composition and solubilities in water at 293 K have been determined. The IR spectra of the hydrated complexes have been recorded and their thermal decomposition in air determined. During heating, the hydrated complexes $Ln(C_7H_5O_4)O_3 \cdot nH_2O$ ($n = 4$ for La–Pr, $n = 7$ for in Y, Nd–Lu) lose water of crystallization in one step and then the anhydrous complexes decompose directly to oxides (Sm–Gd, Dy–Lu, Y) or with intermediate formation of $Ln_2O_2CO_3$ (La, Nd). The conditions of thermal decomposition of 2, 4- and 3, 5-dihydroxybenzoates are compared.

Keywords: Complexes; 3, 5-Dihydroxybenzoates; IR; Rare earth elements; Thermal analysis

1. Introduction

A survey of the literature shows that the complexes of dihydroxybenzoic acid with rare earth elements are not very well known. The studies are not complete and concern only complexes of some rare earth elements [1–7]. In previous papers, we have described the complexes of rare earth elements (Y, La–Lu) with 2, 4- [8] and 3, 4-dihydroxybenzoic acids [9], their preparation, properties in the solid state, and thermal decomposition in air. Rare earth element 3, 5-dihydroxybenzoates in the solid state were previously unknown.

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* Corresponding author.

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The aim of this work was to prepare rare earth element (III) complexes with 3, 5-dihydroxybenzoic acid under the same conditions and to examine systematically their physicochemical properties and thermal decomposition in air, and to compare their properties with those of the complexes of 2, 4- [8] and 3, 4-dihydroxybenzoic acid [9].

2. Experimental

3, 5-Dihydroxybenzoates of Y and lanthanides from La to Lu (without Ce and Pm) were prepared by addition of equivalent quantities of ammonium 3, 5-dihydroxybenzoate (pH 5.0–5.3) to a solution of rare earth chlorides at room temperature, and then crystallization. Cerium (III) complex was prepared by dissolving freshly precipitated cerium (III) carbonate in a solution of 3, 5-dihydrohybenzoic acid at room temperature, followed by crystallization. The precipitate formed was filtered off, washed with water and dried at 303 K to a constant mass.

The quantitative compositions of the prepared 3, 5-dihydroxybenzoates were determined by eemental analysis, by ignition of the complexes to 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 a specified temperature. The IR spectra for the complexes, and spectra for 3, 5-dihydroxybenzoic acid and its sodium salt, were recorded as KBr discs on a Specord M-80 spectrophotometer (Carl Zeiss-Jena) within the range 4000–400 cm^{-1}. The X-ray diffraction pattern of the prepared complexes were taken on a DRON-2 diffractometer using Ni-filtered Cu Kα radiation. The measurements were made within the range $2\phi = 5$–60° according to the Debye–Scherrer method. The solubilities of the rare earth 3, 5-dihydroxybenzoates in water were determined at 293 K. Saturated solutions were prepared under isothermal conditions. After equilibrium had been established, samples of 1, 2 and 5 cm^3 were removed and the concentrations of Ln (III) ions were determined gravimetrically using the oxalate method.

The thermal stabilities of the prepared complexes and the products of their decomposition were studied in air. The TG, DTG and DTA curves were recorded with a Q 1500 D derivatograph (Paulik–Paulik–Erdey) at a heating rate 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_2O_3 was used as a standard.

3. Results and discussion

3, 5-Dihydroxybenzoates of Y (III) and lanthanides (III) from La to Lu were prepared as solids, grey-beige in colour, with a molar ratio of metal to organic ligand of 1:3, general formulae $Ln[C_6H_3(OH)_2COO]_3 \cdot nH_2O$. The complexes of La (III), Ce (III) and Pr (III) were obtained as tetrahydrates and those of Y (III) and Nd (III)–Lu (III) as heptahydrates (Table 1). The prepared complexes are crystalline solids of low symme-

Table 1
Analytical data of Y and lanthanide 3, 5-dihydroxybenzoates

Complex[a]	H %		C %		M %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$YL_3 \cdot 7H_2O$	4.33	4.69	37.40	37.28	13.18	13.4
$LaL_3 \cdot 4H_2O$	3.46	3.63	37.62	37.68	20.72	20.8
$CeL_3 \cdot 4H_2O$	3.45	3.65	37.56	37.95	20.86	20.8
$PrL_3 \cdot 4H_2O$	3.44	3.69	37.51	37.42	20.95	21.0
$NdL_3 \cdot 7H_2O$	4.00	4.13	34.57	34.34	19.76	19.6
$SmL_3 \cdot 7H_2O$	3.97	3.84	34.27	34.07	20.43	20.6
$EuL_3 \cdot 7H_2O$	3.96	3.79	34.21	34.05	20.61	20.2
$GdL_3 \cdot 7H_2O$	3.93	3.90	33.96	34.06	21.16	21.8
$TbL_3 \cdot 7H_2O$	3.92	3.81	33.88	33.56	21.88	21.6
$DyL_3 \cdot 7H_2O$	3.90	3.90	33.72	33.78	21.73	21.6
$HoL_3 \cdot 7H_2O$	3.89	3.72	33.61	33.41	21.97	21.8
$ErL_3 \cdot 7H_2O$	3.88	3.62	33.51	33.40	22.22	22.4
$TmL_3 \cdot 7H_2O$	3.87	3.71	33.43	33.29	22.39	22.6
$YbL_3 \cdot 7H_2O$	3.85	3.80	33.25	33.34	22.81	22.6
$LuL_3 \cdot 7H_2O$	3.84	3.70	33.17	33.28	23.01	23.2

[a] L is $[C_6H_3(OH)_2COO)^-$.

try and large unit cells, being isostructural in the groups: La–Pr, and Nd–Lu and Y [10].

3, 5-Dihydroxybenzoates are soluble in water. Their solubilities are of the order 10^{-2}–10^{-3} mol dm^{-3} and change periodically in the lanthanide series with increasing atomic number Z of the metal. The solubilities of tetrahydrated complexes of La(III), Ce(III) and Pr(III) are similar, whereas the solubilities of heptahydrated 3, 5-dihydroxybenzoates decrease from Nd(III) to Tb(III) and then increase from Tb(III) to Lu(III) (Fig. 1). The solubilities of the lanthanide complexes with carboxylic acids very often change in a similar way in the isostructural series, and in different ways for light and heavy lanthanides [12, 13]. The periodic changes of the properties of the lanthanide compounds are connected with the change of in electronic structure and orbital number L.

3, 5-Dihydroxybenzoates of La(III)–Pr(III) show similar solid-state IR spectra, which differ a little from those of the complexes of Nd(III)–Lu(III) (Table 2). The characteristic frequencies related to the carbonyl group are altered markedly in going from acid to complex. In the IR spectrum of 3, 5-dihydroxybenzoic acid, there is an absorption band at 3208 cm^{-1} due to the valency vibration of the OH group, the band of the COOH group at 1684 cm^{-1}, and the bands of δ(OH) and ν(OH) at 1420, 856 and 1328 cm^{-1}, respectively. In the IR spectra of tetrahydrated 3, 5-dihydroxybenzoates of La(III)–Pr(III), there are bands at 1512–1508 cm^{-1} and 1408 cm^{-1} of asymmetric and symmetric vibrations of the OCO$^-$ group, respectively, broad absorption bands with a maximum at 3368–3328 cm^{-1} and narrow bands at 1612–1608 cm^{-1} confirming the

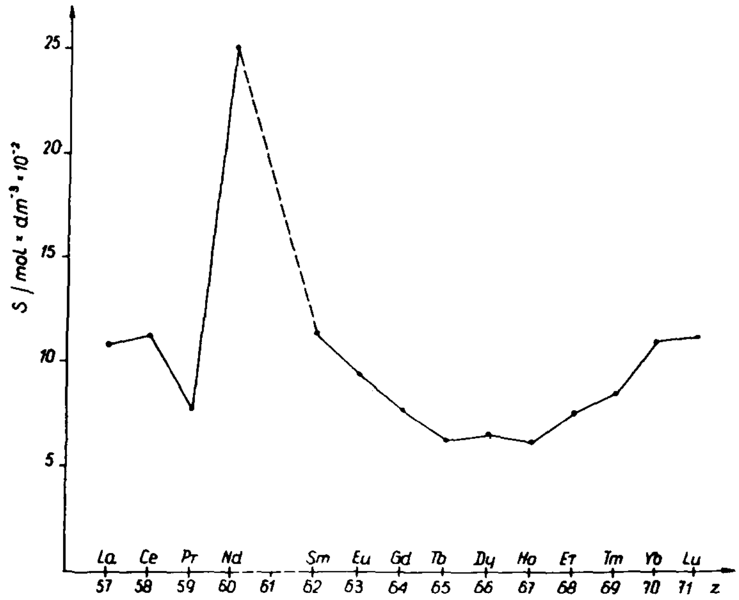

Fig. 1. Relationship between the solubilities (S) of rare earth element 3, 5-dihydroxybenzoates and Z (atomic number of metal).

Table 2

Frequencies (cm^{-1}) of the absorption bands of OCO^- and OH groups of 3, 5-dihydroxybenzoic acid and its compounds and their solubilities ($mol \times dm^{-3} \times 10^{-2}$) in water at 293 K

Compounds	$\nu_{as}(OCO^-)$	$\Delta\nu_{as}^{b}$	$\nu_s(OCO^-)$	$\Delta\nu_s^{b}$	$\nu_{as} - \nu_s$	$\delta(OH)$	$\nu(OH)$	$\nu(M-O)$	Solubil.
HL[a]						856	1328		
NaL	1564		1416		148	840	1292	416	
$YL_3 \cdot 7H_2O$	1528	−36	1420	+4	108	852	1300	428	10.89
$LaL_3 \cdot 4H_2O$	1512	−52	1408	−8	104	848	1304	424	10.80
$CeL_3 \cdot 4H_2O$	1508	−56	1408	−8	100	852	1304	424	11.27
$PrL_3 \cdot 4H_2O$	1508	−56	1408	−8	100	852	1300	424	7.87
$NdL_3 \cdot 7H_2O$	1524	−40	1420	+4	104	848	1300	424	25.14
$SmL_3 \cdot 7H_2O$	1524	−40	1420	+4	104	848	1296	424	11.47
$EuL_3 \cdot 7H_2O$	1524	−40	1420	+4	104	848	1296	424	9.54
$GdL_3 \cdot 7H_2O$	1528	−36	1420	+4	108	852	1296	424	7.83
$TbL_3 \cdot 7H_2O$	1528	−36	1420	+4	108	848	1300	424	6.26
$DyL_3 \cdot 7H_2O$	1528	−36	1420	+4	108	848	1300	424	6.64
$HoL_3 \cdot 7H_2O$	1528	−36	1424	+8	104	848	1300	424	6.24
$ErL_3 \cdot 7H_2O$	1528	−36	1424	+8	104	848	1300	428	7.68
$TmL_3 \cdot 7H_2O$	1528	−36	1424	+8	104	848	1300	424	8.58
$YbL_3 \cdot 7H_2O$	1528	−36	1424	+8	104	848	1300	424	11.12
$LuL_3 \cdot 7H_2O$	1532	−32	1424	+8	108	848	1300	424	11.30

[a] L is $[C_6H_3(OH)_2COO]^-$.

[b] Shift of absorption bands $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ compared with bands of sodium 3, 5-dihydroxybenzoate.

presence of lattice water, and bands of the metal–oxygen bond at 424 cm^{-1} (Table 1). In the IR spectra of heptahydrated complexes of Y (III) and Nd (III)–Lu (III), the bands of the asymmetric and symmetric vibrations of the OCO$^-$ group are observed at 1532–1524 cm^{-1} and 1424–1420 cm^{-1}, respectively, and also the bands characteristic for the presence of lattice water with a maximum at 3400–3340 cm^{-1} and 1612–1604 cm^{-1}, and the bands of the metal–oxygen bond at 428–424 cm^{-1}. The absorption band δ(OH) at 1420 cm^{-1} (of the C–OH group) observed in the spectrum of the acid, is obscured by the absorption band of the symmetric vibration of the OCO$^-$ group in the spectra of the complexes. The remaining absorption bands δ(OH) and ν(OH) are shifted insignificantly relative to the absorption bands in the spectrum of the 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 $\nu_{as}(OCO^-)$ vibrations in the complexes of Y (III) and all the lanthanides are shifted to lower frequencies compared to the bands of sodium salt but those values for the tetrahydrates are greater ($\Delta\nu_{as}$ = 52–56 cm^{-1}) than those for the heptahydrates ($\Delta\nu_{as}$ = 32–40 cm^{-1}). The absorption bands of the symmetric $\nu_s(OCO^-)$ vibrations in the tetrahydrated complexes are shifted to lower frequencies ($\Delta\nu = -8$ cm^{-1}), whereas in the heptahydrated ones they are shifted to higher frequencies ($\Delta\nu$ = 4–8 cm^{-1}) compared to those of sodium salt (Table 2). The values of splitting for the absorption bands of the valency vibrations $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ ($\Delta\nu = \nu_{as} - \nu_s$) are insignificantly lower for the tetrahydrates ($\Delta\nu$ = 100–104 cm^{-1}) than for the heptahydrates ($\Delta\nu$ = 104–108 cm^{-1}). The $\Delta\nu$ values for all the studied complexes are lower than those found for the sodium salt ($\Delta\nu$ = 148 cm^{-1}). The $\Delta\nu$ values 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 the 3, 5-dihydroxybenzoate ligand is thought to be a bidentate chelating one for the tetrahydrates and bidentate bridging for the heptahydrates [11]. A more precise interpretation of the coordination mode of the metal–3, 5-dihydroxybenzoate ligand can be determined on the basis of the molecular and crystallographic structure of the monocrystals.

The hydrated 3,5-dihydroxybenzoates of rare earth elements (III) 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 La (III) and Nd (III) complexes (Table 3, Figs. 2–4).

The hydrated 3, 5-dihydroxybenzoates of rare earth elements are stable up to 318–328 K and then all the complexes are dehydrated in one step at 318–445 K to form anhydrous compounds, which are stable at 413–553 K (Fig. 5). The anhydrous complexes heated undergo polymorphic change at 453–488 K (Table 3) and next decompose directly to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. Only the lanthanum and neodymium complexes decompose to oxides Ln_2O_3 with intermediate formation of very unstable oxycarbonates $Ln_2O_2CO_3$ at 983–993 K and 938–958 K, respectively (Table 3). The temperatures of polymorphic change (T_P) of the studied complexes decrease in the lanthanide series (Fig. 6), which can be explained by the contraction effect and the increasing polarization in the lanthanide series with increasing atomic number Z of the metal.

Table 3
Data for decomposition of Y and lanthanide 3,5-dihydroxybenzoates in air

Compounds	ΔT_1/K	Mass loss%		n H_2O	T_p/K	ΔT_2/K	Mass loss %		T_K/K	$T_t(Ln_2O_2CO_3)$
		Calcd.	Found				Calcd.	Found		
$YL_3 \cdot 7H_2O$	323–433	18.69	18.2	7	453	473–926	83.25	84.6	926	
$LaL_3 \cdot 4H_2O$	320–445	10.75	11.0	4	483	533–1053	76.33	76.2	1053	983–993
$CeL_3 \cdot 4H_2O$	318–438	10.73	10.8	4	488	543–968	74.36	74.6	968	
$PrL_3 \cdot 4H_2O$	323–431	10.71	10.4	4	468	500–953	74.68	74.8	953	
$NdL_3 \cdot 7H_2O$	320–435	17.28	17.2	7	488	538–1015	75.34	76.0	1015	938–958
$SmL_3 \cdot 7H_2O$	328–433	17.12	17.2	7	485	498–973	76.29	76.4	973	
$EuL_3 \cdot 7H_2O$	328–440	17.10	16.8	7	483	513–933	76.13	76.5	933	
$GdL_3 \cdot 7H_2O$	318–435	16.98	16.8	7	485	540–915	75.59	75.2	915	
$TbL_3 \cdot 7H_2O$	320–423	16.90	16.6	7	468	505–968	74.88	74.4	968	
$DyL_3 \cdot 7H_2O$	318–433	16.85	16.8	7	478	513–943	75.06	75.4	943	
$HoL_3 \cdot 7H_2O$	323–428	16.80	16.2	7	473	553–968	74.82	75.2	968	
$ErL_3 \cdot 7H_2O$	328–433	16.75	16.5	7	468	503–958	74.58	74.6	958	
$TmL_3 \cdot 7H_2O$	330–413	16.71	16.2	7	463	526–956	73.74	73.4	956	
$YbL_3 \cdot 7H_2O$	328–423	16.62	16.4	7	456	473–898	73.39	73.4	898	
$LuL_3 \cdot 7H_2O$	328–423	16.58	16.3	7	453	486–908	72.53	72.8	908	

Key: L is $[C_6H_3(OH)_2COO]$; ΔT_1, temp. range of dehydration; ΔT_2, temp. range of decomposition; T_p, temp. of polymorphic change; T_k, temp. of oxide formation.

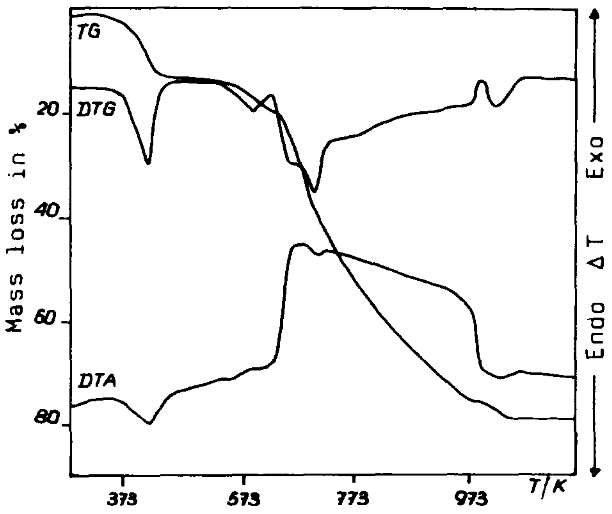

Fig. 2. TG, DTG and DTA curves of La$(C_7H_5O_4)_3 \cdot 4H_2O$.

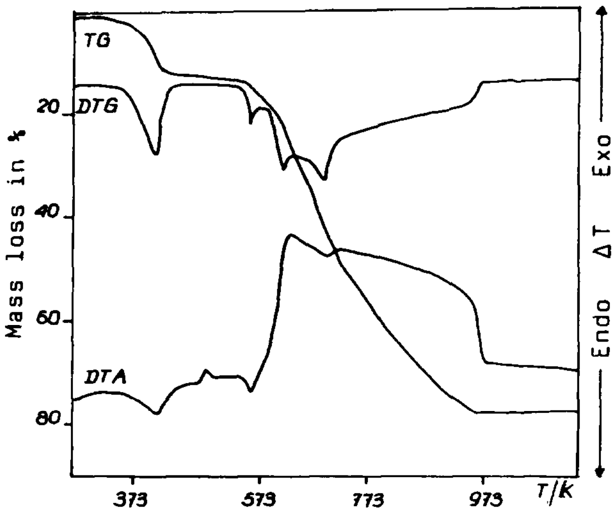

Fig. 3. TG, DTG and DTA curves of Ce$(C_7H_5O_4)_3 \cdot 4H_2O$.

Generally, the thermal decomposition of hydrated rare earth element 3,5-dihydroxybenzoates can be presented as

$$Ln(C_7H_5O_4)_3 \cdot nH_2O \rightarrow Ln(C_7H_5O_4)_3 \rightarrow Ln_2O_3, Pr_6O_{11}, Tb_4O_7$$

$$(Ln = Sm\text{–}Gd, Dy\text{–}Lu, Y)$$

$$Ln(C_7H_5O_4)_3 \cdot nH_2O \rightarrow Ln(C_7H_5O_4)_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3 \; (Ln = La, Nd)$$

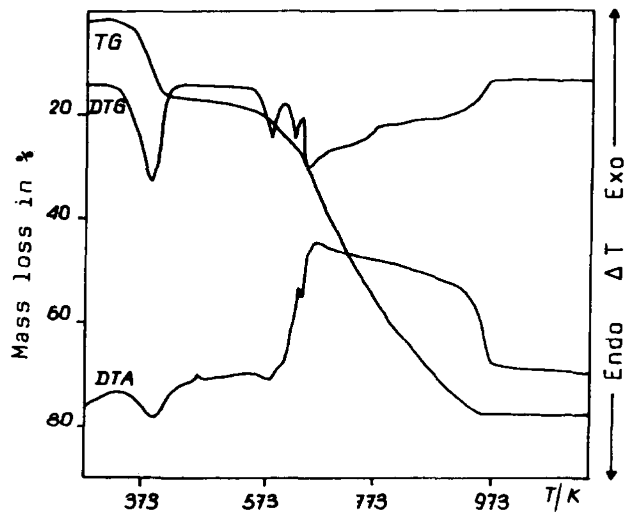

Fig. 4. TG, DTG and DTA curves of $Ho(C_7H_5O_4)_3 \cdot 7H_2O$.

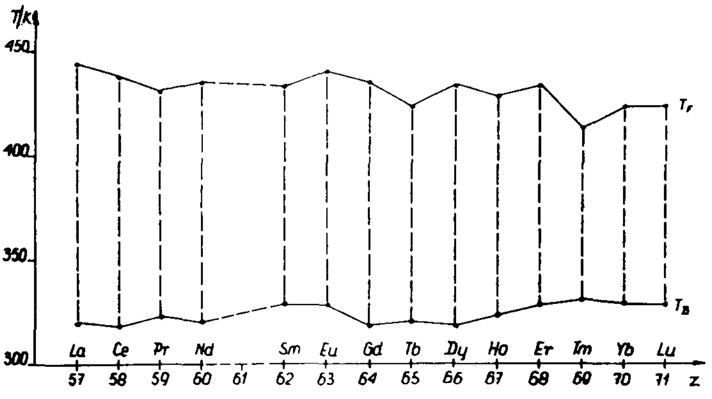

Fig. 5. Relationship between the initial T_B and final T_F temperatures of dehydration, and Z.

The temperatures of oxide formation (T_K) change insignificantly in the lanthanide series (Fig. 7) with the exception of La_2O_3 and Nd_2O_3, which are formed at the highest temperatures (1053 and 1015 K, respectively) and Gd_2O_3, Yb_2O_3 and Lu_2O_3 which are formed at the lowest ones (915, 898, 908 K, respectively) (Fig. 7). The high temperatures of La_2O_3 and Nd_2O_3 formation can be due to formation of oxocarbonates as intermediate products of the complex decomposition. The lower temperature of Gd_2O_3 formation compared to the oxides of other lanthanides is not unusual and can be interpreted as the "gadolinium break". The low temperatures of Yb_2O_3 and Lu_2O_3

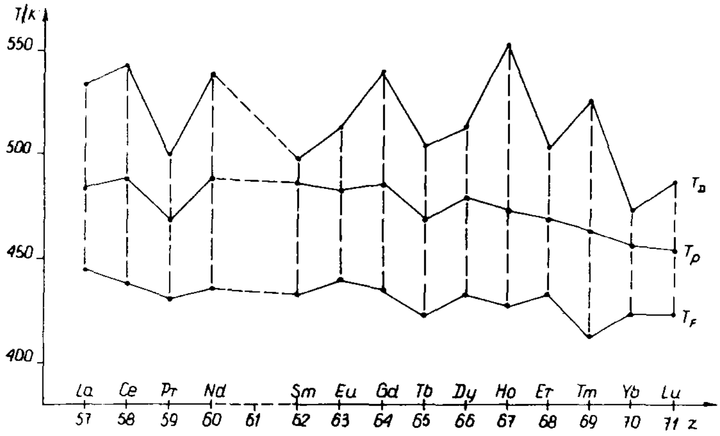

Fig. 6. Relationship between the final temperatures of dehydration, and T_F, the temperatures of polymorphic change T_P, and the temperatures of decomposition T_D of the anhydrous complexes, and Z.

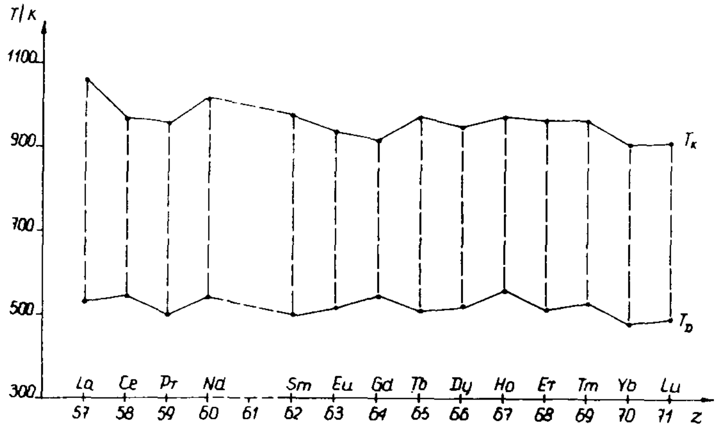

Fig. 7. Relationship between the temperatures of decomposition T_D of anhydrous complexes, and oxide formation T_K, and Z.

formation may be due to increasing polarization with decreasing ionic radius in the lanthanide series.

The processes of dehydration and decomposition are connected with a strong endothermic effect, whereas the processes of combustion of the organic ligand and its decomposition are accompanied by exothermic effects.

Comparing the properties of the three systematically studied series of rare earth element, dihydroxybenzoates it is possible to state that the solubilities of the complexes increase in the order

$$3,4-(10^{-4}\,\mathrm{mol\,dm^{-3}}) < 2,4-(10^{-2}\,\mathrm{mol\,dm^{-3}}) < 3,5-(10^{-1}\,\mathrm{mol\,dm^{-3}})$$

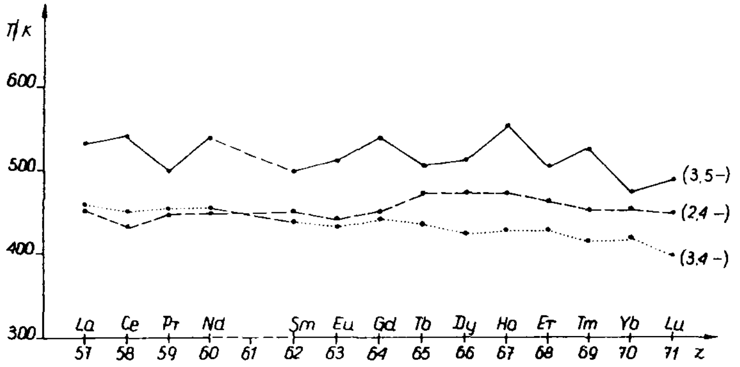

Fig. 8. The decomposition temperatures of the anhydrous 3,5-, 2,4- and 3,4-dihydroxybenzoates of rare earth elements.

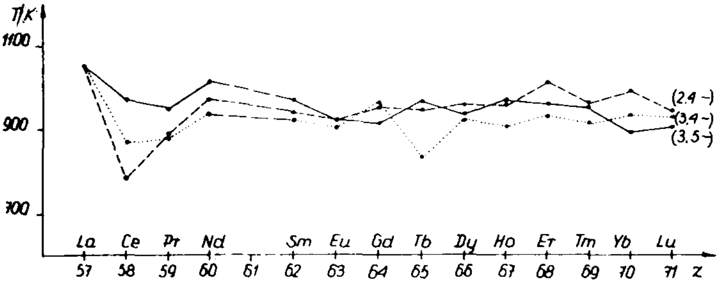

Fig. 9. The temperatures of oxide formation from 3,5-, 2,4- and 3,4-dihydroxybenzoates.

The thermal stabilities of anhydrous complexes change in a similar way (Fig. 8). The temperatures of oxide formation for 3,5-dihydroxybenzoates of the heavy lanthanides are similar to the 3,4- and 2,4-dihydroxybenzoates, whereas those of the light lanthanides are notable higher (Fig. 9).

On this basis it is possible to confirm that the position of the two OH groups in the benzene ring influences the electron cloud density on the carbon atom in the OCO^- group and causes the changes of the properties and thermal stabilities of the rare earth dihydroxybenzoates.

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