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THE COMPLEXES OF RARE EARTH ELEMENTS WITH 2,5-DIHYDROXYBENZOIC ACID
Preparation, properties and thermal decomposition

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Abstract

The conditions of the formation of rare earth(III) 2,5-dihydroxybenzoates have been studied; their compositions and solubilities in water at 293 K have been determined. The IR spectra of the anhydrous complexes with the general formula $Ln(C_7H_5O_4)_3$ have been recorded and their thermal decompositions in static air determined. During heating the anhydrous complexes of Y, Pr–Lu decompose to the oxides Ln_2O_3, Pr_6O_{11} and Tb_4O_7 with formation of the intermediate $Ln_2(C_7H_4O_4)_3$. The lanthanum complex decomposes to the oxide in three steps forming $La_2(C_7H_4O_4)_3$ and $La_2O_2CO_3$ as intermediates and the Ce(III) complex decomposes directly to CeO_2. The properties of rare earth 2,5- and 2,4-dihydroxybenzoates have been compared.

Keywords: 2,5-dihydroxybenzoates, IR, rare earth elements, thermal analysis

Introduction

A survey of the literature shows that the complexes of dihydroxybenzoic acid are not very well known. Studies are usually not comprehensive and concern only the 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- [8–9], 3,4- [10] and 3,5-dihydroxybenzoic acids [11], their preparation, IR spectra and thermal decomposition in an air atmosphere. The authors of [1] have prepared 2,5-dihydroxybenzoates of La, Pr, Nd, Sm and Gd in solid state as hydrates, registered their IR spectra and also UV spectra in methanol and ethanol solutions. The stability constants and thermodynamic functions have been determined for the lanthanide complexes with the general formula $Ln(C_7H_5O_4)^{2+}$ [12].

The aim of this work was to prepare the complexes of all the rare earth elements(III) with 2,5-dihydroxybenzoic acid under the same conditions and to examine systematically their physico-chemical properties and thermal decomposi-

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tion in air, to describe the changes of the properties of the complexes in the lanthanide series, and to compare the properties of 2,5-dihydroxybenzoates with those of 2,4-dihydroxybenzoates.

Experimental

2,5-dihydroxybenzoates of Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by dissolving the freshly precipitated lanthanide(III) hydroxides or carbonates in a solution of 2,5-dihydroxybenzoic acid and crystallization at room temperature. The precipitate formed was filtered off, washed with water and methanol, and dried at 303 K to a constant mass.

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

The IR spectra for the complexes, and the spectra of 2,5-dihydroxybenzoic acid and its sodium salt, were recorded as KBr discs on a Specord M-80 spectrophotometer (Carl Zeiss – Jena) in the range 4000–400 cm^{-1}. The X-ray diffraction patterns of the prepared complexes were taken on a DRON-2 diffractometer using Ni-filtered CuK_α radiation. The measurements were made in the range 2θ=5–60° by means of the Debye-Scherrer method.

The solubilities of rare earth 2,5-dihydroxybenzoates were determined in water at 293 K. Saturated solutions were prepared under isothermal conditions. After equilibrium had been established, samples of 2 and 5 cm^3 volume were withdrawn 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 an OD-102 Derivatograph (Paulik-Paulik-Erdey) at a heating rate of 10 K min^{-1}. The samples (100 mg) were heated to 1273 K in platinum crucibles. Al_2O_3 was used as a reference.

Results and discussion

2,5-Dihydroxybenzoates of Y(III) and lanthanides(III) were prepared as solids, grey-beige in colour, with a molar ratio of metal to organic ligand of 1:3 and general formula $[Ln\{C_6H_3(OH)_2COO\}_3]$. On the basis of X-ray patterns it was found that the prepared complexes are amorphous. They form glassy solids.

Anhydrous 2,5-dihydroxybenzoates are soluble in water. Their solubilities are of the order of 10^{-2} mol dm^{-3} and change periodically in the lanthanide series with increasing atomic number Z of the metal (Table 1). The solubilities of the complexes of the light lanthanides are remarkably less than those of the heavy ones. The solubilities of the complexes of lanthanides with carboxylic acids very often change in different ways for light and heavy lanthanides [12]. The periodic

change of the properties of lanthanide compounds are connected with the change in the electronic structure and orbital number L, and the change of ionic potential of metal ions in the lanthanide series. The solubility of the Y(III) complex is similar to those of heavy lanthanide complexes, which is connected with the similarity of the ionic radii. Comparison of the solubilities of rare earth 2,4- and 2,5-dihydroxybenzoates revealed that solubilities of the 2,5-dihydroxybenzoates of the light lanthanides from La to Tb are greater than those of the 2,4-dihydroxybenzoates, whereas the solubilities of the 2,5-dihydroxybenzoates of Y(III) and heavy lanthanides are smaller than those of the 2,4-dihydroxybenzoates [8].

All rare earth 2,5-dihydroxybenzoates show similar solid-state IR spectra (Table 1). However, the characteristic frequencies related to the carbonyl group are altered markedly in going from the acid to the salt. In the IR spectrum of 2,5-dihydroxybenzoic acid, there is an absorption band at 3136 cm^{-1} due to the valence vibration of the OH group, the band of the COOH group at 1668 cm^{-1}, and the bands of δ(OH) and ν(OH) at 1440, 840 and 1280 cm^{-1}, respectively. In the IR

Table 1 Frequencies (cm^{-1}) of the absorption bands of OCO^- and OH groups of 2,5-dihydroxybenzoic acid and its compounds and their solubilites (mol $dm^{-3}\times10^{-2}$) in water at 293 K

Compound	$\nu_{as}OCO^-$	$\Delta\nu_{as}^{**}$	ν_sOCO^-	$\Delta\nu_{as}^{**}$	$\nu_{as}-\nu_s$	δOH	νM–O	Solub.
HL*						1440.840		
NaL	1592		1400		192	1464.828	426	
YL_3	1552	–40	1392	–8	160	1464.828	436	3.19
LaL_3	1548	–44	1400	0	148	1464.824	436	1.29
CeL_3	1548	–44	1400	0	148	1464.824	436	0.99
PrL_3	1548	–44	1400	0	148	1464.824	436	1.53
NdL_3	1548	–44	1400	0	148	1464.824	436	2.44
SmL_3	1548	–44	1400	0	148	1464.828	436	3.90
EuL_3	1548	–44	1400	0	148	1464.828	436	1.87
GdL_3	1548	–44	1400	0	148	1464.832	436	3.36
TbL_3	1552	–40	1400	0	152	1464.828	436	3.91
DyL_3	1552	–40	1392	–8	160	1464.824	436	4.07
HoL_3	1552	–40	1392	–8	160	1464.824	436	3.23
ErL_3	1556	–36	1392	–8	164	1464.824	436	4.44
TmL_3	1556	–36	1388	–12	168	1464.824	436	3.72
YbL_3	1558	–34	1388	–12	170	1464.824	436	4.26
LuL_3	1560	–32	1392	–8	168	1464.824	436	2.66

* L is $[C_6H_3(OH)_2COO]$

** shift of absorption bands $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ compared with bands of sodium 2,5-dihydroxybenzoate

spectra of the prepared complexes, there are bands at 1560–1548 cm^{-1} and 1400–1388 cm^{-1} of the asymmetric and symmetric vibrations of the COO^{-1} group, respectively and bands of the metal–oxygen bonds at 436 cm^{-1}. The absorption bands of δ(OH) and ν(OH) are shifted insignificantly relative to the absorption bands in the spectrum of the acid, which suggests that OH groups do not play any direct part in the coordination of the metal ion. The absorption bands of the asymmetric vibrations $\nu_{as}(OCO^-)$ are shifted to lower frequencies compared to the bands of the sodium salt. The absorption bands of symmetric vibrations of the OCO^- group, $\nu_s(OCO^-)$ in the IR spectra of the complexes of light lanthanides from La to Tb appear at the same frequency as those for the sodium salt, whereas in the spectra of Y(III) and heavy lanthanides these bands are shifted to lower frequencies compared to those in the spectrum of the sodium salt.

The values of splitting for the absorption bands of the valence vibrations $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ ($\Delta\nu=\nu_{as}-\nu_s$) are ($\Delta\nu$=148–170 cm^{-1}) smaller for the prepared complexes than for the sodium salt ($\Delta\nu$=192 cm^{-1}). The values $\Delta\nu$ in the spectra of the complexes of light lanthanides ($\Delta\nu$=148 cm^{-1}) are smaller than those for the heavy lanthanide complexes ($\Delta\nu$=152–170 cm^{-1}). On this basis it is possible to state that the 2,5-dihydroxybenzoate ligand acts as a bidentate chelating agent [13] and the participation of the ionic bond in the metal–ligand bond in the prepared complexes is smaller than that in the sodium salt, and that it changes in the lanthanide complexes with increasing ionic potential of the metal. In this case one can observe the change of the bond character for the complexes of light and heavy lanthanides. This tendency is very often observed for the complexes in the lanthanide series.

The values of $\Delta\nu$ in the spectra of rare earth 2,5-dihydroxybenzoates ($\Delta\nu$= 148–170 cm^{-1}) are remarkably less than those of 2,4-dihydroxybenzoates ($\Delta\nu$= 230–240 cm^{-1}), which indicates a change in the participation of ionic bond of metal–ligand and in the mode of coordination of M–L with the change of the position of the OH groups in the benzene ring of the ligands. In rare earth 2,5-dihydroxybenzoates the carboxylate group probably acts as a bidentate whereas in the 2,4-dihydroxybenzoates as a monodentate ligand [8]. A more precise interpretation of the coordination mode of the metal-dihydroxybenzoate ligands might offered on the basis of the molecular and crystallographic structure of monocrystals, but it has not been made so far.

Anhydrous 2,5-dihydroxybenzoates of Y(III) and lanthanides(III) are stable in air up to 333–353 K (Table 2). The temperatures of decomposition are very similar for all the prepared complexes. The complexes heated decompose in a similar way except for the lanthanum(III) and cerium(III) complexes (Figs 1–3, Table 2). During heating, the complexes of Y, La, Pr–Lu decompose to the oxides Ln_2O_3, Pr_6O_{11} and Tb_4O_7 with formation of unstable intermediates $Ln_2(C_7H_4O_4)_3$ with a metal to ligand molar ratio of 2:3. The lanthanum(III) complex forms moreover the stable oxocarbonate $La_2O_2CO_3$ as an intermediate over the tem-

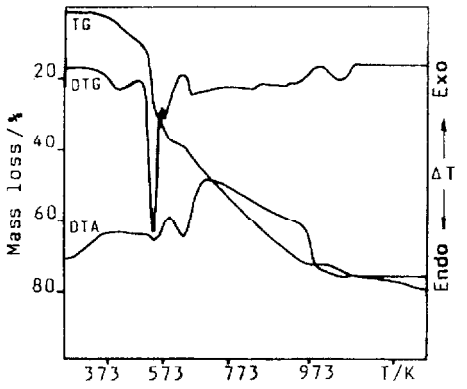

Fig. 1 TG, DTG and DTA curves of $La(C_7H_5O_4)_3$

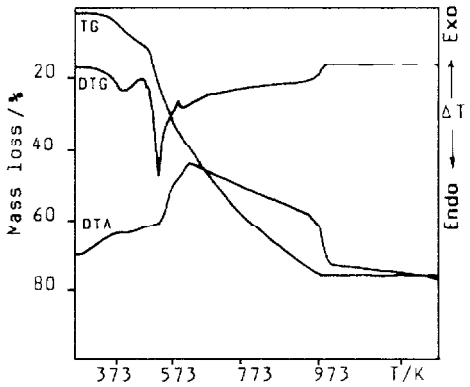

Fig. 2 TG, DTG and DTA curves of $Ce(C_7H_5O_4)_3$

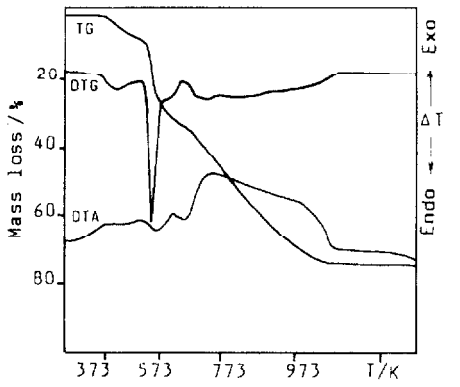

Fig. 3 TG, DTG and DTA curves of $Er(C_7H_5O_4)_3$

Table 2 Data for decomposition of Y and lanthanide 2,5-dihydroxybenzoates in air

Complex	ΔT/ K	Mass loss/%		$Ln_2[C_6H_3(O)(OH)COO]_3$/%			$(Ln_2O_2CO_3)$	T_k/ K
		calcd.	found	T/K	calcd.	found	T_t/K	
YL_3	353–1116	79.40	79.9	673	53.45	53.8		1116
LaL_3	351–1071	72.76	73.0	630	57.34	57.5	973–1071	1071
CeL_3	333– 980	71.29	72.0					980
PrL_3	343–1020	71.63	72.0	640	57.48	57.8		1020
NdL_3	341–1001	72.12	72.0	630	57.72	58.5		1001
SmL_3	353– 991	71.39	71.0	643	58.14	59.0		991
EuL_3	353– 953	71.21	71.0	631	58.25	59.0		953
GdL_3	353– 995	70.60	71.0	658	58.61	59.1		995
TbL_3	353– 993	70.41	70.5	640	58.72	58.7		993
DyL_3	353–1040	70.01	70.0	653	58.96	59.0		1040
HoL_3	350–1041	69.74	70.0	646	59.12	60.0		1041
ErL_3	353–1055	69.48	69.8	648	59.27	59.5		1055
TmL_3	353–1043	69.23	69.2	656	59.38	59.8		1043
YbL_3	353–1053	68.85	69.0	651	59.64	59.5		1053
LuL_3	353–1038	68.63	68.5	660	59.76	60.0		1038

ΔT – temperature range of decomposition
T – temperature of $Ln_2[C_6H_3(O)(OH)COO]_3$ formation
T_t – temperature of $(Ln_2O_2CO_3)$ formation
T_k – temperature of oxide formation

perature range 973–1017 K. The anhydrous cerium(III) complex decomposes directly to CeO_2.

Generally, the thermal decomposition of anhydrous rare earth 2,5-dihydroxybenzoates can be described as:

$Ln(C_7H_5O_4)_3 \rightarrow Ln_2(C_7H_4O_4)_3 \rightarrow Ln_2O_3, Pr_6O_{11}, Tb_4O_7$

Ln = Y, Pr–Lu

$La(C_7H_5O_4)_3 \rightarrow La_2(C_7H_4O_4)_3 \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$

$Ce(C_7H_5O_4)_3 \rightarrow CeO_2$

The temperatures of oxide formation (T_K) change insignificantly in the lanthanide series (Fig. 4), with the exception of La_2O_3, which is formed at the highest temperature (1071 K), and CeO_2 and Eu_2O_3, which are formed at the lowest temperatures (980 and 953 K, respectively). Similar changes of oxide formation temperatures are observed for 2,4-dihydroxybenzoates (min. for CeO_2 and Eu_2O_3 and max. for La_2O_3).

Comparing the thermal stabilities of rare earth 2,4- and 2,5-dihydroxybenzoates [8], it is possible to state that the decomposition of anhydrous complexes begins at very similar temperatures whereas the temperatures of oxide formation from 2,5-dihydroxybenzoates are higher than those for 2,4-dihydroxybenzoates (Fig. 5). The differences in the temperatures of oxide formation of yttrium and lanthanides from 2,5-dihydroxybenzoates are greater than those from 2,4-dihydroxybenzoates [8] (ΔT=50–90 K), and those of light lanthanides are smaller

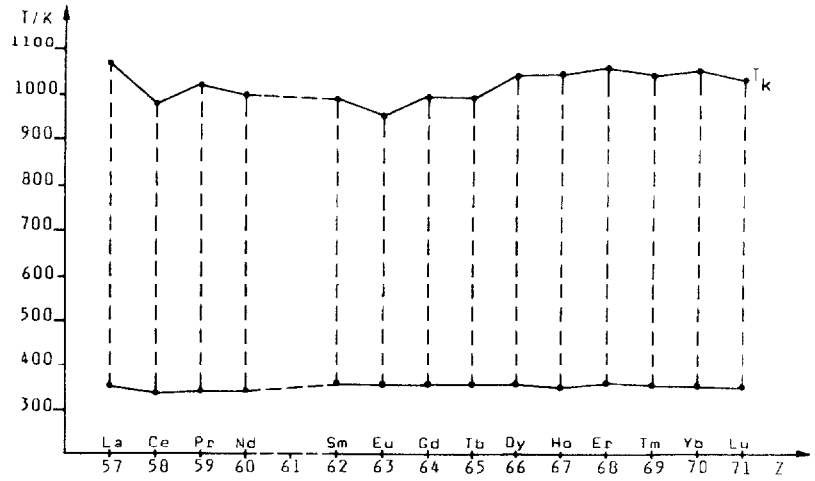

Fig. 4 Relation between the decomposition temperature (T) of anhydrous complexes and oxide formation (T_K), and the atomic number (Z) of metal

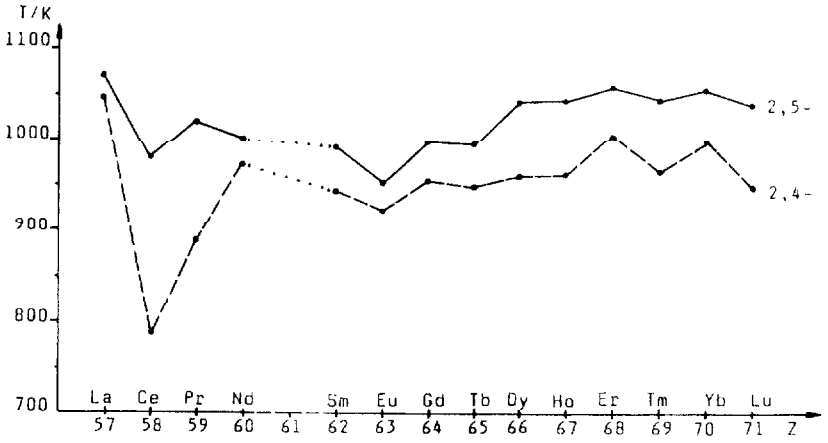

Fig. 5 The temperatures of rare earth oxide formation from 2,4- and 2,5-dihydroxybenzoates

(ΔT=20–40 K). The greatest difference between the temperatures of oxide formation is observed for cerium(III) complexes (ΔT=192 K).

The differences in the thermal stabilities of rare earth complexes with 2,5- and 2,4-dihydroxybenzoic acids are caused by the change in the position of OH groups in the benzene ring of the ligands and the change in electron cloud density on the carbon atom of the OCO^- group. The M–L bonds in the complexes of rare earth elements with 2,5-dihydroxybenzoic acid are probably stronger than that in the complexes of the 2,4-dihydroxybenzoic acid.

On this basis it is possible to confirm that the position of two OH groups in the benzene ring influences the structures and properties of rare earth dihydroxybenzoates.

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