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THERMAL DECOMPOSITION OF LANTHANIDE(III) AND Y(III) 3,4,5-TRIHYDROXYBENZOATES
Preparation, properties

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Abstract

Complexes of lanthanides(III) (La–Lu) and Y(III) with 3,4,5-trihydroxybenzoic acid (gallic acid) were obtained and their thermal decomposition, IR spectra and solubility in water have been investigated. When heated, the complexes with a general formula $Ln(C_7H_5O_5)(C_7H_4O_5)\cdot nH_2O$ (n=2 for La–Ho and Y: n=0 for Er–Lu) lose their crystallization water and decompose to the oxides Ln_2O_3, CeO_2, Pr_6O_{11}, and Tb_4O_7, except of lanthanum and neodymium complexes, which additionally form stable oxocarbonates such as $Ln_2O_2CO_3$. The complexes are sparingly soluble in water ($0.3\cdot10^{-5}$–$8.3\cdot10^{-4}$ mol dm^{-3}).

Keywords: complexes, IR spectra, lanthanides, synthesis, thermal analysis, 3,4,5-trihydroxybenzoates

Introduction

The crystal structure of 3,4,5-trihydroxybenzoic acid (gallic acid) monohydrate has been studied [1–2]. Biochemical investigation showed that gallic acid had selective cytotoxicity against tumour cells [3–6]. Solid Y, La, Ce, Nd, Ho and Er gallate with a general formula $NH_4[M(C_7H_4O_5)_2]$ were prepared and IR spectra of the compounds were recorded. They have asymmetric and symmetric vibration bands at 1603 and 1429 cm^{-1}, respectively [7]. Neodymium gallate was reported as a solid, in which metal to ligand ratio is 1:2. Phenolic OH vibrations were defined at 1282 and 1212 cm^{-1} [8]. The thermal stability of the complexes was till now not investigated.

Previously have been described the preparation, solubility in water, IR and X-ray spectra and thermal decomposition in air of the complexes of lanthanide(III) from La(III) to Lu(III) and Y(III) with 2,3- [9], 2,4- [10, 11], 2,5- [12], 2,6- [13–15], 3,4- [16], and 3,5-dihydroxybenzoic acids [17, 18]. The present work is a continuation of past papers.

The aim of this work was the preparation and study of thermal and spectral properties of the complexes of lanthanide(III) and Y(III) with 3,4,5-trihydroxybenzoic

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acid as solids as well as examination of influence of the OH group in benzene ring on the properties of the complexes.

Experimental

3,4,5-Trihydroxybenzoates of lanthanides(III) from La(III) to Lu(III) and Y(III) were prepared by addition of equivalent quantities of 0.2 M ammonium 3,4,5-trihydroxybenzoate (pH 5.2–6.0) to a solution of rare earth chlorides (Ce(III) was used as its nitrate) at 323 K. The precipitate formed was filtered off, washed with water and dried at 303 K to a constant mass.

The quantitative composition of the prepared complexes was determined by elemental analysis, by ignition of the complexes to the oxides and from TG curve. The content of crystallisation water was determined from TG curve and by isothermal heating of the complexes at a specified temperature. The analytical data of the complexes were in agreement with the theoretical calculations. The X-ray diffraction patterns of the complexes obtained were taken on a HZG 4 A2 diffractometer, using Ni-filtered radiation. The measurements were made in the range of $2\theta=5–60°$ by the Debye–Scherrer method.

The solubility of the complexes in water at 293 K were determined. The saturated solutions were prepared under isothermal conditions. The content of lanthanide(III) was determined spectrophotometrically by the arsenazo-III method, using a Specord M-40 spectrophotometer.

The IR spectra of 3,4,5-trihydroxybenzoate acid, the lanthanide complexes and the sodium salt were recorded in the range of 4000–400 cm^{-1}, using M-80 Carl-Zeiss Jena spectrophotometer. The samples were prepared as KBr discs.

The thermal stability of the complexes obtained, the processes of their dehydration and decomposition as well as the solid product of decomposition were studied in air, using SETSYS 16/18 (Setaram) derivatograph; samples were heated to 1273 K at a heating rate of 10 K min^{-1}.

Results and discussion

3,4,5-Trihydroxybenzoates of lanthanides(III) from La(III) to Lu(III) and Y(III) were obtained as solids, with a molar ratio of metal to organic ligand 1:2 and general formulae $LnLL'\cdot nH_2O$; L is $[C_6H_2(OH)_3COO]^-$ and L′ is $[C_6H_2(OH)_2(O)COO]^{2-}$. In these complexes a lanthanide ion substitutes three hydrogen atoms, two of which come from carboxylic groups and one from a phenolic group. Nevertheless, it is difficult to judge from the IR spectra which phenolic group the hydrogen atom comes from. A similar case was previously described by Burns and Baldwin [19]. They defined the structure of samarium salicylate and proved that only one phenolic group from six ligands coordinated to metal takes part in the bond. Complexes from La(III) to Ho(III) and Y(III) were obtained as crystalline and isostructural dihydrates, whereas complexes of Er(III), Tm(III), Yb(III), and Lu(III) as amorphous anhydrates. These complexes are sparingly soluble in water. Their solubility changes in the wide range of $0.3\cdot10^{-5}$–$8.3\cdot10^{-4}$ mol dm^{-3}. It also changes periodically in the lanthanide series (Table 1).

Table 1 Solubility of Y(III) and lanthanide(III) 3,4,5-trihydroxybenzoates in water at 293 K

Complex	Solubility/mol·dm^{-3}·10^{-5}	Complex	Solubility/mol·dm^{-3}·10^{-5}
LaLL′·2H$_2$O	3.7	DyLL′·2H$_2$O	0.3
CeLL′·2H$_2$O	14.8	HoLL′·2H$_2$O	23.4
PrLL′·2H$_2$O	0.6	ErLL′	83.3
NdLL′·2H$_2$O	1.7	TmLL′	57.5
SmLL′·2H$_2$O	1.3	YbLL′	71.1
EuLL′·2H$_2$O	0.6	LuLL′	59.9
GdLL′·2H$_2$O	1.1	YLL′·2H$_2$O	56.9
TbLL′·2H$_2$O	0.4		

$L=C_7H_5O_5^-$
$L'=C_7H_4O_5^{2-}$

The thermal stability of the complexes obtained was studied in air and the data are presented in Table 2. Dihydrates of lanthanides(III) from La(III) to Ho(III) and Y(III) are stable in air to temperature of 319–340 K. Other anhydrous complexes from Er(III) to Lu(III) are much more stable than the dihydrates; they are stable to temperature of 373–393 K. When heated in air dihydrates lose their crystallization water. The loss of water molecules is a slow, continuous process; the DTA curve shows slight, unclear endoeffect, which is associated with this process. This may suggest that water molecules are loosely bound in space lattice of the complex (Fig. 1).

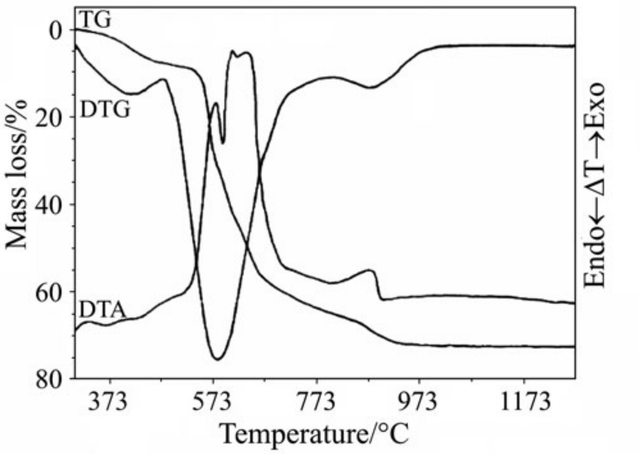

Fig. 1 TG, DTG and DTA curves of Sm(C$_7$H$_5$O$_5$)(C$_7$H$_4$O$_5$)·2H$_2$O

Table 2 Data of decomposition of yttrium(III) and lanthanide(III) 3,4,5-trihydroxybenzoates in air

Complex	ΔT_1	Mass loss/%			ΔT_2	Mass loss/%		T_0	DTA effect			
		calc.	found	nH$_2$O		calc.	found		endo/K	exo/K		
LaLL′·2H$_2$O	341–393	7.02	6.7	2	481–1089	68.2	67.5	1089	383	561	637	695
CeLL′·2H$_2$O	333–388	7.01	6.9	2	442–716	66.5	67.0	716	381	540	606	715
PrLL′·2H$_2$O	333–398	7.00	6.8	2	459–873	66.9	66.8	873	391	558	626	713
NdLL′·2H$_2$O	340–403	6.95	7.0	2	487–975	66.8	66.0	975	383	568	608	627
SmLL′·2H$_2$O	334–378	6.87	7.1	2	475–971	66.7	67.1	971	385	576	607	637
EuLL′·2H$_2$O	330–385	6.85	7.1	2	455–968	66.5	67.0	968	387	547	585	610
GdLL′·2H$_2$O	330–388	6.78	6.9	2	470–978	65.8	65.7	978	380	554	609	
TbLL′·2H$_2$O	319–385	6.76	6.7	2	502–883	65.4	64.7	883	383	554	628	
DyLL′·2H$_2$O	323–398	6.72	6.7	2	443–968	65.2	65.5	967	392	541	640	
HoLL′·2H$_2$O	323–390	6.70	6.9	2	438–981	64.9	63.3	981	394	540	647	
ErLL′					373–991	60.0	60.0	991		550	668	
TmLL′					385–1005	59.0	59.0	1005		549	670	
YbLL′					393–1007	57.0	57.7	1007		553	679	
LuLL′					388–1035	57.0	57.4	1035		555	685	
YLL′·2H$_2$O	323–400	7.79	8.1	2	448–978	75.6	76.4	978		553	668	

L=C$_7$H$_5$O$_5^-$
L'=C$_7$H$_4$O$_5^{2-}$
ΔT_1 – range of dehydration temperature
ΔT_2 – range of decomposition temperature
T_0 – temperature of oxide formation (Ln$_2$O$_3$, CeO$_2$, Pr$_6$O$_{11}$, Tb$_4$O$_7$)

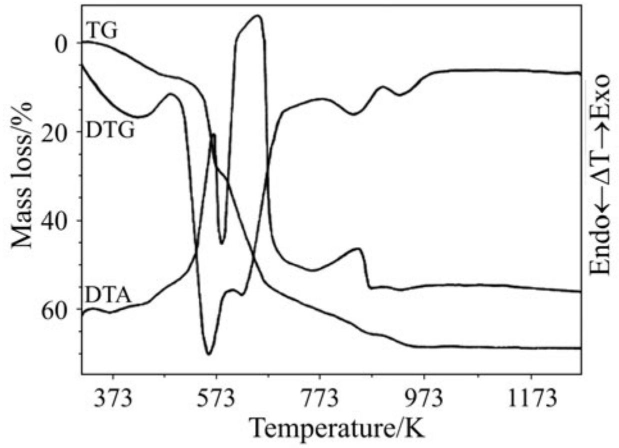

Fig. 2 TG, DTG and DTA curves of $Nd(C_7H_5O_5)(C_7H_4O_5)\cdot 2H_2O$

The dehydration temperature of dihydrated complexes is similar, which is associated with their isostructural properties. After dehydration anhydrous complexes are stable to temperature of 378–438 K; when heated they decompose to oxides: Ln_2O_3, CeO_2, Pr_6O_{11}, and Tb_4O_7. The intermediate decomposition of complexes of La(III) and Nd(III) are oxocarbonates $Ln_2O_2CO_3$; they are stable in temperature of 658–893 K (Fig. 2). When heated anhydrous complexes of lanthanides(III) from Er(III) to Lu(III) as well as hydrous ones decompose to oxides Ln_2O_3. The temperatures of oxide formation in the case of decomposition of lanthanide dihydrates are similar, except Ce(III) complex, which has the lowest (716 K), and La(III) complex, which has the highest temperature (1089 K). Thermal decomposition of obtained lanthanide(III) and Y(III) complexes with 3,4,5-trihydroxybenzoic acid can be presented as follows:

$$LnLL'\cdot 2H_2O \rightarrow LnLL' \rightarrow Ln_2O_3\ (CeO_2,\ Pr_6O_{11},\ Tb_4O_7) \quad (Ln=\text{Ce, Pr, Sm–Ho})$$

$$LnLL'\cdot 2H_2O \rightarrow LnLL' \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3 \quad (Ln=\text{La, Nd})$$

$$LnLL' \rightarrow Ln_2O_3 \quad (Ln=\text{Er–Lu})$$

The temperatures of the oxide formation (T_0) increases with increasing of the atomic number Z of the metal. These temperatures of oxide formations from anhydrous complexes /Er(III)–Lu(III)/ are much higher than the temperatures in the case of dihydrates (Figs 3 and 4). The thermal stability of Y(III) complex is similar to heavy lanthanide complexes, which is connected with the similarity of the ionic radii.

IR spectra of 3,4,5-trihydroxybenzoic acid, its sodium salt and lanthanide(III) complexes obtained were recorded. They are presented in Table 3. In the IR spectrum of the free 3,4,5-trihydroxybenzoic acid there is a sharp absorption band of carboxylic group – COOH at 1664 cm^{-1}, absorption bands of δOH at 1428 and at 864 cm^{-1} as well as νCOH at 1320 cm^{-1}.

Table 3 Frequencies of absorption bands of OCO^- and OH groups of 3,4,5-trihydroxybenzoic acid and its compounds (cm^{-1})

Compound	$\nu_{as}OCO^-$	ν_sOCO^-		$\nu_{as}–\nu_s$		δOH	νCOH	δOH	$\nu M–O$
$LaLL'·2H_2$	1538	1360	1336	168	192	1442	1292	856	464
$CeLL'·2H_2$	1538	1360	1336	168	192	1440	1290	860	468
$PrLL'·2H_2O$	1538	1356	1336	172	192	1442	1290	862	472
$NdLL'·2H_2$	1532	1360	1336	172	196	1440	1290	856	472
$SmLL'·2H_2$	1532	1360	1336	172	196	1442	1292	856	472
$EuLL'·2H_2$	1532	1360	1336	172	196	1442	1292	858	476
$GdLL'·2H_2$	1532	1360		172		1440	1290	856	476
$TbLL'·2H_2$	1532	1360		172		1442	1292	856	476
$DyLL'·2H_2$	1532	1360		172		1440	1290	856	476
$HoLL'·2H_2$	1532	1360		172		1440	1292	854	476
ErLL′	1540	1278		162		1442	1290	860	450
TmLL′	1544	1384		160		1442	1292	862	450
YbLL′	1540	1380		160		1440	1292	864	450
LuLL′	1552	1392		160		1442	1292	860	452
$YLL'·2H_2O$	1532	1360		172		1440	1292	854	476
NaL	1540	1344		196		1408	1290	850	468
HL						1428	1320	864	

$L=[C_6H_2(OH)_3COO]^-$
$L'=[C_6H_2(OH)_2(O)COO]^{2-}$

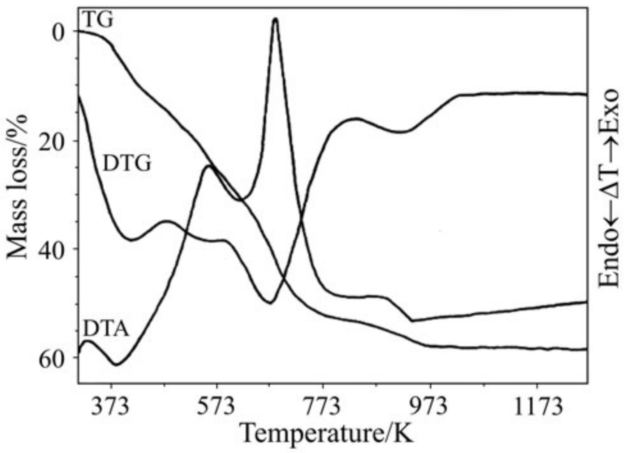

Fig. 3 TG, DTG and DTA curves of Yb($C_7H_5O_5$)($C_7H_4O_5$)

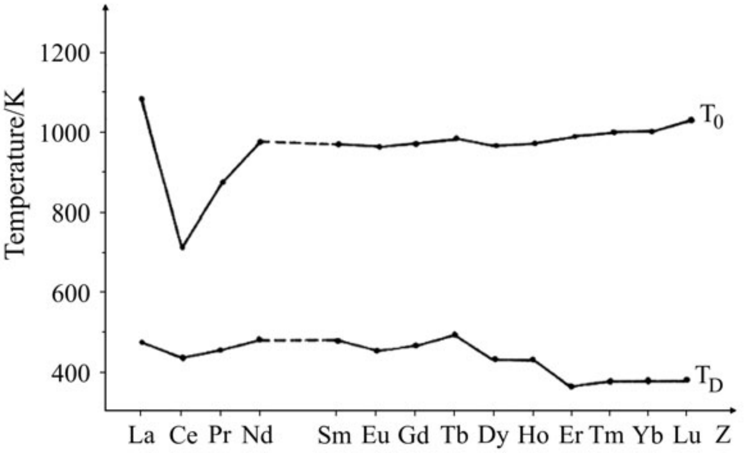

Fig. 4 Relationship between temperature of anhydrous complexes decomposition (T_D) and oxide formation (T_0) for lanthanide complexes with 3,4,5-trihydroxybenzoic acid

In the IR spectra of the complexes obtained asymmetric absorption bands of $\nu_{as}(OCO^-)$ at 1544–1528 cm^{-1} can be observed. The asymmetric absorption bands of dihydrated complexes are shifted to lower frequencies of about 8–12 cm^{-1} or have not changed their position (for anhydrous complexes Er–Lu) in comparison with sodium salt. The symmetric absorption bands $\nu_s(OCO^-)$ of dihydrated complexes from La(III) to Er(III) are split, forming a double band at 1360 and 1336 cm^{-1}. The symmetric absorption bands of complexes from Gd(III) to Lu(III) are not split but shifted about 16 cm^{-1} (for Gd–Ho), and 34–48 cm^{-1} (for Er–Lu) to higher frequencies in comparison with sodium salt. The splitting of asymmetric bands $\nu_{as}(OCO^-)$ and the separation value $\Delta\nu$ indicates that organic ligands may be found as mono-, bi- and tetradentate. The deformation vibration bands of phenolic group δ(OH) at 1428 cm^{-1} in free acid are shifted to higher frequencies, the bands at 864 cm^{-1} and the bands νOH at 1320 cm^{-1} are shifted to lower frequencies in the lanthanide complexes. Shifting of the bands may be the result of the disappearance of hydrogen bonding in the ligand molecule and participation of the phenolic group in the metal coordination. In the IR spectra of hydrated complexes a broad valency absorption band of the OH groups from H_2O at 3480–3420 cm^{-1} can be observed. In all complexes an absorption band at 476–450 cm^{-1} due to metal–oxygen bond appears.

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