

## **THERMAL AND SPECTRAL STUDIES OF RARE EARTH ELEMENT 3-methoxy-4-methylbenzoates**

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### **Abstract**

3-Methoxy-4-methylbenzoates of Y(III) and lanthanide(III) (La–Lu) were prepared as crystalline compounds with molar ratio of metal to organic ligand of 1.0:3.0 and general formula  $\text{Ln}(\text{C}_9\text{H}_9\text{O}_3)_3 \cdot n\text{H}_2\text{O}$ , where  $n=2$  for Y, La–Er and  $n=0$  for Tm–Lu. IR spectra of the prepared complexes suggest that carboxylate groups are bidentate chelating. During heating dihydrated complexes lose crystallization water molecules in one (Y, La, Pr–Er) or two steps (Ce) and then all the anhydrous complexes decompose directly to oxides  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$ .

**Keywords:** complexes, IR spectra, 3-methoxy-4-methylbenzoic acid, rare earth element, thermal analysis

### **Introduction**

3-Methoxy-4-methylbenzoic acid  $\text{C}_6\text{H}_3(\text{OCH}_3)(\text{CH}_3)\text{COOH}$  is a crystalline solid, sparingly soluble in water [1]. The complexes of 3-methoxy-4-methylbenzoic acid with rare earth elements were previously unknown. In our previous work [2] we have studied the complexes of rare earth elements with 4-methoxy-2-methylbenzoic acid.

4-Methoxy-2-methylbenzoates were prepared as crystalline complexes with general formula  $\text{Ln}(\text{C}_9\text{H}_9\text{O}_3)_3$ . Only La(III) and Pr(III) complexes were prepared as monohydrates. Monohydrates heated lose crystallization water molecules and then all the anhydrous complexes decompose directly to oxides. Only La(III) complex decompose to oxide with intermediate formation  $\text{La}_2\text{O}_2\text{CO}_3$ . The carboxylate group in the studied complexes is a tridentate chelating – bridging or bidentate chelating (Y).

In the literature there are some papers on the preparation and thermal and spectral properties of rare earth complexes with 2,3- [3, 4], 2,4- [4, 5] and 3,4-dimethoxybenzoic [4, 5] acids.

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As a continuation of our work on the rare earth element carboxylate [2, 6–8], we now report on the preparation, and spectral and thermal studies of rare earth element complexes with 3-methoxy-4-methylbenzoic acid in solid-state.

## Experimental

3-Methoxy-4-methylbenzoates of rare earth element(III) (Y, La–Lu, without Pm) were prepared by reaction of stoichiometric quantities of 0.2 M solution of ammonium 3-methoxy-4-methylbenzoate (pH 5.5) and 0.2 M solution of rare earth element(III) chlorides (Ce was used as its nitrate). The precipitation formed was heating in the mother solution for 0.5 h at 343–353 K, was then filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass. The sodium salt was prepared by adding 3-methoxy-4-methylbenzoic acid to solution of NaOH and crystallizing at room temperature.

The carbon and hydrogen in the prepared complexes were determined by elemental analysis on a Perkin Elmer CHN 2400 analyser. The metal content was determined from TG curve and by ignition of the complexes prepared in air to 1273 K. The content of crystallization water was determined from TG curve and by heating the samples isothermally at suitable temperature to a constant mass.

The IR spectra of 3-methoxy-4-methylbenzoic acid, its sodium salt and the separated rare earth complexes were recorded over the range 4000–400  $\text{cm}^{-1}$  on a Specord M 80 spectrophotometer. The samples were prepared as KBr discs. The X-ray patterns were recorded with a HZG (Zeiss Jena) diffractometer by Debye–Scherrer powder method using Ni filtered  $\text{CuK}_\alpha$  radiation. The measurements were made over the range  $2\theta=5\text{--}80^\circ$ .

The solubility of the prepared complexes in water was determined at 293 K. The saturated solution were prepared under isothermal conditions. The content of metal(III) ions was determined by spectrophotometric analysis using UV-VIS Specord M 40 spectrophotometer, with arsenazo III. The solubility of the complexes was calculated on the basis of the metal(III) concentration in the saturated solution.

The thermal stability of the prepared complexes was determined using a Paulik–Paulik–Erdey Q 1500 derivatograph with Derill converter. Measurements were made with a sensitivity of 100 mg (TG). The sensibility of DTG and DTA curves were recorded by Derill computer program. Samples of 100 mg were heated in air static atmosphere in platinum crucibles to 1273 K at a heating rate  $10 \text{ K min}^{-1}$  with a full scale. The hydrated complexes were also heated isothermally at a set temperature to a constant mass. The products of decomposition were confirmed by the IR spectra and X-ray diffractograms.

## Results and discussion

3-Methoxy-4-methylbenzoates of rare earth elements(III) (Y, La–Lu, without Pm) were prepared as crystalline solids with a colour characteristic for rare earth element(III) ions and with molar ratio of metal to organic ligand of 1.0:3.0 and general formula

$\text{Ln}(\text{C}_9\text{H}_9\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$ . Only the complexes of the heaviest lanthanides, Tm–Lu, were prepared as anhydrous complexes (Table 1). The complexes prepared are sparingly soluble in water. Their solubility is of the order  $10^{-4} \text{ mol dm}^{-3}$  and change periodically in the lanthanide series. It changes from  $1.30 \cdot 10^{-4}$ – $3.40 \cdot 10^{-4} \text{ mol dm}^{-3}$  (only solubility of Ce(III) complex is equal  $5.50 \cdot 10^{-4} \text{ mol dm}^{-3}$ ).

**Table 1** Analytical data and solubilities in water at 293 K of Y(III) and lanthanide(III) 3-methoxy-4-methylbenzoates

Complex	Ln/%		C/%		H/%		Solubility/ $10^{-4} \text{ mol dm}^{-3}$
	calcd.	found	calcd.	found	calcd.	found	
$\text{YL}_3 \cdot 2\text{H}_2\text{O}^*$	14.34	14.3	52.25	52.0	5.00	4.9	2.62
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	20.73	20.7	48.35	48.4	4.62	4.5	1.55
$\text{CeL}_3 \cdot 2\text{H}_2\text{O}$	20.88	20.8	48.28	47.9	4.62	4.5	5.50
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	20.97	21.0	48.22	48.0	4.61	4.6	2.96
$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$	21.36	21.4	47.98	47.7	4.59	4.6	3.65
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	22.06	22.0	47.55	47.5	4.55	4.5	1.30
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	22.25	22.0	47.44	47.4	4.54	4.5	1.65
$\text{GdL}_3 \cdot 2\text{H}_2\text{O}$	22.84	22.8	47.07	47.0	4.50	4.5	2.35
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	23.03	23.0	46.96	47.0	4.49	4.5	2.20
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	23.43	23.4	46.72	46.7	4.47	4.5	2.11
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	23.70	23.8	46.56	46.5	4.45	4.4	3.10
$\text{ErL}_3 \cdot 2\text{H}_2\text{O}$	23.95	24.0	46.40	46.3	4.44	4.4	2.58
$\text{TmL}_3$	25.49	25.5	48.77	48.8	4.06	4.0	3.40
$\text{YbL}_3$	25.90	26.0	48.50	48.5	4.04	4.0	2.74
$\text{LuL}_3$	26.11	26.0	48.36	48.4	4.03	4.0	2.02

\* $L = [\text{C}_6\text{H}_3(\text{OCH}_3)(\text{CH}_3)\text{COO}]^-$

The IR spectra of the prepared 3-methoxy-4-methylbenzoates are similar to each other (except of Tm–Lu) and have many bands. When the acid is converted to complexes the absorption band of C=O group at  $1684 \text{ cm}^{-1}$  disappears and the bands of asymmetrical ( $\nu_{\text{as}}$ ) and symmetrical ( $\nu_{\text{s}}$ ) vibrations of  $\text{OCO}^-$  group appear at  $1525$ – $1520$  and  $1425$ – $1420 \text{ cm}^{-1}$ , respectively (for Ce, Pr and Eu complexes at  $1510$  and  $1410 \text{ cm}^{-1}$ ), the bands of  $\text{OCH}_3$  with max. at  $1388$ – $384$ ,  $1288$ – $1284$ ,  $1248$ – $1244 \text{ cm}^{-1}$ , the bands of  $\text{CH}_3$  group at  $2930$  and  $2830$ ,  $1408$ – $1404$ ,  $1320$ – $1313 \text{ cm}^{-1}$  and the bands of M–O bond at  $570$ – $550 \text{ cm}^{-1}$ . In the IR spectra of the prepared complexes there are the bands of aromatic ring  $1172$ ,  $1168$ ,  $1106$ ,  $1104$  and  $1040 \text{ cm}^{-1}$ , and the CH bond at  $884$ – $880$ ,  $816$ – $804$ ,  $776$ – $770 \text{ cm}^{-1}$  [9–12]. These bands are shifted insignificantly ( $8$ – $4 \text{ cm}^{-1}$ ) or do not change their position compared to the respective bond of 3-methoxy-4-methylbenzoic acid, what indicates that Ln(III) ions have only a weak influence on the benzene ring.

The frequencies of M–O bond for all the complexes have similar value (Table 2). Accordingly, it may be suggested that 3-methoxy-4-methylbenzoates of rare earth have similar stability [13]. The separation value ( $\Delta\nu$ ) of  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  in the spectra of the prepared 3-methoxy-4-methylbenzoates have similar values ( $\Delta\nu=100\text{--}90\text{ cm}^{-1}$ ) and are smaller than for the sodium salt ( $\Delta\nu=150\text{ cm}^{-1}$ ), what shows on smaller degree of ionic bond in the prepared complexes compared to the sodium salt [9, 11]. The bands of asymmetric vibrations of OCO group are shifted to lower frequencies ( $\Delta=50\text{--}35\text{ cm}^{-1}$ ) and the symmetric vibrations of OCO group to higher frequencies ( $\Delta=25\text{--}10\text{ cm}^{-1}$ , only for Pr and Eu  $\Delta=0$ ) compared to these bands for the sodium salt. From the shifts of  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  and value  $\Delta\nu$  in the IR spectra of the prepared complexes, compared to the bands for sodium salt, it is possible to suggest that OCO group is bonded as bidentate chelating [9–13]. In the IR spectra of the prepared complexes of Y and La–Er there are broad bands of  $\nu(\text{OH})$  with max. at  $3410\text{--}3300\text{ cm}^{-1}$  and narrow bands  $\delta(\text{H}_2\text{O})$  at  $1630\text{--}1620\text{ cm}^{-1}$ , that are characteristic for hydrates. In the IR spectra of Tm–Lu these bands are absent, what confirms anhydrous character of these complexes.

The rare earth element 3-methoxy-4-methylbenzoates are crystalline solids of low symmetry and different structure. They are isostructural in the groups: Y, La, Ce–Sm, Gd–Er, Tm–Lu.

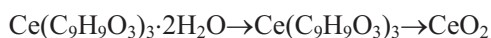
**Table 2** Frequencies of characteristic absorption bands in IR spectra of Na(I) and rare earth 3-methoxy-4-methylbenzoates ( $\text{cm}^{-1}$ )

Complex	$\nu(\text{OH})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu_{\text{as}}\text{--}\nu_{\text{s}}$	$\nu(\text{M--O})$
$\text{YL}_3\cdot 2\text{H}_2\text{O}^*$	3300	1524	1425	99	560
$\text{LaL}_3\cdot 2\text{H}_2\text{O}$	3400	1510	1420	90	560
$\text{CeL}_3\cdot 2\text{H}_2\text{O}$	3410	1510	1420	90	560
$\text{PrL}_3\cdot 2\text{H}_2\text{O}$	3300	1510	1410	100	560
$\text{NdL}_3\cdot 2\text{H}_2\text{O}$	3300	1520	1420	100	570
$\text{SmL}_3\cdot 2\text{H}_2\text{O}$	3300	1520	1425	95	570
$\text{EuL}_3\cdot 2\text{H}_2\text{O}$	3300	1510	1410	100	560
$\text{GdL}_3\cdot 2\text{H}_2\text{O}$	3300	1520	1425	95	570
$\text{TbL}_3\cdot 2\text{H}_2\text{O}$	3300	1520	1420	100	560
$\text{DyL}_3\cdot 2\text{H}_2\text{O}$	3300	1525	1425	100	570
$\text{HoL}_3\cdot 2\text{H}_2\text{O}$	3300	1520	1420	100	560
$\text{ErL}_3\cdot 2\text{H}_2\text{O}$	3350	1525	1425	100	560
$\text{TmL}_3$	-	1520	1420	100	560
$\text{YbL}_3$	-	1520	1420	100	560
$\text{LuL}_3$	-	1525	1425	100	550
$\text{NaL}\cdot n\text{H}_2\text{O}$	3400	1560	1410	150	480

\* $L=[\text{C}_6\text{H}_3(\text{OCH}_3)(\text{CH}_3)\text{COO}]^-$

3-Methoxy-4-methylbenzoates of rare earth elements are stable in air and do not change their composition. Hydrated complexes are stable up to 323–363 K, whereas the anhydrous complexes (Tm–Lu) up to 563 K. When heated in air (Table 1, Figs 1–4) the hydrated complexes of Y, La–Er lose crystallization water molecules in one (Y, La, Pr–Er) or two (Ce) steps over the range 333–363 to 398–413 K (only La and Ce complexes up to 508 K, respectively). The water molecules in the hydrated complexes is probably in inner sphere. According to Nikolaev *et al.* [14] and Singh *et al.* [15] water released below 423 K can be considered crystallization water, whereas that eliminated above 423 K are chemically bonded to central ions through coordination bond, but generally it is possible to say that temperature of dehydration is not connected directly with position of water molecules in inner or outer sphere [10, 11].

All the anhydrous complexes heated decompose directly to oxides  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$  over the range 523–563 to 1078–1173 K. The results indicate that the thermal decomposition of rare earth(III) 3-methoxy-4-methylbenzoates can be presented in following way:



The dehydration and decomposition of the complexes are connected with endothermic effects at 373–383 and 673–678 K, respectively (for Ce(III) complex at 373, 473, 673 K), whereas the combustion of the organic ligand and products of its decomposition shows exothermic effects. The temperature of beginning of dehydration

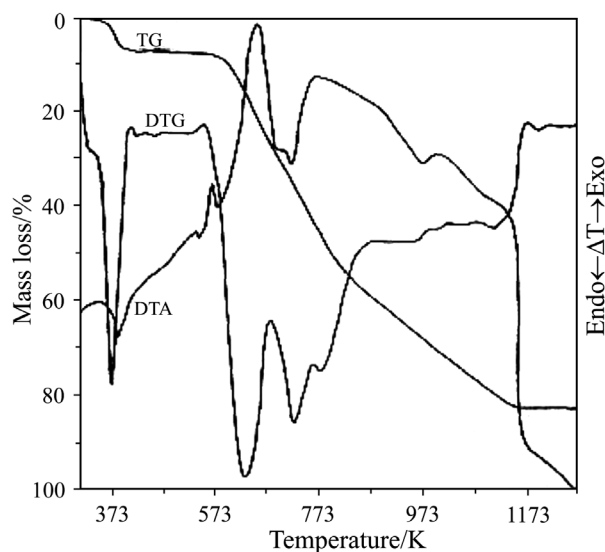


Fig. 1 TG, DTG and DTA curves of  $\text{Y}(\text{C}_9\text{H}_9\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$

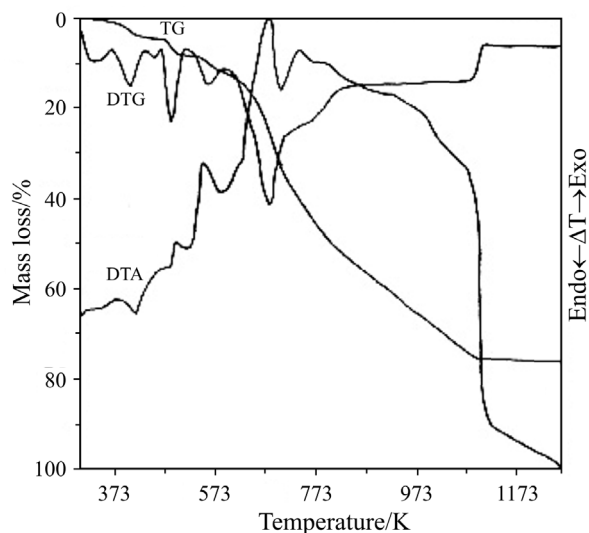


Fig. 2 TG, DTG and DTA curves of  $\text{Ce}(\text{C}_9\text{H}_9\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$

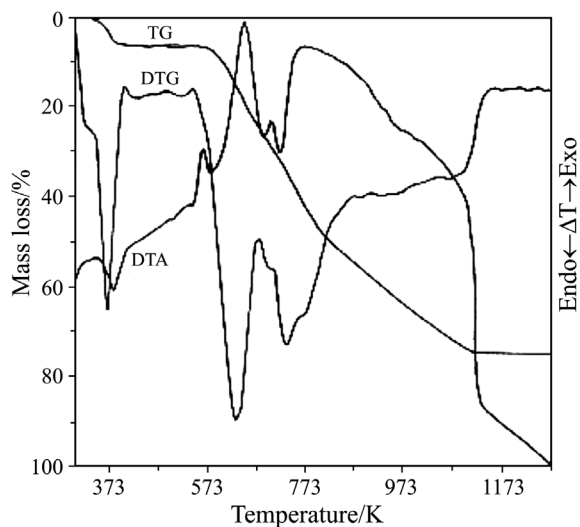


Fig. 3 TG, DTG and DTA curves of  $\text{Er}(\text{C}_9\text{H}_9\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$

( $T_1$ ) and of the beginning of decomposition ( $T_2$ ) change insignificantly with increasing atomic number  $Z$  of the metal (Table 3, Fig. 5). The temperature of the beginning of decomposition for the heaviest rare earth complexes (Tm–Lu) having the smallest ionic radius attain the highest value (563 K). The temperatures over which oxides ( $T_K$ ) exist change irregularly in the lanthanide series:  $\text{Yb}_2\text{O}_3$  forms at the lowest temperature (1078 K) and  $\text{Y}_2\text{O}_3$  at the highest (1173 K). Generally  $\text{La}_2\text{O}_3$  obtained by decomposition of the complexes with different organic ligands forms at the highest temperature [6–9].

Comparing the obtained results with the properties of rare earth elements with 4-methoxy-2-methylbenzoates [2] it is possible to state that the change of position of  $\text{CH}_3$  and  $\text{OCH}_3$  groups in benzene ring in relation to carboxylate group influences on number of crystallization water molecules, mode of coordination of  $\text{OCO}^-$  group, the position of asymmetric and symmetric vibration bands of carboxylate group in their IR spectra and the temperature over the oxides exist (the  $T_K$  for 3-methoxy-4-methylbenzoates are higher than for 4-methoxy-2-methylbenzoates of suitable elements).

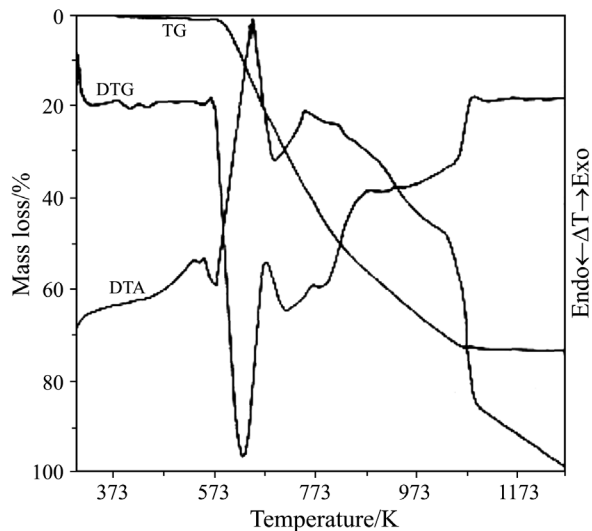


Fig. 4 TG, DTG and DTA curves of  $\text{Lu}(\text{C}_9\text{H}_9\text{O}_3)_3$

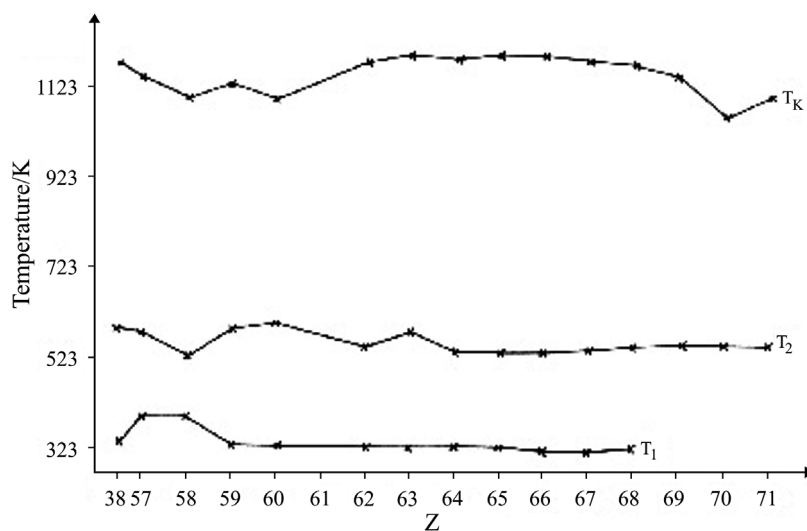


Fig. 5 Relationship between  $T_1$ ,  $T_2$ ,  $T_K$  and  $Z$

**Table 3** Thermoanalytical data of Y(III) and lanthanide(III) 3-methoxy-4-methylbenzoates

Complex	$\Delta T_1/\text{K}$	Mass loss/%		$n\text{H}_2\text{O}$ mol	$\Delta T_2/\text{K}$	Mass loss/%		$T_k/\text{K}$
		calcd.	found			calcd.	found	
$\text{YL}_3 \cdot 2\text{H}_2\text{O}$	333–403	5.80	5.8	2	558–1173	80.65	80.6	1173
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	363–508	5.37	5.5	2	553–1133	74.29	74.0	1133
$\text{CeL}_3 \cdot 2\text{H}_2\text{O}$	363–413	2.68	2.7	1	523–1113	72.89	73.0	1113
	465–503	2.68	2.7	1				
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	343–413	5.35	5.3	2	558–1128	73.23	73.0	1128
$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$	343–413	5.33	5.3	2	563–1113	73.68	74.0	1113
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	343–413	5.28	5.2	2	538–1153	72.98	73.0	1153
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	343–413	5.27	5.3	2	553–1158	72.80	72.6	1158
$\text{GdL}_3 \cdot 2\text{H}_2\text{O}$	343–413	5.23	5.2	2	533–1153	72.21	72.0	1153
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	342–413	5.21	5.2	2	533–1158	71.41	71.4	1158
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	323–400	5.20	5.2	2	533–1158	71.63	71.6	1158
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	323–400	5.20	5.2	2	543–1153	71.36	71.3	1153
$\text{ErL}_3 \cdot 2\text{H}_2\text{O}$	333–398	5.15	5.1	2	553–1153	71.12	71.1	1153
$\text{TmL}_3$	–	–	–	–	563–1118	70.89	71.0	1118
$\text{YbL}_3$	–	–	–	–	563–1076	70.50	70.5	1078
$\text{LuL}_3$	–	–	–	–	563–1108	70.30	70.3	1108

\*L –  $[\text{C}_6\text{H}_3(\text{OCH}_3)(\text{CH}_3)\text{COO}]^-$

$\Delta T_1$  – temperature range of dehydration

$\Delta T_2$  – temperature range of decomposition to oxides

$T_k$  – temperature over which oxides exist

## Conclusions

3-Methoxy-4-methylbenzoates of rare earth element(III) (Y, La–Lu) were prepared as crystalline solids with molar ratio of metal to organic ligand of 1.0:3.0. Complexes of Y(III), La(III) to Er(III) were prepared as dihydrates, whereas the complexes of Tm–Lu as anhydrous ones. The prepared complexes are sparingly soluble in water (their solubility is of the order  $10^{-4}$  mol dm<sup>-3</sup>). They are stable in air at room temperature. During heating the hydrated complexes lose crystallization water in one (Y, La, Pr–Er) or two (Ce) steps. All the anhydrous complexes heated decompose directly to oxides ( $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Tb}_4\text{O}_7$ ). The temperatures over which exist oxides changes irregularly in the lanthanide series. The yttrium oxide have the highest formation temperature (1173 K), while the ytterbium oxide has the lowest one (1078 K). The carboxylate group in the studied complexes acts probably as bidentate chelating and the water is inner sphere of the complexes.



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