

## NEW COMPLEXES OF RARE EARTH ELEMENTS WITH 3-METHYLADIPIC ACID

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### Abstract

Rare earth element 3-methyladipates were prepared as crystalline solids with general formula  $\text{Ln}_2(\text{C}_7\text{H}_{10}\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ , where  $n=6$  for La,  $n=4$  for Ce, Sm–Lu,  $n=5$  for Pr, Nd and  $n=5.5$  for Y. Their solubilities in water at 293 K were determined ( $2 \cdot 10^{-3}$ – $1.5 \cdot 10^{-4}$  mol dm<sup>-3</sup>). The IR spectra of the prepared complexes suggest that the carboxylate groups are bidentate chelating. During heating the hydrated 3-methyladipates lose all crystallization water molecules in one (Ce–Lu) or two steps (Y) (except of La(III) complex which undergoes to monohydrate) and then decompose directly to oxides (Y, Ce) or with intermediate formation of oxocarbonates  $\text{Ln}_2\text{O}_2\text{CO}_3$  (Pr–Tb) or  $\text{Ln}_2\text{O}(\text{CO}_3)_2$  (Gd–Lu). Only La(III) complex decomposes in four steps forming additionally unstable  $\text{La}_2(\text{C}_7\text{H}_{10}\text{O}_4)(\text{CO}_3)_2$ .

**Keywords:** complexes, IR spectra, 3-methyladipic acid, thermal analysis

### Introduction

3-Methyladipic acid  $\text{C}_7\text{H}_{10}(\text{COOH})_2$  is a crystalline solid soluble in water, ether, acetone, chloroform and acetic acid, sparingly soluble in benzene, toluene and xylene, and practically insoluble in petroleum benzin [1]. The salts of Na(I) and K(I) [1, 2] are solid soluble in water, whereas the complexes of Cu(II), Ag(I) and Ba(II) are sparingly soluble in water [1]. Ikeda *et al.* [3] determined the stability constants of rare earth element 3-methyladipates by potentiometric method. The stability constants of 3-methyladipates are smaller than those of adipates. The complexes of rare earth elements in solid state has not been prepared.

The aim of our work was to prepare the complexes of Y(III) and lanthanides(III) with 3-methyladipic acid in solid under the same conditions and to study their properties and thermal decomposition in air.

### Experimental

The complexes of Y(II) and lanthanide(III) from La to Lu (except of Pm) were prepared by adding stoichiometric quantities of 0.1 M solution of ammonium 3-methyl-

adipate (pH 5.5) to a hot solution of separated lanthanide chlorides (cerium(III) was used as nitrate). The precipitate formed was heated in mother solution for 0.5 h and then was filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass. The carbon and hydrogen in the prepared complexes were determined by elemental analysis on a Perkin Elmer CHN 2400 analyser. The number of crystallization water molecules was determined from TG curves and by isothermal heating the hydrated complexes at define temperature. The experimental data confirm the calculated data (Table 1). The IR spectra of the complexes and spectra of 3-methyladipic acid and its sodium salt were recorded as KBr discs on a Specord M-80 spectrophotometer ( $4000\text{--}400\text{ cm}^{-1}$ ). The solubility of rare earth complexes was determined by measuring the concentration of lanthanide(III) ions in saturated (under isothermal conditions) solution by spectroscopic method using arsenazo(III). Thermal stability of the prepared complexes were investigated by TG, DTA and DTG curves. Measurements were made with a Q-1500 D derivatograph by method described in [4]. The products of decomposition were calculated from TG curve and verified by diffractogram registration. The activation energy of decomposition was determined by using Pletniev and Fotiyev method [5].

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

Complex	M%		C%		H%		Solubility/ $10^{-4}\text{ mol dm}^{-3}$	$E_a$ / $\text{kJ mol}^{-1}$
	calc.	found	calc.	found	calc.	found		
$\text{Y}_2\text{L}_3\cdot 5.5\text{H}_2\text{O}$	23.68	23.6	33.56	34.0	5.46	5.6	3.2	38.9
$\text{La}_2\text{L}_3\cdot 6\text{H}_2\text{O}$	32.30	32.4	29.30	30.0	4.48	4.4	20.9	31.8
$\text{Ce}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	33.90	33.8	30.51	29.9	4.49	4.7	20.0	36.3
$\text{Pr}_2\text{L}_3\cdot 5\text{H}_2\text{O}$	33.30	33.0	29.78	29.9	4.73	4.7	13.0	36.1
$\text{Nd}_2\text{L}_3\cdot 5\text{H}_2\text{O}$	33.81	33.6	29.60	30.0	4.60	4.6	7.2	37.6
$\text{Sm}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	35.50	35.1	29.79	29.8	4.50	4.4	3.5	37.6
$\text{Eu}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	35.76	36.0	29.63	29.8	4.47	4.4	2.3	38.1
$\text{Gd}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	36.53	36.4	29.27	29.2	4.41	4.4	2.4	31.8
$\text{Tb}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	36.80	36.6	29.16	29.2	4.40	4.4	1.5	33.7
$\text{Dy}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	37.31	37.5	28.93	29.1	4.36	4.4	2.1	30.0
$\text{Ho}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	37.61	37.5	28.76	28.9	4.34	4.3	2.0	32.0
$\text{Er}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	37.95	38.2	28.63	28.6	4.30	4.2	2.2	32.4
$\text{Tm}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	38.52	39.0	28.51	28.7	4.28	4.2	2.5	35.8
$\text{Y}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	38.78	38.6	28.24	28.4	4.26	4.2	3.8	35.9
$\text{Lu}_2\text{L}_3\cdot 4\text{H}_2\text{O}$	39.04	39.1	28.11	28.3	4.24	4.2	3.9	37.3

$L = \text{C}_3\text{H}_{10}\text{O}_4^{2-}$

$E_a$  – activation energy of dehydration reaction

## Results and discussion

3-Methyladipates of Y(III) and lanthanide(III) from La to Lu (without Pm) were prepared as crystalline solids with colour characteristic of lanthanide(III) ions and with molar ratio of metal to organic ligand of 2.0 : 3.0 and general formula  $Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$ , where  $n=4$  for Ce, Sm–Lu,  $n=5$  for Pr and Nd,  $n=5.5$  for Y and  $n=6$  for La (Table 1). The prepared complexes are characterised by low symmetry and diversity of their structure. 3-Methyladipates are isostructural in the groups Pr–Nd and Eu–Lu [6].

3-Methyladipates of rare earth are sparingly soluble in water. Their solubility is of the order  $10^{-3}$ – $10^{-4}$  mole  $dm^{-3}$  and changes (Table 1) from  $1.51 \cdot 10^{-4}$  mole  $dm^{-3}$  for Tb to  $3.80 \cdot 10^{-3}$  mol  $dm^{-3}$  for Y. Generally, it is possible to state, that solubility of lanthanide complexes decreases from La to Tb and then increases to Lu.

All the prepared complexes exhibit similar solid state IR spectra (Table 2). When the acid is converted to the salt, the stretching vibration of C=O group,  $\nu(C=O)$  in COOH at  $1700\text{ cm}^{-1}$  disappears, whereas the bands of asymmetric vibrations  $\nu_{as}(OCO)$  at  $1540$ – $1552\text{ cm}^{-1}$  and the bands of symmetric vibration  $\nu_s(OCO)$  at  $1412\text{ cm}^{-1}$  (La–Nd) and  $1440$ – $1450\text{ cm}^{-1}$  (Y, Sm–Lu) appear.

**Table 2** Frequencies of characteristic bands in IR spectra of Na(I) and rare earth(III) 3-methyladipates

Complex	$\nu(OH)$	$\delta(H_2O)$	$\nu_{as}(OCO)$	$\nu_s(OCO)$	$\nu_{as}-\nu_s$
$Y_2L_3 \cdot 5.5H_2O$	3352	1650	1552	1448	104
$La_2L_3 \cdot 6H_2O$	3432	1630	1540	1412	128
$Ce_2L_3 \cdot 4H_2O$	3416	1630	1552	1412	140
$Pr_2L_3 \cdot 5H_2O$	3329	1640	1544	1412	132
$Nd_2L_3 \cdot 5H_2O$	3352	1650	1548	1412	136
$Sm_2L_3 \cdot 4H_2O$	3360	1650	1552	1440	112
$Eu_2L_3 \cdot 4H_2O$	3368	1650	1552	1444	108
$Gd_2L_3 \cdot 4H_2O$	3360	1650	1552	1450	102
$Tb_2L_3 \cdot 4H_2O$	3392	1650	1552	1444	108
$Dy_2L_3 \cdot 4H_2O$	3352	1650	1548	1444	102
$Ho_2L_3 \cdot 4H_2O$	3352	1650	1552	1448	104
$Er_2L_3 \cdot 4H_2O$	3360	1650	1552	1448	104
$Tm_2L_3 \cdot 4H_2O$	3344	1650	1552	1448	104
$Yb_2L_3 \cdot 4H_2O$	3344	1650	1552	1450	102
$Lu_2L_3 \cdot 4H_2O$	3344	1650	1552	1450	102
$Na_2L$	3424	1650	1568	1408	160



In the IR spectra of the prepared complexes there are broad absorption bands of  $\nu(\text{OH})$  with max. at  $3344\text{--}3432\text{ cm}^{-1}$  and narrow bands of  $\delta(\text{H}_2\text{O})$  at  $1630\text{--}1650\text{ cm}^{-1}$  confirming the presence of water molecules linked by hydrogen bonds, the bands of  $\text{CH}_3$  vibrations at  $2960, 2930\text{ cm}^{-1}$  and  $1164\text{--}1172\text{ cm}^{-1}$ , the bands of C–H vibrations at  $1330\text{--}1350\text{ cm}^{-1}, 1100, 900\text{--}700\text{ cm}^{-1}$ . The splitting for the absorption bands of valency vibrations  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  ( $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ ) in the IR spectra of La–Nd complexes have values  $128\text{--}140\text{ cm}^{-1}$  and those of Sm–Lu and Y are smaller and amount  $102\text{--}112\text{ cm}^{-1}$ . The values of  $\Delta\nu$  of the prepared complexes are smaller than for the sodium salt ( $\Delta\nu = 160\text{ cm}^{-1}$ ) suggesting a smaller degree of ionic bond character in these complexes compared to the sodium salt. Similarly, in the complexes of heavy lanthanide 3-methyladipates the degree of ionic bond is smaller than in the light lanthanide complexes, which is connected with the decrease of the part of the ionic bond with increasing the atomic number  $Z$  of metal and the contraction effect. The bands of  $\nu_{\text{as}}(\text{OCO})$  in the IR spectra of the prepared complexes are shifted to lower frequencies ( $\Delta\nu = 16\text{--}28\text{ cm}^{-1}$ ) and the  $\nu_{\text{s}}(\text{OCO})$  to higher frequencies ( $\Delta\nu = 4\text{--}42\text{ cm}^{-1}$ ). On the basis of spectroscopic criteria [7–8] and our previous work [9, 10] it is possible to suggest that the carboxylate groups are bidentate chelating. Taking into account the high value of the coordination number characteristic of lanthanides (CN=9 for light element and CN=8 for heavy ones) it can suggest that the water molecules are probably in the inner and outer sphere of the complexes, but the coordinated and uncoordinated water molecules are not distinguished by thermogravimetric curve. Full interpretation of the mode of coordination of metal–ligand would be possible after the determination of the crystallographic and molecular structure of the monocrystals, but they have not been obtained so far.

The prepared 3-methyladipates are stable at room temperature and can be stored for several months without change. During heating in air they decompose in two, three or four steps. (Table 3, Figs 1–3). The hydrated 3-methyladipates are stable up to  $273\text{--}378\text{ K}$  and on further heating they are dehydrated in one step (without Y, which is dehydrated in two steps) forming anhydrous complexes stable up to  $513\text{--}593\text{ K}$ . The lanthanum complex loses 5 water molecules forming monohydrate, which is dehydrated and decomposed simultaneously. The dehydrating process is connected with strong endothermic effect at  $393\text{--}418\text{ K}$  (for Y at  $418$  and  $473\text{ K}$ ). The anhydrous 3-methyladipates heated decompose in different ways over the range  $493\text{--}1088\text{ K}$ . On heating the anhydrous complexes of Pr(III)–Eu(III) decompose over the range  $513\text{--}558\text{ K}$  to  $903\text{--}1033\text{ K}$  to oxides  $\text{Ln}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  with intermediate formation oxocarbonates  $\text{Ln}_2\text{O}_2\text{CO}_3$ . The anhydrous complexes of Gd–Lu then heated decompose over the range  $683\text{--}1013\text{ K}$  to oxides  $\text{Ln}_2\text{O}_3$  and  $\text{Tb}_4\text{O}_7$  with intermediate formation oxocarbonates  $\text{Ln}_2\text{O}(\text{CO}_3)_2$ . The anhydrous complex of Y(III) and Ce(III) decomposes over the range  $493\text{--}972\text{ K}$  directly to oxides  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$ . Lanthanum(III) 3-methyladipate monohydrate decomposes to oxide  $\text{La}_2\text{O}_3$  with intermediate formation unstable  $\text{La}_2\text{L}(\text{CO}_3)_2$  (probably) and  $\text{La}_2\text{O}(\text{CO}_3)_2$ . The combustion of organic ligand and products of decomposition are connected with a strong exothermic effect at  $483\text{ K}$  (Ce) to  $753\text{ K}$  (Nd). The decomposition of oxocarbonates is accompanied by endothermic effect at  $691\text{ K}$  (Lu) to  $1023\text{ K}$  (Nd).

**Table 3** Thermoanalytical data of Y(III) and lanthanide(III) 3-methyadipates

Complex	$\Delta T_1/K$	Mass loss/%		$n$ H <sub>2</sub> O	$\Delta T_2/K$	Mass loss/%		$\Delta T_3/K$	Mass loss/%		$T_K/K$
		calc.	found			calc.	found		calc.	found	
Y <sub>2</sub> L <sub>3</sub> ·5.5H <sub>2</sub> O	273–428	9.58	9.5	4				523–978	69.90	70	978
	463–483	13.17	13.0	1.5							
La <sub>2</sub> L <sub>3</sub> ·6H <sub>2</sub> O	333–423	10.46	10.5	5	533–783	51.98	52	993–1088	62.12	62	1088
Ce <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	358–412	8.70	9.0	4				493–833	58.32	58	833
Pr <sub>2</sub> L <sub>3</sub> ·5H <sub>2</sub> O	343–418	10.80	10.6	5	558–813	57.00	56	998–1033	62.30	62	1033
Nd <sub>2</sub> L <sub>3</sub> ·5H <sub>2</sub> O	368–438	10.55	10.5	5	543–813	55.40	55	948–1058	60.61	61	1058
Sm <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	368–438	8.52	8.5	4	513–828	53.68	54	883–913	58.90	60	913
Eu <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	378–443	8.46	8.5	4	528–798	53.45	54	868–903	58.72	59	903
Gd <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	363–443	8.36	8.3	4	548–663	47.68	48*	688–893	57.26	58	893
Tb <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	378–441	8.33	8.3	4	573–668	47.49	47*	693–913	56.75	57	913
Dy <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	378–433	8.27	8.5	4	583–668	47.10	47*	703–998	57.18	57	998
Ho <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	378–433	8.21	8.0	4	598–663	46.80	46*	703–1013	56.84	57	1013
Er <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	378–433	8.17	8.0	4	593–653	46.59	47*	683–1008	56.59	56	1008
Tm <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	368–428	8.14	8.0	4	593–658	46.42	47*	673–1005	56.33	56	1005
Yb <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	348–413	8.08	8.0	4	558–658	45.98	46*	678–793	55.84	56	793
Lu <sub>2</sub> L <sub>3</sub> ·4H <sub>2</sub> O	358–413	8.03	8.0	4	583–673	45.80	46*	693–793	55.60	56	793

$\Delta T_1$  – temperature range of dehydration

$\Delta T_2$  – temperature range of decomposition to Ln<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> or \* to Ln<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub>

$\Delta T_3$  – temperature range of decomposition to oxides Ln<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Tb<sub>4</sub>O<sub>7</sub>

$T_K$  – temperature of oxide formation

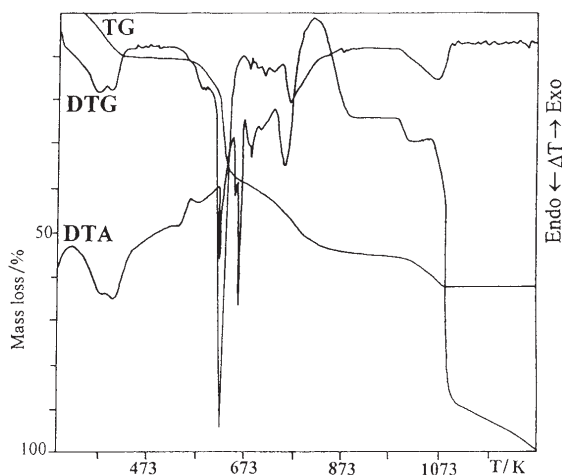


Fig. 1 TG, DTG and DTA curves of  $\text{La}_2(\text{C}_5\text{H}_{10}\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$

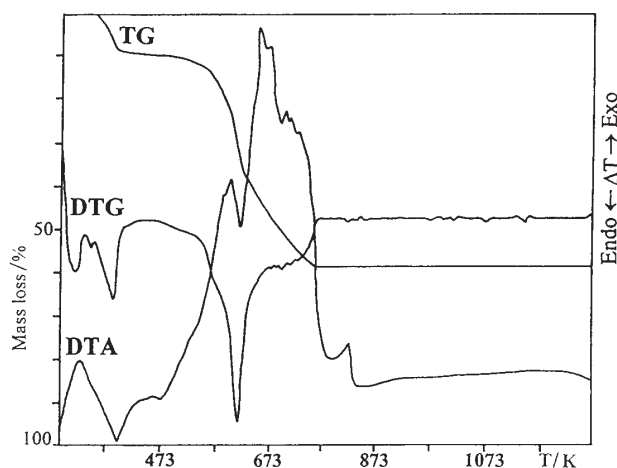
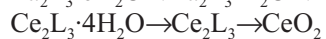
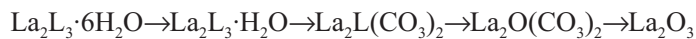


Fig. 2 TG, DTG and DTA curves of  $\text{Ce}_2(\text{C}_5\text{H}_{10}\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$

The results indicate, that the prepared complexes decompose in the following way:



The temperatures of dehydration ( $T_0$ ) of different lanthanide complexes are similar to each other and change insignificantly in the lanthanide series (Fig. 3) from 333–378 K. Only Y(III) complex begins to lose crystallization water molecules at

273 K. Temperatures of decomposition ( $T_D$ ) change in the lanthanide series from 493 for Ce(III) to 538 K for Ho(III). Temperature of oxide formation ( $T_K$ ) change periodically in the lanthanide series. Neodymium oxide is formed at the highest temperature (1058 K), whereas CeO<sub>2</sub> at the lowest one (833 K). The temperatures of oxide formation for Dy (998 K) to  $T_m$  (1005 K) are similar to each other and for the last lanthanides (Yb and Lu) violently decreases to 783 K and 793 K, respectively. The tem-

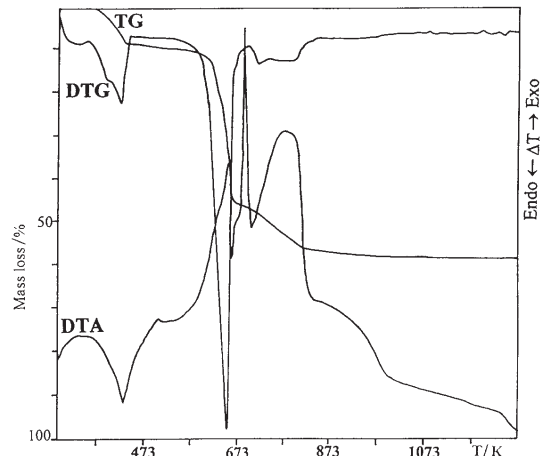


Fig. 3 TG, DTG and DTA curves of  $H_2(C_5H_{10}O_4)_3 \cdot 4H_2O$

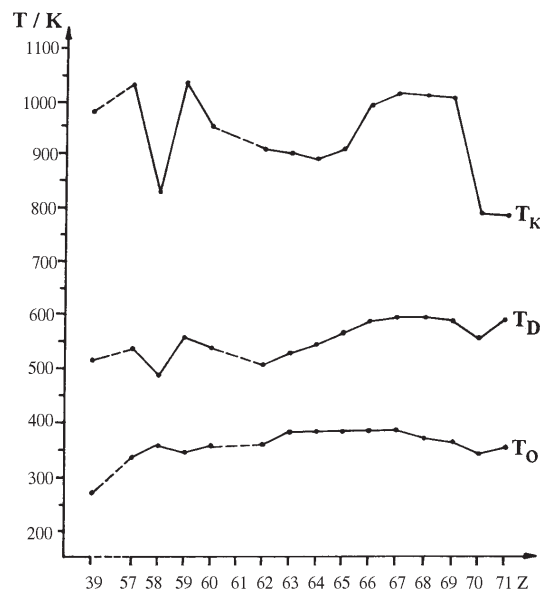


Fig. 4 The relationship between  $T_0$ ,  $T_D$ ,  $T_K$  and  $Z$  of Ln(III)

perature of  $Y_2O_3$  formation (978 K) is similar to those of heavy lanthanide oxide formation, which is connected with the contraction effect and similarity of the ionic radii. The temperature of  $CeO_2$  formation almost always has the lowest value in the lanthanide series [9, 10].

The activation energy of the dehydration reaction for the prepared complexes (Table 1) has similar values from 30.0 to 38.9  $\text{kJ mol}^{-1}$  and changes irregularly in the lanthanide series, which indicates on the similar energy of bonding the water molecules in the prepared complexes.

## Conclusions

Complexes of Y(III) and lanthanide(III) with 3-methyladipic acid were prepared as solids with a molar ratio of metal to organic ligand of 2:3, sparingly soluble in water. The carboxylate groups in the complexes are bidentate chelating. The oxygen atoms of the carboxylate groups are not only coordinated to metal ion, but they linked with hydrogen bonds to the water of crystallization. The water molecules are probably in inner and outer coordination sphere. During heating the hydrated complexes lose all water molecules in one step except for Y(III) complex, which is dehydrated in two steps and La(III) complex, which loses 5 water molecules transforming to the monohydrate. Next, the complexes heated decompose to oxides directly (Y Ce) or with intermediate formation of oxocarbonates  $\text{Ln}_2\text{O}_2\text{CO}_3$  (Pr–Eu) or  $\text{Ln}_2\text{O}(\text{CO}_3)_2$  (Gd–Lu). Only La(III) complex decomposes to oxide  $\text{Ln}_2\text{O}_3$  in four steps forming  $\text{La}_2\text{L}(\text{CO}_3)_2$  additionally. The temperature of oxide formation changes in the lanthanide series from 833 K for cerium(III) complex to 1058 K for neodymium(III) one.

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