

## **THERMAL DECOMPOSITION OF RARE EARTH SALICYLATES IN AIR ATMOSPHERE**

*W. Brzyska and A. Kula*

DEPARTMENT OF INORGANIC AND GENERAL CHEMISTRY, INSTITUTE OF CHEMISTRY, MARIE CURIE SKŁODOWSKA UNIVERSITY, 20-031 LUBLIN, POLAND

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The conditions of decomposition of Y, La and lanthanide (from Ce(III) to Lu) salicylates have been studied. On heating, the hydrated salicylates of Y and lanthanides from Nd to Lu lose crystallization water in one step to yield the anhydrous salts. The anhydrous complexes of Y, La, Ce(III), Pr, Nd, Sm, Eu(III), Gd and Tb subsequently decompose in several steps to the oxides  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$ . The anhydrous complexes of the remaining lanthanides decompose directly to the oxides  $\text{Ln}_2\text{O}_3$ .

The structures of some rare earth complexes with salicylic acid have been investigated by spectroscopic [1-15] and X-ray [15] methods by many authors. The proposed composition of the complexes is, in general,  $\text{Ln}(\text{C}_6\text{H}_4\text{OHCOO})_3$  [1-7], except in the work of Kanekar et al. [8], who suggested that the formula for the ytterbium complex is  $\text{Yb}_2(\text{C}_6\text{H}_4\text{OCOO})_3$ . Lewandowska et al. [16] have prepared complexes of Y, La and all lanthanides except promethium with the general formula  $\text{Ln}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot n\text{H}_2\text{O}$  ( $n$  is not given). Some authors [1-4, 9, 10, 14] are of the opinion that the lanthanide-salicylate bond is formed by replacing the proton from the COOH group only, whereas others [5, 8] have suggested that both the carboxylic and the phenolic groups are involved. Sinha and Irving [3] have suggested the formation of a coordination bond between the central ion and the oxygen of the phenolic group. The bonding mode between the central ion and the carboxylic group can be monodentate [12] or simultaneously monodentate and bidentate [9]. According to Kanekar [8], the salicylic anion behaves as a tridentate ligand and the coordination number of  $\text{Ln}^{3+}$  is 9. Burns and Baldwin [14] have investigated the crystal structure of samarium salicylate,  $\text{Sm}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$ . The X-ray data indicate that both the carboxylic and the phenolic oxygen atoms participate in the coordination. Thus, there is no uniform opinion concerning the structures of these rare earth complexes.

The thermal decompositions of Y, La and Nd salicylate hydrates [4, 17] have been studied. It was found that dehydration takes place in the range 313–433 K, and decomposition at 433–1023 K [17].

Systematic studies on the thermal decompositions of rare earth complexes with salicylic acid have not been reported.

The aim of our work was to obtain rare earth complexes with salicylic acid in the solid state and to study their thermal decompositions on heating in air atmosphere.

## Experimental

The complexes of Y, La and lanthanides (from Ce(III) to Lu) with salicylic acid were prepared by adding an equivalent amount of a saturated solution of ammonium salicylate to a hot solution of the rare earth chloride (Ce(III) was used as nitrate). The precipitate formed was heated in the mother liquor for 0.5 h, then filtered off, washed with hot water to remove  $\text{NH}_4^+$  ions and dried to constant weight at 303 K. The rare earth salicylates were prepared as crystalline solids with the weak colours characteristic of the  $\text{Ln}^{3+}$  ions.

The compositions of the prepared complexes were established on the basis of elemental analysis. The contents of carbon and hydrogen were determined by elemental analysis, with  $\text{V}_2\text{O}_5$  as oxidizing agent. The contents of rare earth

**Table 1** Analytical data

Complex	H, %		C, %		M, %	
	calcd.	found	calcd.	found	calcd.	found
$\text{Y}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot 4\text{H}_2\text{O}$	4.05	4.44	44.07	44.26	15.53	15.74
$\text{La}(\text{C}_6\text{H}_4\text{OHCOO})_3$	2.74	2.90	45.84	46.30	25.24	24.72
$\text{Ce}(\text{C}_6\text{H}_4\text{OHCOO})_3$	2.74	3.24	45.73	45.29	25.40	25.01
$\text{Pr}(\text{C}_6\text{H}_4\text{OHCOO})_3$	2.73	3.03	45.47	45.93	25.51	24.58
$\text{Nd}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.98	3.79	43.97	43.05	25.14	24.85
$\text{Sm}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.95	3.41	43.50	43.14	25.94	25.44
$\text{Eu}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.94	3.40	43.39	42.60	26.14	25.90
$\text{Gd}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.92	3.04	43.00	43.30	26.80	26.88
$\text{Tb}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.91	3.17	42.87	41.99	27.02	26.93
$\text{Dy}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.89	3.25	42.61	42.05	27.45	27.44
$\text{Ho}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot \text{H}_2\text{O}$	2.88	2.91	42.44	41.97	27.75	27.93
$\text{Er}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot 4\text{H}_2\text{O}$	3.56	3.67	38.76	38.46	25.86	25.95
$\text{Tm}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot 4\text{H}_2\text{O}$	3.55	3.69	38.66	37.33	25.89	25.33
$\text{Yb}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot 4\text{H}_2\text{O}$	3.53	3.68	38.42	38.54	26.35	26.34
$\text{Lu}(\text{C}_6\text{H}_4\text{OHCOO})_3 \cdot 4\text{H}_2\text{O}$	3.67	3.75	38.31	38.03	26.57	25.94

elements were determined by ignition of the complexes to the oxides at 1173 K and from the TG curves. The contents of crystallization water were determined from the TG curves and by heating the complexes at suitable temperatures. The results are given in Table 1.

The salicylates of La, Ce(III) and Pr(III) were prepared as anhydrous complexes, those of Nd, Sm, Eu(III), Gd, Tb, Dy and Ho as monohydrates, and those of Er, Tm, Yb, Lu and Y as tetrahydrates, with a molar ratio of metal to ligand of 1 : 3.

The IR spectra of salicylic acid and the complexes were recorded over the range 4000–400  $\text{cm}^{-1}$ . Analysis of the IR spectra confirmed the elemental analysis data. When the acid is converted to a salt, the absorption band of the COOH group at 1655  $\text{cm}^{-1}$  disappears and the absorption bands of asymmetric and symmetric vibrations of the COO<sup>-</sup> group appear at 1590–1560  $\text{cm}^{-1}$  and 1400–1380  $\text{cm}^{-1}$ , with the absorption band of the metal-oxygen bond at 490–470  $\text{cm}^{-1}$ . In the spectra of the hydrated salicylates a strong broad absorption band is observed with maximum at 3420–3320  $\text{cm}^{-1}$ , and a sharp band at 1620–1600  $\text{cm}^{-1}$ , which confirm the presence of crystallization water. In the spectra of salicylic acid and of the prepared salicylates, the absorption band of the phenolic group is present at 1480  $\text{cm}^{-1}$ , which indicates that the OH group does not take part in coordination to the metal ion. The IR spectra of all lanthanide salicylates have been studied in detail by Lewandowska et al. [16]. Our results are comparable to those obtained by Lewandowska.

The thermal stabilities and decomposition products of the rare earth complexes were studied on heating in air atmosphere. On OD-102 derivatograph was used to record the TG, DTG and DTA curves. The samples were heated in ceramic crucibles at a heating rate of 9  $\text{deg}/\text{min}^{-1}$ . The decomposition products were determined from the derivatographic curves and by recording IR spectra. The results are presented in Figs 1–3 and Tables 2–4.

## Results

The results demonstrated that the anhydrous salicylates of La, Ce(III) and Pr are stable up to 448–463 K. On heating, they decompose in several steps. During the decompositions of the La and Ce(III) complexes, the unstable products  $\text{Ln}_2(\text{C}_6\text{H}_4\text{OCOO})_3$  and  $\text{Ln}_4\text{O}_3(\text{C}_6\text{H}_4\text{OCOO})_3$  formed; the cerium intermediates decomposed directly to  $\text{CeO}_2$ , whereas those of lanthanum gave  $\text{La}_2\text{O}_3$  via the intermediate formation of  $\text{La}_2\text{O}_2\text{CO}_3$ , which was stable in the range 843–963 K (Fig. 1, a, b, c, Tables 2 and 3).

The monohydrated salicylates of Nd, Sm(III), Eu(III), Gd, Tb, Dy and Ho and the tetrahydrated salicylates of Er, Tm, Yb, Lu and Y are fully dehydrated in one

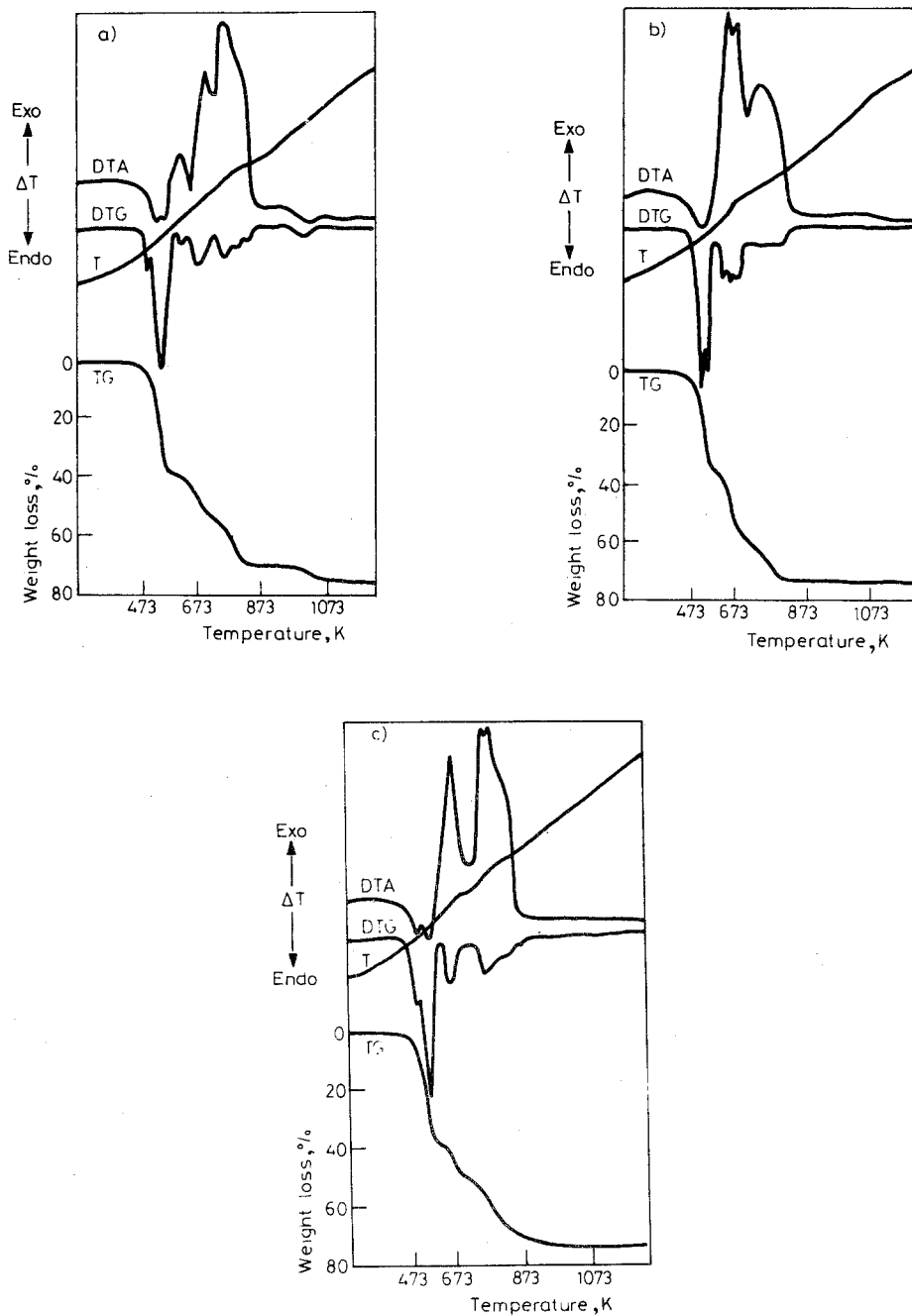


Fig. 1 TG, DTG and DTA curves of salicylate of: a) La, b) Ce(III), c) Pr(III)

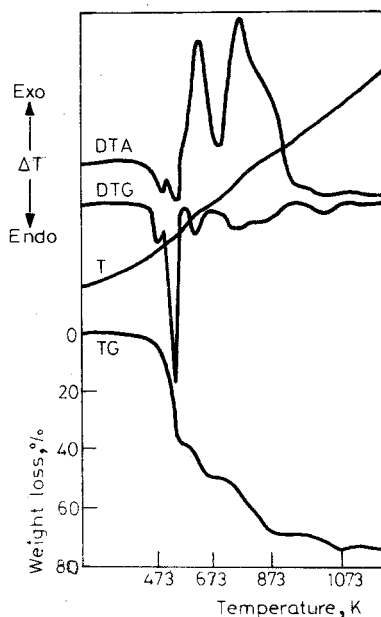


Fig. 2 TG, DTG and DTA curves of Nd salicylate

step in the range 313–493 K to the accompaniment of an endothermic effect. The anhydrous salicylates of Nd and Sm are very unstable, whereas those of the remaining rare earth are stable in the range 408–493 K. The stability range differs for the complexes of the various rare earth elements.

When heated, the anhydrous salicylates of Y, Pr, Sm(III), Gd and Tb decompose to  $\text{Ln}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$ , with the intermediate formation of unstable  $\text{Ln}_2(\text{C}_6\text{H}_4\text{OCOO})_3$  and  $\text{Ln}_2\text{O}(\text{C}_6\text{H}_4\text{OCOO})_2$ . Anhydrous neodymium salicylate decomposes to  $\text{Nd}_2\text{O}_3$ , with the intermediate formation of unstable  $\text{Nd}_2(\text{C}_6\text{H}_4\text{OCOO})_3$ , and  $\text{Nd}_2\text{O}(\text{C}_6\text{H}_4\text{OCOO})_2$  and  $\text{Nd}_2\text{O}_2\text{CO}_3$ , whereas the europium complexes decomposes first to  $\text{Eu}_2\text{O}_2\text{CO}_3$ , and then to  $\text{Eu}_2\text{O}_3$ . On heating, the anhydrous salicylates of the heavy lanthanides Dy, Er, Tm, Yb and Lu decompose directly to  $\text{Ln}_2\text{O}_3$ .

The results permit the conclusion that the temperatures of complex dehydration and oxide formation vary periodically with increase of the atomic number of the metal. The hydrated salicylates of the heavy lanthanides from Er to Lu are less stable than those of the previous elements. The temperature of  $\text{CeO}_2$  formation is the lowest, and that of  $\text{La}_2\text{O}_3$  formation the highest.

The dehydration process is accompanied by an endothermic effect, and the ignition of the organic ligand by an exothermic one (Figs 1–3).

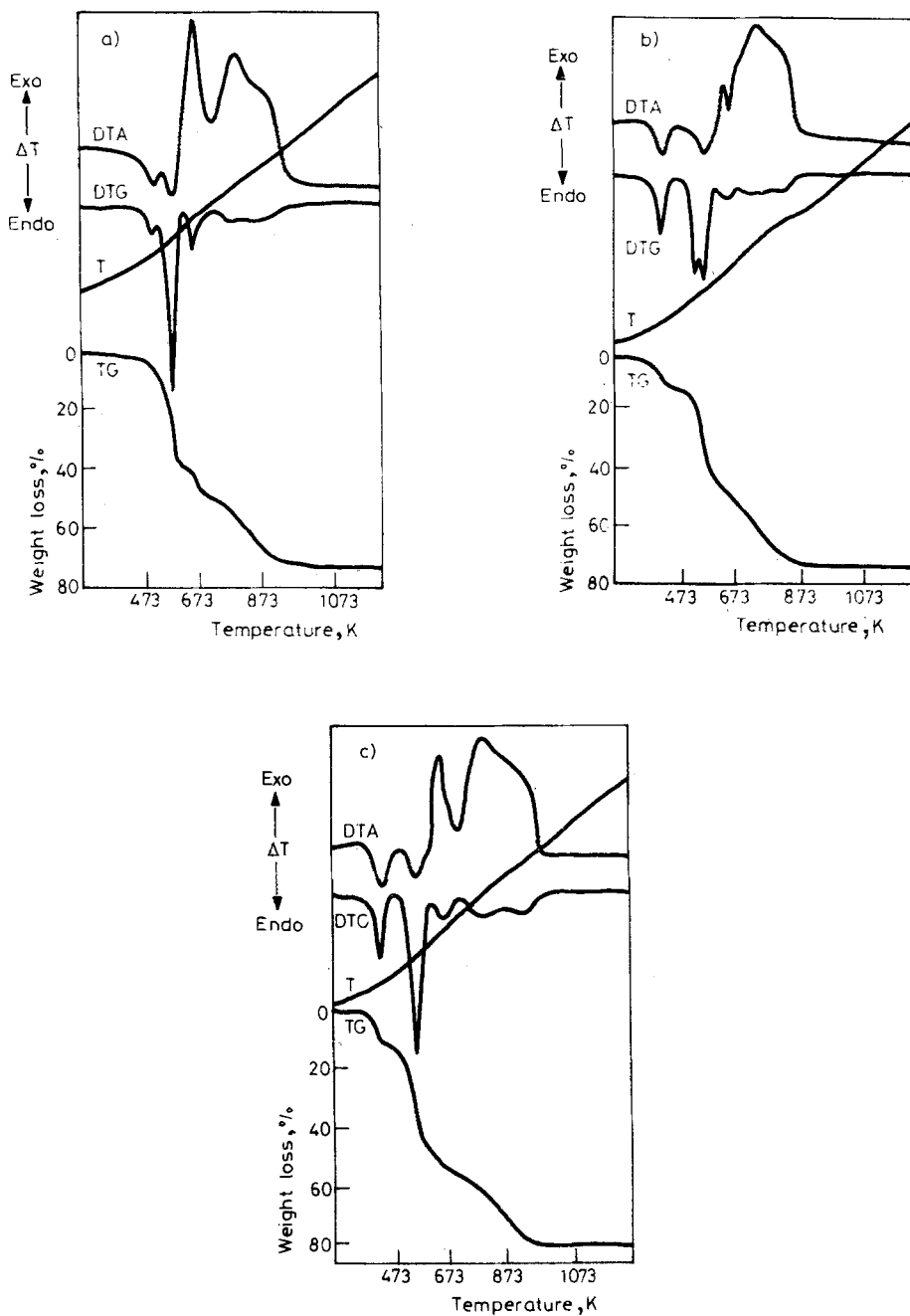


Fig. 3 TG, DTG and DTA curves of salicylate: a) Sm, b) Tm, c) Y

Table 2 Temperature range of thermal stability of Y, La and lanthanide salicylates and their stable decomposition products in air atmosphere

Ln	Ln(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>3</sub> · nH <sub>2</sub> O		Ln(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>3</sub>		Ln <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>		Ln <sub>2</sub> O <sub>3</sub> *	
	Temp. range, K	H <sub>2</sub> O, n	Temp. range, K	% calcd. found	Temp. range, K	% calcd. found	Temp. range, K	% calcd. found
Y	293-348	4	418-468	87.41 88.0			953	19.73 20.0
La			293-463		843-968	33.61 33.0	1123	29.41 29.0
Ce			293-458				803	31.22 30.5
Pr			293-448				983	30.83 30.5
Nd	293-448	1	448	96.86 96.5	893-968	33.68 34.0	973	29.34 29.0
Sm	293-453	1	493	96.89 96.5			913	30.08 29.5
Eu	293-423	1	473-483	96.91 97.0	863-895	31.89 32.0	933	30.28 30.0
Gd	293-431	1	468-478	96.93 97.0			931	30.91 31.0
Tb	293-433	1	473-493	96.94 97.0			918	31.10 31.0
Dy	293-428	1	473-483	96.96 97.0			913	31.80 31.5
Ho	293-418	1	458-473	96.97 97.0	833-878	35.49 35.5	943	31.80 32.0
Er	293-348	4	428-483	88.93 89.5			913	29.40 29.5
Tm	293-313	4	408-468	88.96 89.5			963	29.64 29.0
Yb	293-353	4	428-463	89.04 90.5			873	30.02 30.0
Lu	293-353	4	428-473	89.07 89.5			833	30.21 29.5

Ln<sub>2</sub>O<sub>3</sub>\* (Ln = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu) and CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>

**Table 3** The temperature range of formation of unstable intermediate products of Y, La and lanthanide salicylate decomposition

Ln	$\text{Ln}_2[\text{C}_6\text{H}_4(\text{O})\text{COO}]_3$			$\text{Ln}_2\text{O}[\text{C}_6\text{H}_4(\text{O})\text{COO}]_2$			$\text{Ln}_4\text{O}_3[\text{C}_6\text{H}_4(\text{O})\text{COO}]_3$		
	Temp., K	%		Temp., K	%		Temp., K	%	
		calcd.	found		calcd.	found		calcd.	found
Y	583	51.20	52.0	693	40.71	42.0			
La	573	62.34	62.0				733	45.97	46.0
Ce	573	62.43	63.0				693	46.09	45.0
Pr	578	62.48	61.0	683	51.60	51.5			
Nd	563	60.73	61.0	673	50.26	51.0			
Sm	583	61.16	61.5	673	50.79	51.0			
Gd	563	61.61	62.0	663	51.36	53.0			
Tb	573	61.72	63.0	693	51.51	52.5			

A comparison of the stabilities of the rare earth salicylates (2-hydroxybenzoates) with those of the 3-hydroxybenzoates reveals that the salicylates are less stable than the 3-hydroxybenzoates [18, 19] and the rare earth oxides are formed at lower temperatures. This is connected with the different position of the phenolic groups with respect to the carboxylic group, the different polarisation of the ligand, and the differences in bonding energy.

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**Zusammenfassung** — Die Zersetzungsreaktionsbedingungen von Y-, La- und Lanthanid-(Ce(III) bis Lu) salicylaten wurden untersucht. Beim Erhitzen geben hydrierte Salicylate von Y und der Lanthanide Nd bis Lu Kristallwasser in einem Schritt ab und bilden wasserfreie Salze. Die wasserfreien Komplexe von Y, La, Ce(III), Pr, Nd, Sm, Eu(III), Gd und Tb zersetzen sich in mehreren Schritten und bilden die Oxide  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  und  $\text{Tb}_4\text{O}_7$ . Die wasserfreien Komplexe der übrigen Lanthaniden zerfallen direkt in  $\text{Ln}_2\text{O}_3$  Oxide.

**Резюме** — Изучены условия разложения салицилатов иттрия, лантана и лантаноидов от трехвалентного церия до лютетия. Гидраты салицилатных комплексов иттрия и лантаноидов от неодима до лютетия при нагревании теряют кристаллизационную воду в одну стадию, давая при этом безводные соли. Безводные комплексы иттрия, лантана, трехвалентного церия, празеодима, неодима, самария, трехвалентного европия, гадолиния и тербия последовательно разлагаются в несколько стадий, давая окиси  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  и  $\text{Tb}_4\text{O}_7$ . Безводные комплексы оставшихся лантаноидов разлагаются прямо до окисей  $\text{Ln}_2\text{O}_3$ .