

## **THERMAL DECOMPOSITION OF RARE EARTH COMPLEXES WITH O-AMINOBENZOIC ACID**

*W. Brzyska and Z. Rzączyńska*

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

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The conditions of thermal decomposition of La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu anthranilates have been studied. The anhydrous La, Ce(III), Pr(III), Nd and Sm anthranilates decompose in one step directly to the oxides  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$  or  $\text{Pr}_6\text{O}_{11}$ . The mono- and dihydrated anthranilates of the remaining rare earths first lose crystallization water when heated, and then decompose exothermally to the oxides  $\text{Ln}_2\text{O}_3$  or  $\text{Tb}_4\text{O}_7$ .

The complexes of metals with aminoacids have been studied by many authors. Ortho-Aminobenzoic acid, also known as anthranilic acid, one of the biologically important  $\alpha$ -aminoacids, reacts with monovalent metal ions to form compounds that may be used for the investigation of the behaviour of potassium in biological systems [1]. It also forms stable, very sparingly soluble complexes with di- and trivalent metal ions, these reactions being used for the quantitative determination of these ions [2-4]. In recent years, several studies have been made on the mode of coordination of rare earth ions with anthranilic acid [5-7]. As a continuation of our work on the thermal decomposition of rare earth carboxylates [8-11], we now report on the thermal decomposition of rare earth anthranilates during heating in an air atmosphere.

### **Experimental**

The anthranilates of Y, La and the lanthanides from Ce(III) to Lu(III) were prepared by adding an anthranilic acid solution (1 g acid/100 cm<sup>3</sup> of H<sub>2</sub>O) at 363 K to freshly precipitated, colloidal hydroxides of Y, La and lanthanides, with an acid to  $\text{Ln}^{3+}$  molar ratio of 3:1. The precipitates formed were filtered off, washed with water and dried at 303 K to constant weight.

The contents of carbon, nitrogen and hydrogen were determined by elemental

analysis using  $V_2O_5$  as oxidizing agent. The contents of rare earth elements were determined by ignition of the complexes to  $Ln_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$  or  $Tb_4O_7$  at 1273 K and by derivatography from the TG curves.

The contents of water were established from the TG curves and by isothermal heating at a definite temperature. The elemental analysis data are given in Table 1.

**Table 1** Analytical data

Complex	% C		% H		% N		% M	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$YL_3 \cdot H_2O$	48.94	48.28	3.91	3.70	8.15	8.10	17.25	17.50
$LaL_3$	46.09	46.44	3.32	3.51	7.67	8.21	25.38	25.08
$CeL_3$	45.98	45.97	3.31	3.40	7.66	7.41	25.54	25.40
$PrL_3$	45.92	44.12	3.30	3.41	7.65	7.33	26.38	26.60
$NdL_3$	45.64	44.33	3.28	3.31	7.60	7.65	26.10	25.70
$SmL_3$	45.14	45.80	3.25	3.41	7.52	7.40	26.92	26.70
$EuL_3 \cdot H_2O$	43.61	43.41	3.14	3.02	7.26	7.58	26.27	26.40
$GdL_3 \cdot H_2O$	43.21	43.04	3.11	3.20	7.20	7.78	26.94	26.10
$TbL_3 \cdot 2H_2O$	41.80	41.54	3.67	3.43	6.96	6.96	26.34	26.02
$DyL_3 \cdot 2H_2O$	41.56	41.54	3.65	3.58	6.92	6.54	26.77	26.92
$HoL_3 \cdot 2H_2O$	41.39	41.98	3.64	3.55	6.90	6.80	27.06	27.00
$ErL_3 \cdot 2H_2O$	41.23	41.43	3.62	3.51	6.87	6.56	26.34	27.31
$TmL_3 \cdot 2H_2O$	41.09	41.42	3.61	3.99	6.85	6.53	27.59	27.14
$YbL_3 \cdot 2H_2O$	40.85	39.49	3.59	3.47	6.80	6.68	28.02	27.89
$LuL_3 \cdot 2H_2O$	40.72	41.26	3.54	3.76	6.78	7.07	28.25	27.99

\*  $L = C_6H_7O_2N^-$

The data obtained indicated that the prepared anthranilates of La, Ce(III), Pr, Nd and Sm were anhydrous salts with a metal to ligand molar ratio of 1:3. The complexes of the remaining rare earths were prepared as hydrated salts with a metal to ligand ratio of 1:3. The anthranilates of Y, Eu and Gd were obtained as monohydrates, and those of the elements from Tb to Lu as dihydrates.

The IR spectra of the prepared complexes were recorded [8] over the range  $4000-400\text{ cm}^{-1}$ . Analysis of the spectra confirmed the elemental analysis results. On the basis of the IR spectra it was found that the metal ions were simultaneously coordinated through amino and carboxyl groups, the coordination number being nine.

The prepared complexes are crystalline solids readily soluble in water.

The thermal stabilities of the complexes of Y, La and the lanthanides with anthranilic acid were studied. The TG, DTG and DTA curves were recorded. The measurements were made with an OD-102 derivatograph at a heating rate of  $9\text{ deg} \cdot \text{min}^{-1}$ . The samples were heated to 1173 K in a ceramic crucible in an air

atmosphere with the sensitivity TG = 100 mg, DTG - 1/5, DTA - 1/10. The curves obtained for the Y complex as an example are presented in Fig. 1. From the thermal curves of the prepared anthranilates, the temperatures of thermal decomposition were evaluated and are presented in Table 2. The decomposition products obtained during heating were established from the TG curves and confirmed by recording their IR and X-ray spectra.

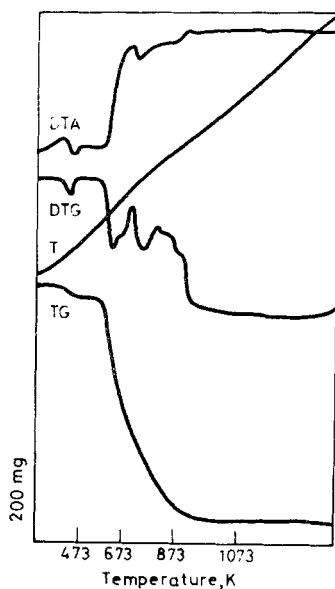


Fig. 1 TG, DTA and DTG curves of  $Y(C_6H_7O_2N)_3 \cdot H_2O$

## Results and discussion

The results indicate that the prepared complexes decompose in various manners. The anhydrous complexes of La, Ce(III), Pr, Nd and Sm decompose in one step in the temperature range 548–983 K, yielding the oxides  $La_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $Nd_2O_3$  and  $Sm_2O_3$ , respectively. The ignition of the organic ligand is accompanied by exothermic effects. The hydrated rare earth anthranilates decompose in two stages. In the first step, the complexes of Y, Eu and Gd lose one molecule of crystallization water at 373–453 K, with an accompanying strong endothermic effect, and the resulting anhydrous complexes are then decomposed exothermally to the oxides  $Ln_2O_3$  in the temperature range 563–953 K. The dihydrated heavy lanthanide anthranilates (from Tb to Lu) lose two water

Table 2 Data on decomposition of Y, La and lanthanide anthranilates

Complex	Temperature range of dehydration, K		Loss in weight, %		Loss of H <sub>2</sub> O, mole	Temperature range of decomposition, K	Loss in weight, %		Temperature of oxide** formation, K	Exothermic peaks, K	Endothermic peaks, K		
	calcd.	found	calcd.	found			calcd.	found					
YI <sub>3</sub> ·H <sub>2</sub> O	393-453	3.50	3.50	3.50	1	590-933	78.08	78.0	933	403	618	813	453
LaL <sub>3</sub>	—	—	—	—	—	553-913	70.24	70.0	913	343	563	813	—
CeL <sub>3</sub>	—	—	—	—	—	548-813	68.62	68.0	813	383	513	763	—
PrL <sub>3</sub>	—	—	—	—	—	553-883	69.00	69.0	883	343	673	793	—
NdL <sub>3</sub>	—	—	—	—	—	573-983	69.56	70.0	983	403	673	793	—
SmL <sub>3</sub>	—	—	—	—	—	573-893	68.80	69.5	893	413	693	823	—
EuL <sub>3</sub> ·H <sub>2</sub> O	373-433	3.11	3.0	3.0	1	563-893	69.58	70.0	893	393	563	753	423
GdL <sub>3</sub> ·H <sub>2</sub> O	373-453	3.09	3.3	3.3	1	563-953	68.95	69.0	953	273	673	908	433
TbL <sub>3</sub> ·2H <sub>2</sub> O	333-448	5.97	6.0	6.0	2	563-863	69.02	69.0	863	283	648	743	423
DyL <sub>3</sub> ·2H <sub>2</sub> O	323-438	5.94	6.0	6.0	2	568-978	69.27	68.5	978	368	653	753	418
HoL <sub>3</sub> ·2H <sub>2</sub> O	333-443	5.91	6.0	6.0	2	573-986	69.00	69.0	986	368	653	753	423
ErL <sub>3</sub> ·2H <sub>2</sub> O	323-441	5.89	6.0	6.0	2	573-914	68.73	70.0	914	373	668	768	418
TmL <sub>3</sub> ·2H <sub>2</sub> O	341-455	5.87	6.0	6.0	2	599-943	68.50	69.0	943	393	688	758	433
YbL <sub>3</sub> ·2H <sub>2</sub> O	340-450	5.84	6.0	6.0	2	583-903	68.09	68.8	903	368	673	758	427
LuL <sub>3</sub> ·2H <sub>2</sub> O	343-438	5.82	5.8	5.8	2	593-879	67.88	68.0	879	388	688	758	433

\* L = C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>N<sup>-</sup>; \*\* Ln<sub>2</sub>O<sub>3</sub> (Ln = La, Nd, Sm, Eu, Gd, Dy-Lu), CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, Tb<sub>4</sub>O<sub>7</sub>

molecules when heated, undergoing dehydration in the temperature range 323–455 K, and the anhydrous complexes then decompose directly to the oxides  $\text{Ln}_2\text{O}_3$  or  $\text{Tb}_4\text{O}_7$  in the temperature range 563–986 K. The low temperature of dehydration indicates that the crystallization water is probably outer sphere water.

The X-ray spectra of the hydrated rare earth anthranilates and the complexes obtained after dehydration were recorded. It was found that a change in structure takes place during the dehydration process. The anhydrous salts do not change their structure when heated.

The temperature of oxide formation changes irregularly in the lanthanide series with increase of the atomic number. The oxides are formed at 813–986 K. The temperature of  $\text{CeO}_2$  formation has the lowest value, similarly as observed during the decomposition of many series of lanthanide complexes.

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**Zusammenfassung** — Die Bedingungen der thermischen Zersetzung der Anthranilate von La, Ce(III), Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb und Lu wurden untersucht. Die wasserfreien Anthranilate von La, Ce(III), Pr(III) und Nd zersetzen sich in einem Schritt direkt zu den Oxiden  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$  und  $\text{Pr}_6\text{O}_{11}$ . Die ein oder zwei Kristallwasser enthaltenden Anthranilate der übrigen seltenen Erdmetalle werden beim Erhitzen zunächst dehydratisiert und danach exotherm zu den Oxiden  $\text{Ln}_2\text{O}_3$  und  $\text{Tb}_4\text{O}_7$  abgebaut.

**Резюме** — Изучено термическое разложение солей антраниловой кислоты с итрии, лантаном и лантаноидами. Безводные антранилаты лантана, трехвалентных церия, празеодима и неодима разлагаются в одну стадию непосредственно до соответствующих окислов  $\text{Ln}_2\text{O}_3$ ,  $\text{CeO}_2$  и  $\text{Pr}_6\text{O}_{11}$ . Моно- и дигидраты оставшихся антранилатов при нагревании теряют кристаллизационную воду и разлагаются экзотермически до окислов  $\text{Ln}_2\text{O}_3$  и  $\text{Tb}_4\text{O}_7$ .