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THERMAL DECOMPOSITION OF Y, La AND LANTHANIDE BENZENE-1,2-DIOXYACETATES IN AN AIR ATMOSPHERE

W. Brzyska and A. Król

Department of Inorganic and General Chemistry, Faculty of Chemistry, Marie Curie Sklodowska University 20-031 Lublin, Poland

Abstract

The thermal decompositions of Y, La and lanthanide (from Ce(III) to Lu(III) benzene-1,2-dioxyacetates with general formula $Ln_2(C_{10}H_8O_6)_3 \cdot nH_2O$ were studied. The hydrated complexes first lose water of crystallization in one or two steps to yield anhydrous compounds or hydrates containing coordination water molecules, and then decompose to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 with formation of intermediates, carbonates and oxycarbonates (La, Pr–Eu), oxycarbonates (Y, Tb–Lu) or carbonate (Gd) only. Anhydrous cerium(III) benzene-1,2-dioxyacetate decomposes on heating directly to CeO_2.

Keywords: complexes, lanthanides

Introduction

The complexes of rare earth elements with benzene-1,2-dioxyacetic acid $C_6H_4(OCH_2COOH)_2$ are little known. The formation constants and thermodynamic parameters of the complexes of rare earths with benzene-1,2-dioxyacetate $[La(C_{10}H_8O_6)_n]^{(3-2n)+}$ (where Ln=La, Y, Ce–Lu, n=1 and 2) have been determined using potentiometric titration and calorimetry [1]. Formation constants have also been determined by NMR for 1:2 complexes of Pr(III), Eu(III), Yb(III) [2]. Single crystals of $Na[La(C_{10}H_8O_6)_2(H_2O)_2] \cdot H_2O$ have been prepared by overnight evaporation of an aqueous solution containing the sodium salt of the acid and lanthanum chloride and its lattice parameters and molecular structure have been determined [3]. It has been established that the complex anion corresponds to the deca-coordinated species. In a previous work we have presented the preparation of Y, La and lanthanide (from Ce(III) to Lu) benzene-1,2-dioxyacetates with a metal to organic ligand molar ratio of 2:3 and different degrees of hydration [4], their IR and X-ray spectra, solubilities in water and conductivities of their aqueous solutions.

As a continuation of our work on the thermal decomposition of rare earth carboxylates, we now report on the thermal decomposition of Y, La and lanthanide benzene-1,2-dioxyacetate hydrates during heating in an air atmosphere.

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Table 1 Data for the dehydration of Y, La and lanthanide benzene-1,2-dioxyacetates

Complex	Temp. range of dehydration I/ K	Loss of weight/%		Loss of H_2O/ mol	Temp. range of dehydration II/ K	Loss of weight/%		Loss of H_2O/ mol	Residual weight/%		Compounds
		calcd.	found			calcd.	found		calcd.	found	
Y_2L_3*$\cdot 13H_2O$	328–423	9.96	10.0	6	423–478	14.95	15.2	3	85.05	84.8	$Y_2L_3\cdot 4H_2O$
$La_2L_3\cdot 12H_2O$	333–403	6.18	6.4	4	404–470	13.89	13.6	5	87.18	86.4	$La_2L_3\cdot 3H_2O$
$Ce_2L_3\cdot 7H_2O$	328–408	7.25	6.8	4	408–465	11.69	12.0	3	88.31	88.0	Ce_2L_3
$Pr_2L_3\cdot 9H_2O$	328–403	6.45	6.4	4	403–455	12.91	13.6	4	87.09	87.4	$Pr_2L_3\cdot H_2O$
$Nd_2L_3\cdot 7H_2O$	318–433	9.94	10.4	6	433–475	11.60	12.4	1	88.40	87.6	Nd_2L_3
$Sm_2L_3\cdot 16H_2O$	333–468	14.26	14.0	10	–	–	–	–	85.74	86.0	$Sm_2L_3\cdot 6H_2O$
$Eu_2L_3\cdot 8H_2O$	318–423	8.04	8.0	5	423–478	12.86	13.2	3	87.14	86.8	Eu_2L_3
$Gd_2L_3\cdot 16H_2O$	318–413	9.88	9.6	7	413–463	12.71	13.4	2	87.29	86.6	$Gd_2L_3\cdot 7H_2O$
$Tb_2L_3\cdot 10H_2O$	318–423	9.23	8.8	6	423–471	12.31	12.8	2	87.69	87.2	$Tb_2L_3\cdot 2H_2O$
$Dy_2L_3\cdot 13H_2O$	325–423	8.77	8.8	6	423–471	14.62	14.2	4	85.38	85.8	$Dy_2L_3\cdot 3H_2O$
$Ho_2L_3\cdot 11H_2O$	311–423	9.00	9.2	6	423–475	12.00	12.4	2	88.00	87.6	$Ho_2L_3\cdot 3H_2O$
$Er_2L_3\cdot 10H_2O$	312–423	7.59	8.0	5	423–463	13.66	13.6	4	86.36	87.4	$Er_2L_3\cdot H_2O$
$Tm_2L_3\cdot 8H_2O$	318–418	9.36	8.8	6	423–473	12.48	12.8	2	87.52	87.2	Tm_2L_3
$Yb_2L_3\cdot 12H_2O$	318–423	10.21	10.8	7	423–475	14.59	14.4	3	85.41	85.6	$Yb_2L_3\cdot 2H_2O$
$Lu_2L_3\cdot 10H_2O$	313–423	10.49	11.2	7	423–483	14.98	14.8	3	85.02	85.2	Lu_2L_3

* $L - C_6H_4(OCH_2COO)_2^{2-}$

Experimental

The thermal stabilities of Y, La and lanthanide (from Ce(III) to Lu(III) benzene-1,2-dioxyacetates with the general formula $Ln_2(C_{10}H_8O_6)_3 \cdot nH_2O$ (Table 1) were studied in an air atmosphere. The TG, DTG and DTA curves were recorded. The measurements were made with Q-1500 D derivatograph at a heating rate of 10 K min^{-1}. The 100 mg samples were heated to 1273 K in platinum crucibles chart speed. Al_2O_3 was used as a reference material. The samples were heated also at 480–523 K isothermally and the thermal curves were recorded to confirm the results. The intermediates were studied by recording IR and X-ray spectra.

Results and discussion

The results indicate that rare earth benzene-1,2-dioxyacetates hydrates decompose during heating in various manners, in several steps (Figs 1–6, Tables 1, 2). They are stable up to 311–333 K and are then dehydrated in two steps, except the samarium(III) complex which is dehydrated in one step. The hydrated complexes of Ce(III), Nd(III), Eu(III), Tm(III) and Lu(III) lose waters of crystallization and yield the anhydrous compounds at 455–483 K to whereas the complexes of the rest of the rare earths lose some of the water molecules and are transformed at 498–523 K to hydrates containing less water (Table 1). The results permit the conclusion that the water molecules are bonded in the studied complexes in various ways. In the complexes there are [4]:

– waters of crystallization bonded to the anion (lost at 311–468 K)

– waters of crystallization coordinated in the inner sphere of the complex [6] (lost at 405–433 K).

The temperatures of the end of the first (T_1) and the second (T_2) step of dehydration change irregularly in the lanthanide series (Fig. 7), having the highest value T_1 for Sm and Nd, and T_2 – for Y, Eu and Lu.

The completely or partially dehydrated complexes are stable up to 498–538 K and decompose on further heating accompanied by two exothermic peaks with maxima between 598–655 K. The exothermic peaks are due to the oxidation of the organic ligands and escape of carbon and carbon monoxide. In this temperature range unstable intermediates difficult to identify are formed, which is clearly shown by the TG curves of the lanthanum, Pr and Nd complexes recorded at a heating rate of 5 K min^{-1}. In the TG curves of the rest of the rare earth complexes studied only a curve bending is observed. The complexes of light lanthanides from Pr(III) to Eu(III) and La(III) (Table 2) decompose on heating to yield the oxides, Ln_2O_3 and Pr_6O_{11}, with formation of carbonates at 645–750 K and then oxycarbonates at 768–950 K as intermedi-

Table 2 Data for the decomposition of Y, La and lanthanide benzene-1,2-dioxyacetates

Complex	Temp. range of decomp. to $Ln_2(CO_3)_3$/K	$Ln_2(CO_3)_3$ residue/%		Temp. range of decomp. to $Ln_2O_2CO_3$/K	$Ln_2O_2CO_3$ residue/%		Exothermic DTA peak/ K	Temp. of oxide format./K	Lanthanide oxide* residue/%	
		calcd.	found		calcd.	found			calcd.	found
$Y_2L_3·4H_2O$	–	–	–	498–743	24.88	25.2	643	1013	20.82	20.8
$La_2L_3·3H_2O$	525–750	39.25	38.8	750–950	31.70	31.0	618,655	1023	27.93	28.0
Ce_2L_3	–	–	–	–	–	–	598	723	31.90	32.4
$Pr_2L_3·H_2O$	523–645	41.37	42.1	675–768	33.48	33.5	608	843	30.49	30.4
Nd_2L_3	513–723	43.09	42.5	753–853	35.00	34.5	603	993	30.95	31.4
$Sm_2L_3·6H_2O$	523–705	38.16	37.6	705–848	31.19	31.6	621	903	27.62	27.6
Eu_2L_3	508–688	43.19	42.6	701–815	35.33	36.0	623	833	31.40	31.2
$Gd_2L_3·7H_2O$	523–705	38.78	39.0	–	–	–	633	925	28.42	28.4
$Tb_2L_3·2H_2O$	–	–	–	521–723	35.02	35.2	633	1181	31.94	32.0
$Dy_2L_3·3H_2O$	–	–	–	521–711	33.86	33.6	638	1043	30.28	30.4
$Ho_2L_3·3H_2O$	–	–	–	531–703	35.14	35.6	635	993	31.47	31.6
$Er_2L_3·H_2O$	–	–	–	521–718	35.93	36.0	633	985	32.22	32.4
Tm_2L_3	–	–	–	538–715	37.23	37.2	643	968	33.42	33.2
$Yb_2L_3·2H_2O$	–	–	–	528–711	35.48	35.6	640	968	31.91	32.0
Lu_2L_3	–	–	–	528–701	36.75	36.0	640	833	33.09	33.2

* Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7

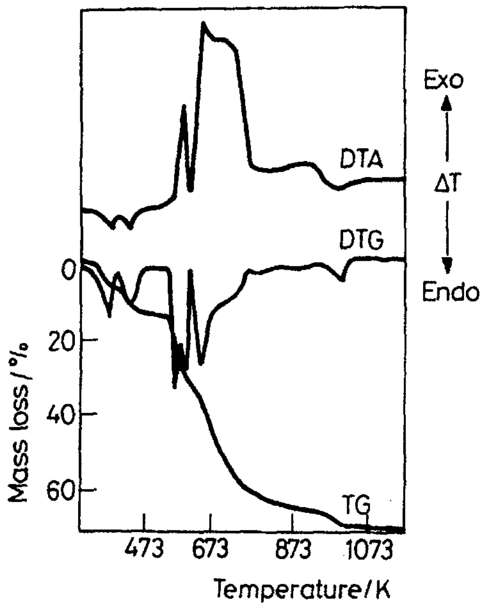

Fig. 1 TG, DTG and DTA curves of $La_2(C_{10}H_8O_6)_3 \cdot 12H_2O$

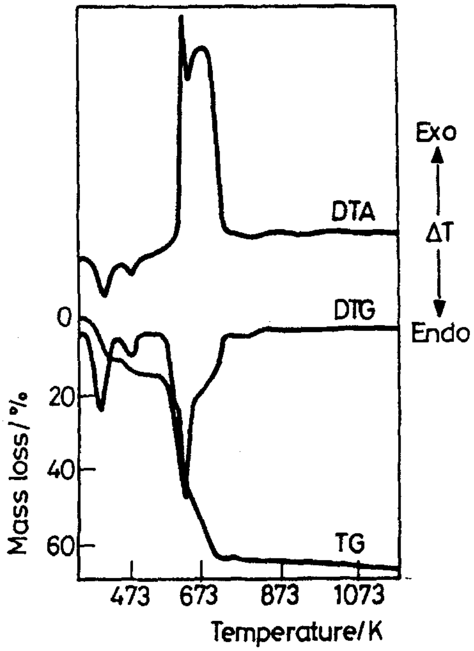

Fig. 2 TG, DTG and DTA curves of $Nd_2(C_{10}H_8O_6)_3 \cdot 7H_2O$

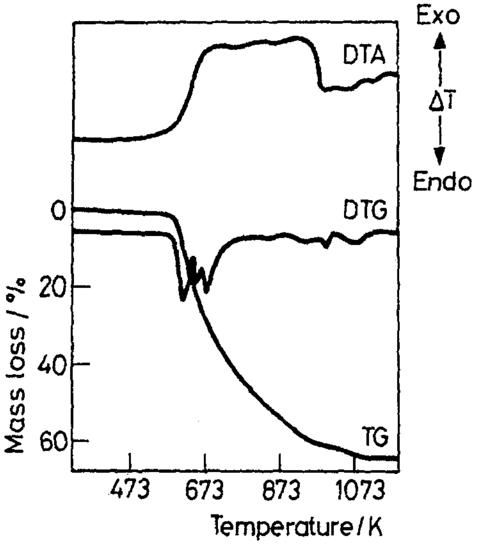

Fig. 3 TG, DTG and DTA curves of $Nd_2(C_{10}H_8O_6)_3$

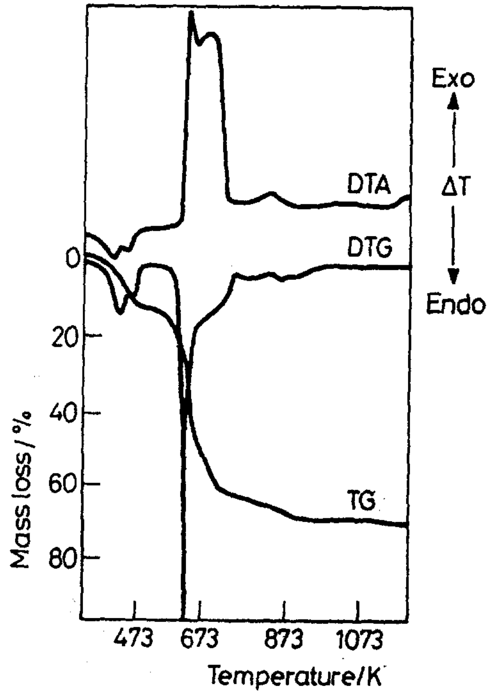

Fig. 4 TG, DTG and DTA curves of $Gd_2(C_{10}H_8O_6)\cdot 16H_2O$

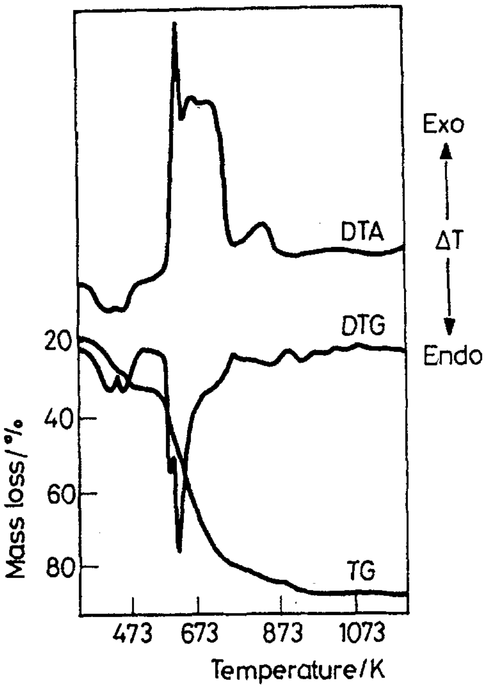

Fig. 5 TG, DTG and DTA curves of $Lu_2(C_{10}H_8O_6)_3 \cdot 10H_2O$

ates. The oxides are formed at 833–1073 K (Fig. 7). The anhydrous cerium(III) complex decomposes directly to CeO_2 at 723 K. Gadolinium(III) benzene-1,2-dioxyacetate heptahydrate forms the carbonate at 705 K, which decomposes to Gd_2O_3 at 925 K. The complexes of heavy lanthanides from Tb(III) to Lu and Y are decomposed to Ln_2O_3 and Tb_4O_7 at 833–1181 K with formation of oxycarbonates as intermediates at 701–743 K. In general, the thermal decomposition of the prepared complexes can be described as follows:

$$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2(CO_3)_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3,\ Pr_6O_{11}$$

$$Ln = \text{La, Pr–Eu},\ y = 0\text{–}6$$

$$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3,\ Tb_4O_7$$

$$Ln = \text{La, Tb–Lu},\ y = 0\text{–}3$$

$$Ce_2L_3 \cdot 7H_2O \rightarrow Ce_2L_3 \rightarrow CeO_2$$

$$Gd_2L_3 \cdot 16H_2O \rightarrow Gd_2L_3 \cdot 7H_2O \rightarrow Gd_2(CO_3)_3 \rightarrow Gd_2O_3$$

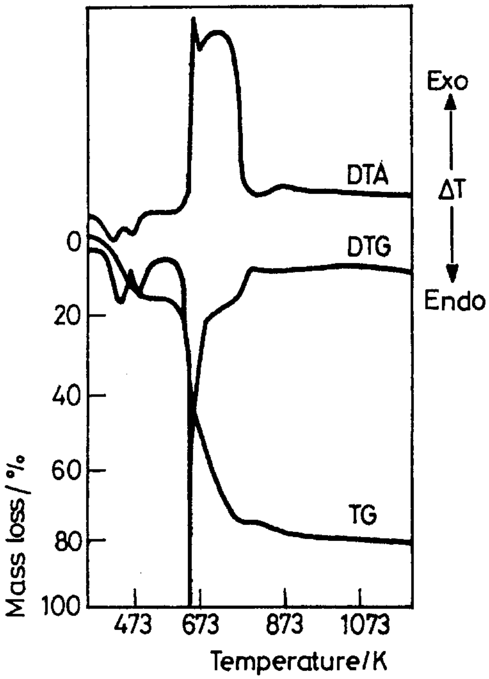

Fig. 6 TG, DTG and DTA curves of $Y_2(C_{10}H_8O_6)_3 \cdot 13H_2O$

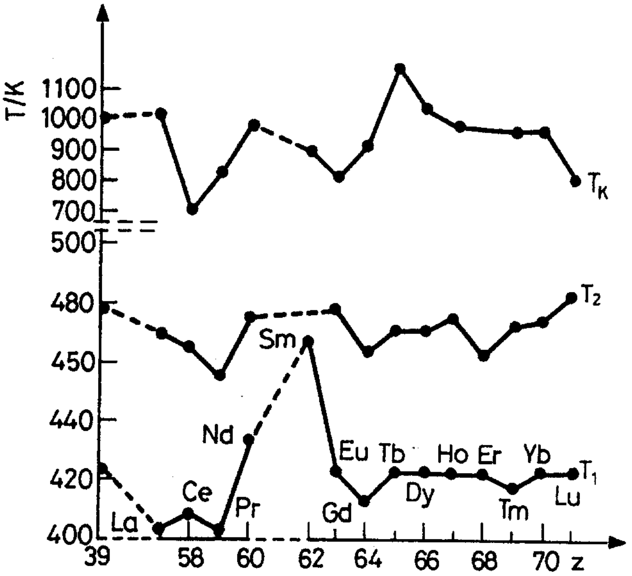

Fig. 7 Relationship between temperatures of the beginning and end of dehydration (T_1, T_2) and oxide formation (T_k) and atomic number Z of metal

The temperature of oxide formation changes irregularly in the lanthanide series. CeO_2 is formed at the lowest (723 K), whereas Tb_4O_7 at the highest (1181 K) temperature (Fig. 7). The temperatures of formation of Y_2O_3, La_2O_3 and Dy_2O_3 are also high (higher than 1000 K).

On the basis of the results obtained it is possible to suggest that the temperatures of the beginning of dehydration (the first and the second step) and of the decomposition of the complexes are similar for the entire lanthanide series, which indicates their similar stabilities.

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