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Thermal decomposition of yttrium and lanthanide benzene-1,4-dioxyacetates in air atmosphere

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Abstract

The thermal decomposition in air of benzene-1,4-dioxyacetates of Y and lanthanides from La(III) to Lu(III) has been studied. During heating, the hydrated complexes $Ln_2[C_6H_4(OCH_2 \cdot COO)_2]_3 \cdot nH_2O$ ($n = 6$–13) lose water of crystallisation in one (Y, La–Pr and Ho–Lu) or two steps (Nd–Dy), then decompose either directly to the oxides or with intermediate formation of very unstable oxycarbonates (La and Nd).

INTRODUCTION

Rare-earth element complexes with benzene-1,4-dioxyacetic acid, $C_6H_4(OCH_2COOH)_2$, were previously unknown. In an earlier study, we described the preparation of Y and lanthanide (from La(III) to Lu(III)) benzene-1,4-dioxyacetates with a molar ratio of metal to organic ligand of 2 : 3 and different degrees of hydration [1], and their IR and X-ray spectra, solubilities in water and the conductivity of their water solutions. As a continuation of our work on the thermal decomposition of rare-earth benzenedioxyacetates [2,3], we now report the thermal decomposition of Y and lanthanide benzene-1,4-dioxyacetate hydrates during heating in an air atmosphere.

EXPERIMENTAL

The thermal stabilities of Y and lanthanide (La(III)–Lu(III)) benzene-1,4-dioxyacetates with general formula $Ln_2(C_{10}H_8O_6)_3 \cdot nH_2O$ (Table 1) were studied in air atmosphere. The TG, DTG and DTA curves were recorded. The measurements were made with a Q-1500D derivatograph at a heating rate of 10 K min^{-1}. The samples of 100 mg were heated to 1273 K in platinum crucibles with the following sensitivities: TG, 100 mg; DTG, 500 μV; DTA, 500 μV. The paper speed was 2,5 mm/min^{-1}. Al_2O_3 was used as a standard. To confirm the results the samples were also heated isother-

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TABLE 1

Data on dehydration of Y and lanthanide benzene-1,4-dioxyacetates

Complex	Temperature range of dehydration I (K)	Weight Loss (%)		Loss of H_2O (mole)	Temperature range of dehydration II (K)	Weight loss (%)		Loss of H_2O (mole)	Weight of residue (%)		Compounds
		Calcd.	Found.			Calcd.	Found.		Calcd.	Found	
$Y_2L_3 \cdot 11H_2O$ [a]	–	–	–	–	423–523	10.31	10.0	6	89.29	90.0	$Y_2L_3 \cdot 5H_2O$
$La_2L_3 \cdot 9H_2O$	–	–	–	–	408–503	8.10	8.0	5	91.90	92.0	$La_2L_3 \cdot 4H_2O$
$Ce_2L_3 \cdot 8H_2O$	–	–	–	–	418–505	8.21	8.4	5	91.79	91.6	$Ce_2L_3 \cdot 3H_2O$
$Pr_2L_3 \cdot 10H_2O$	–	–	–	–	413–498	7.94	8.4	5	92.06	91.6	$Pr_2L_3 \cdot 5H_2O$
$Nd_2L_3 \cdot 8H_2O$	323–428	4.89	4.8	3	438–508	8.15	8.8	2	91.85	91.2	$Nd_2L_3 \cdot 3H_2O$
$Sm_2L_3 \cdot 13H_2O$	318–428	11.93	12.4	8	443–495	16.40	16.0	3	83.60	84.0	$Sm_2L_3 \cdot 2H_2O$
$Eu_2L_3 \cdot 10H_2O$	323–425	10.90	10.8	7	435–501	14.02	14.0	2	85.98	86.0	$Eu_2L_3 \cdot H_2O$
$Gd_2L_3 \cdot 10H_2O$	323–425	10.80	10.4	7	443–503	13.89	13.6	2	86.11	86.4	$Gd_2L_3 \cdot H_2O$
$Tb_2L_3 \cdot 10H_2O$	323–423	10.77	10.0	7	433–505	13.85	13.2	2	86.15	86.8	$Tb_2L_3 \cdot H_2O$
$Dy_2L_3 \cdot 7H_2O$	333–423	3.21	3.2	2	433–518	9.62	9.2	4	90.38	90.8	$Dy_2L_3 \cdot H_2O$
$Ho_2L_3 \cdot 6H_2O$	–	–	–	–	441–518	8.11	8.0	5	91.89	82.0	$Ho_2L_3 \cdot H_2O$
$Er_2L_3 \cdot 7H_2O$	–	–	–	–	425–523	7.95	8.0	5	92.05	92.0	$Er_2L_3 \cdot 2H_2O$
$Tm_2L_3 \cdot 6H_2O$	–	–	–	–	428–521	8.05	8.0	5	91.95	92.0	$Tm_2L_3 \cdot H_2O$
$Yb_2L_3 \cdot 9H_2O$	–	–	–	–	433–543	9.15	9.2	6	90.85	90.8	$Yb_2L_3 \cdot 3H_2O$
$Lu_2L_3 \cdot 9H_2O$	–	–	–	–	438–541	9.12	8.8	6	90.88	91.2	$Lu_2L_3 \cdot 3H_2O$

[a] $L = C_6H_4(OCH_2COO)^{2-}$.

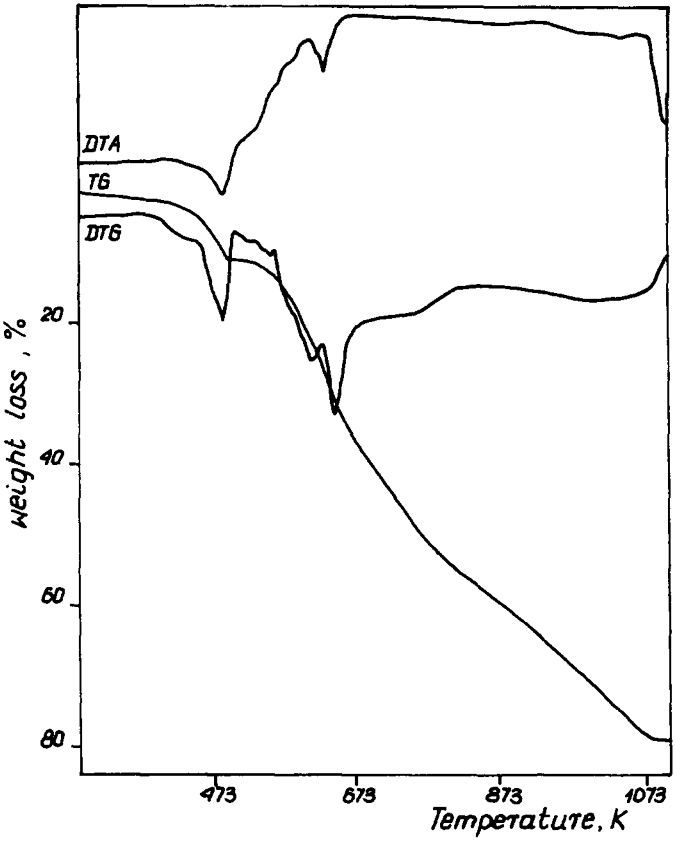

Fig. 1. TG, DTG and DTA curves of $Y_2(C_{10}H_8O_6)_3 \cdot 11H_2O$.

mally at 413 and 473 K and the thermal curves were recorded. The intermediate products were confirmed by IR and X-ray spectra.

RESULTS AND DISCUSSION

The results, shown in Figs. 1–9 and Tables 1 and 2, indicate that the rare earth benzene-1,4-dioxyacetate hydrates prepared decompose in various ways when heated. The hydrated benzene-1,4-dioxyacetates of Nd, Sm, Eu(III), Gd, Tb and Dy are stable up to 318–333 K, and then dehydrate in two steps, whereas the complexes of the remaining rare earth elements are stable up to 408–444 K and then dehydrate in one step. Complexes heated to 445–543 K are partially dehydrated, with 1–5 water molecules remaining. Table 1 gives the ranges of the dehydration temperatures and quantitative descriptions of the dehydration processes of Y and lanthanide benzene-1,4-dioxyacetates.

From these results, it is possible to suggest that water crystallisation molecules are bonded in different ways: with an anion (lost at 423–428 K);

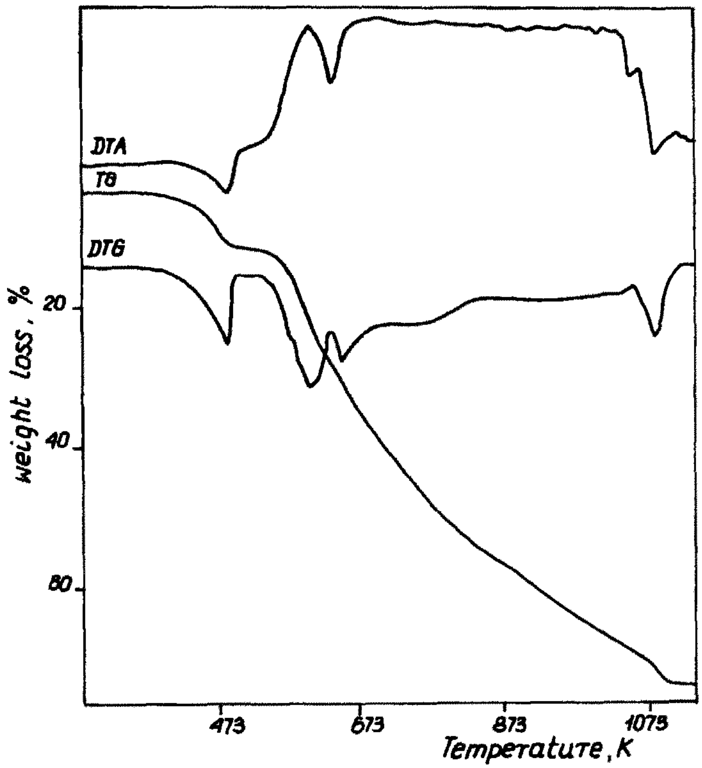

Fig. 2. TG, DTG and DTA curves of $La_2(C_{10}H_8O_6)_3 \cdot 9H_2O$.

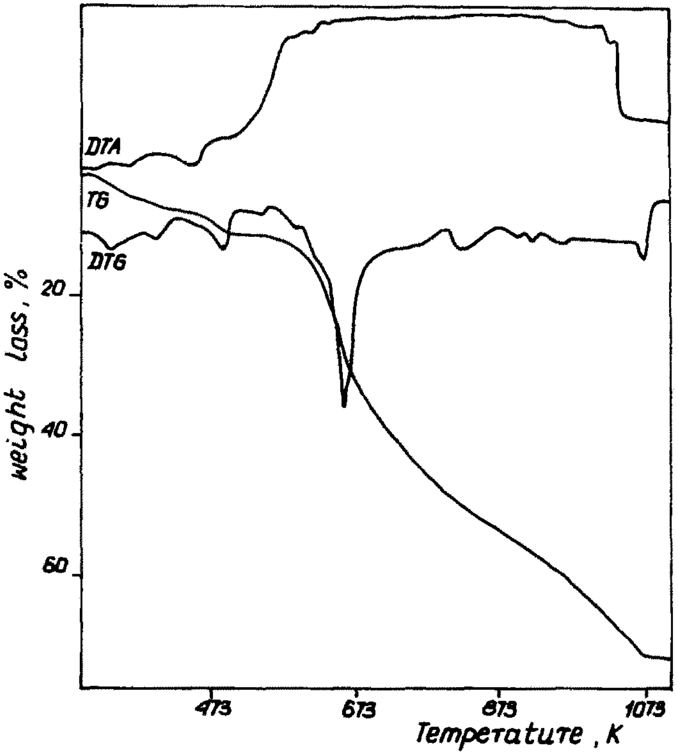

Fig. 3. TG, DTG and DTA curves of $Nd_2(C_{10}H_8O_6)_3 \cdot 8H_2O$.

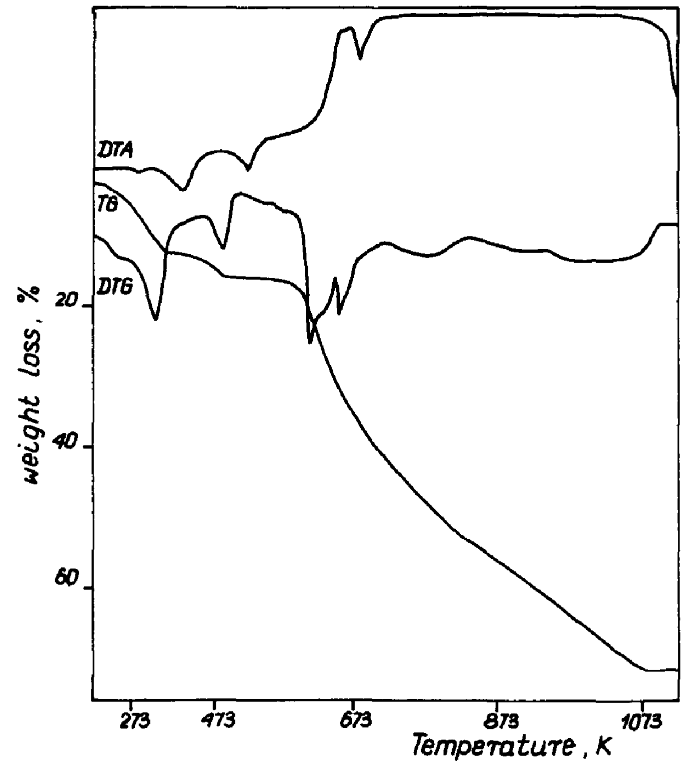

Fig. 4. TG, DTG and DTA curves of $Gd_2(C_{10}H_8O_6)_3 \cdot 10H_2O$.

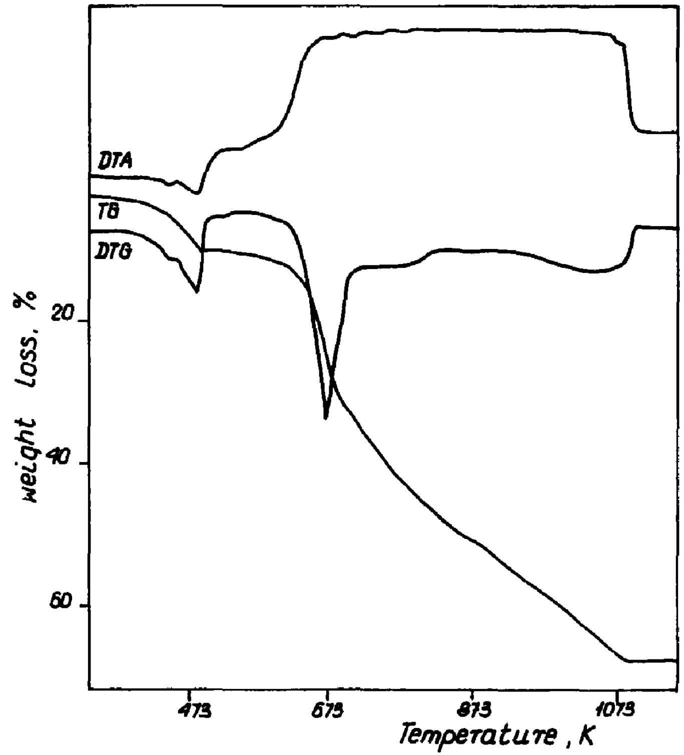

Fig. 5. TG, DTG and DTA curves of $Lu_2(C_{10}H_8O_6)_3 \cdot 9H_2O$.

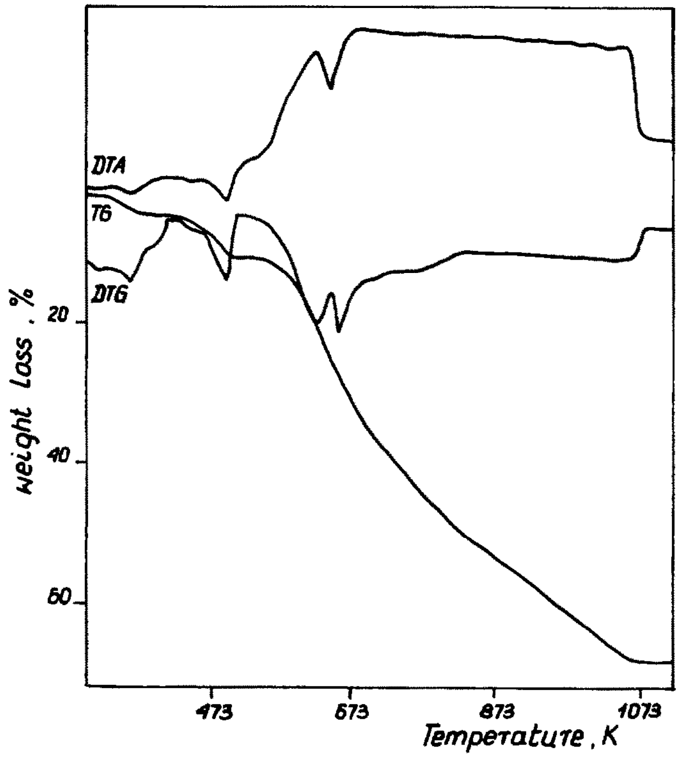

Fig. 6. TG, DTG and DTA curves of $Dy_2(C_{10}H_8O_6)_3 \cdot 7H_2O$.

in the space lattice bonded by a hydrogen bond with an anion or as inner sphere water of the complexes (lost at 495–543 K); and as coordination water which is strongly bonded with metal ion (lost simultaneously with decomposition of the organic ligand leaving 1–5 water molecules). Comparing the final temperatures of dehydration of the various complexes, it is possible to suggest that water of crystallisation molecules are most strongly bonded in Yb(III) and Lu(III) complexes, and least strongly in Sm(III) and Pr(III) complexes. The benzene-1,4-dioxyacetates of rare earth elements lose only some of their water molecules when heated and do not form anhydrous complexes. For a full interpretation of the nature of the bonding of the water molecules, it is necessary to define the coordination and molecular structure of the complexes on the basis of an X-radiographic study of the monocrystals.

Partially dehydrated complexes heated above 525–568 K lose their last water molecules simultaneously with decomposition of the organic ligand. This process is accompanied by a strong exothermic effect, which is observed on the DTA curve as a plateau without maximum. During heating the complexes decompose directly to the oxides, Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7; at 1001 K for Ce, at 1198 K for Tb(III). For the complexes of La

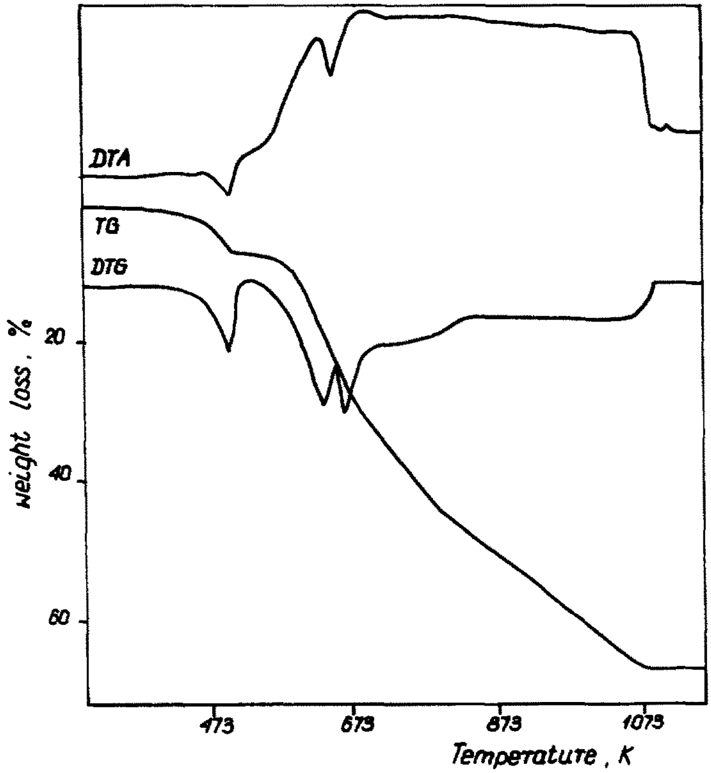

Fig. 7. TG, DTG and DTA curves of $Dy_2(C_{10}H_8O_6)_3 \cdot 5H_2O$.

and Nd only, the DTG curve indicates the formation of very unstable oxycarbonates 1093 and 1063 K, respectively.

The results indicate that the thermal decomposition of hydrated rare earth element benzene-1,4-dioxyacetates can be presented in the following manner

$$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2O_3,\ Tb_4O_7$$

$$n > x > y \qquad Ln = Nd\text{–}Dy$$

$$Ln_2L_3 \cdot nH_2O \rightarrow Ln_2L_3 \cdot xH_2O \rightarrow Ln_2O_3,\ CeO_2,\ Pr_6O_{11}$$

$$n > x \qquad Ln = Y,\ La\text{–}Pr,\ Ho\text{–}Lu$$

In general, it can be suggested that hydrated benzene-1,4-dioxyacetates, when heated in air atmosphere, dehydrate losing some water molecules, and then decompose directly to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7; only La and Nd form very unstable oxycarbonates as intermediate products.

Comparing the final temperatures of complex dehydration (T_D) and the temperatures of oxide formation (T_T) (Fig. 9) it is possible to suggest that hydrates of Y and heavy lanthanide complexes are more stable than those of light ones. The temperatures of oxide formation (T_T) change irregularly with increasing atomic number (Z) of the metal (Fig. 9). The temperature of

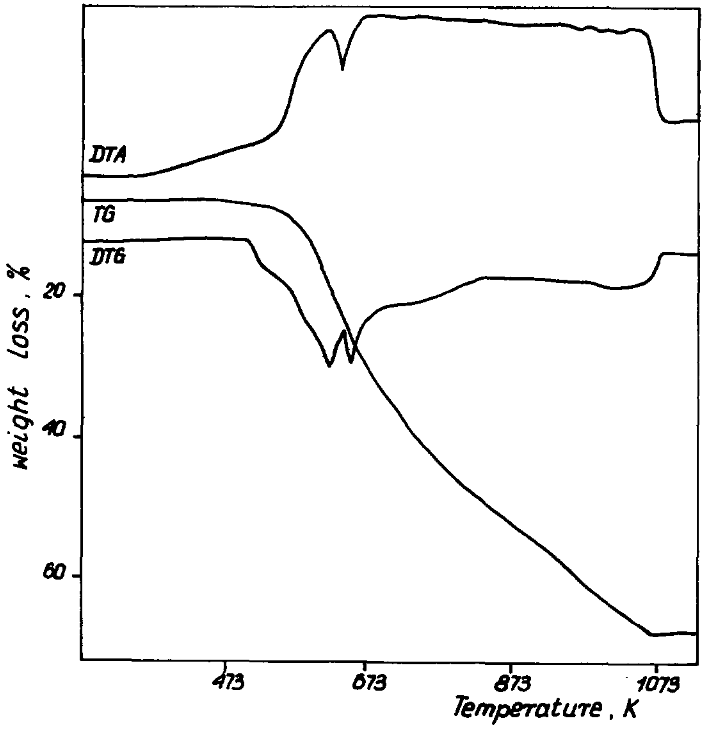

Fig. 8. TG, DTG and DTA curves of $Dy_2(C_{10}H_8O_6)_3 \cdot H_2O$.

TABLE 2

Data on decomposition of Y and lanthanide benzene-1,4-dioxyacetates

Complex	Temperature range of decomposition to oxides (K)	Weight of residue (Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7) (%)	
		Calcd.	Found
$Y_2L_3 \cdot 5H_2O$	528–1135	21.54	21.6
$La_2L_3 \cdot 4H_2O$	528–1133	29.29	29.2
$Ce_2L_3 \cdot 3H_2O$	525–1001	31.38	31.2
$Pr_2L_3 \cdot 5H_2O$	528–1108	30.01	30.0
$Nd_2L_3 \cdot 3H_2O$	543–1095	30.45	30.0
$Sm_2L_3 \cdot 2H_2O$	523–1148	28.86	28.8
$Eu_2L_3 \cdot H_2O$	533–1073	30.43	30.4
$Gd_2L_3 \cdot H_2O$	523–1103	31.06	30.8
$Tb_2L_3 \cdot H_2O$	548–1198	31.94	32.0
$Dy_2L_3 \cdot H_2O$	531–1083	33.20	33.2
$Ho_2L_3 \cdot H_2O$	533–1088	34.02	34.1
$Er_2L_3 \cdot 2H_2O$	531–1093	33.76	33.6
$Tm_2L_3 \cdot H_2O$	528–1118	34.50	34.4
$Yb_2L_3 \cdot 3H_2O$	568–1123	33.38	33.2
$Lu_2L_3 \cdot 3H_2O$	558–1098	33.59	33.6

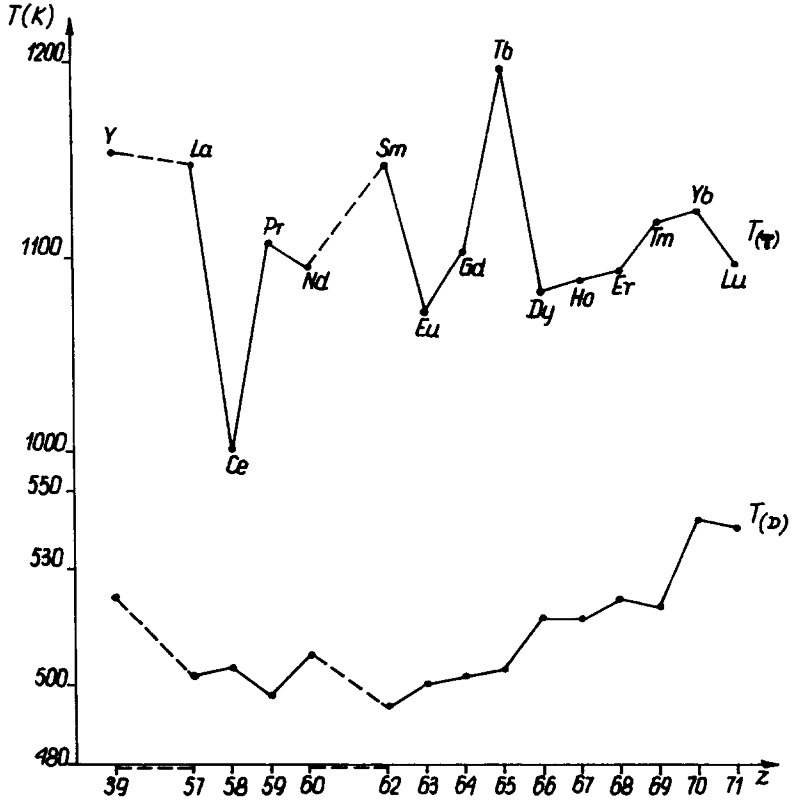

Fig. 9. Relationship between the final temperatures of dehydration, T_D, and of oxide formation, T_T, and atomic number, z, of the metal.

CeO_2 formation is lowest (1001 K) whereas the temperature of Tb_4O_7 formation is highest (1198 K), as observed during the decomposition of many series of lanthanide complexes.

In general, it can be confirmed that the rare earth oxides prepared by the thermal decomposition of benzene-1,4-dioxyacetates are formed at very high temperatures compared to the temperatures of the oxides formed by decomposition of the complexes of rare earth elements with other organic ligands, e.g. benzene-1,2- or benzene-1,3-dioxyacetates [2,3].

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