Journal of Thermal Analysis, Vol. 53 (1998) 285-296

SYNTHESIS AND THERMAL DECOMPOSITION OF COMPLEXES OF RARE EARTH BROMIDES WITH ALANINE

Sun Tong-Shan[1], *Xiao Yu-Mei*[1], *Wang Da-Qing*[2], *Wang Feng-Lian*[1] *and Zhao Yu-Ting*[1]

[1]Department of Chemistry, Shandong University, Jinan, Shandong 250100
[2]Testing Center, Shandong Teacher's University, Jinan, Shandong 250014, People's Republic of China

(Received August 21, 1997; in revised form October 21, 1997)

Abstract

The complexes of rare earth bromides with alanine, $REBr_3 \cdot 3Ala \cdot nH_2O$ (*RE*=Ce, Pr, Sm, Eu, Gd and Tb, n=3; *RE*=Dy and Y, n=2.5 *Ala*=alanine), were prepared and characterized by means of chemical analysis, elemental analysis, molar conductivity, thermogravimetry, IR spectra and X-ray diffraction. The thermal decomposition in N_2 of these complexes was studied by means of TG-DTG techniques from ambient temperature to 1000°C. During heating, the hydrated complexes of Ce, Pr and Y lose waters in one step, but the hydrated complexes of Sm, Eu, Gd, Tb and Dy lose waters in two steps. Then anhydrous complexes lose 2.5 alanine molecules except the complexes of Eu which lose three alanine molecules. Apparently, only the complex of Eu has an intermediate, EuOBr. All complexes finally decompose to oxides.

Keywords: alanine, complexes of rare earth bromides, synthesis, TG-DTG, thermal decomposition

Introduction

With the ever expanding field of application of rare earth elements, the influence of rare earths on the environment and human health has been followed with increasing interest. On the other hand, rare earths have found wide use in wool dyes as dyeing aid [1] and in the study of large biological molecules as probes [2]. α-Amino acids have very important physiological action in the human body. So the studies of rare earth complexes with amino acids will provide basic data for exploring the role of rare earths in the metabolism in the human body and their biological effect. In recent decades efforts have been made to prepare and analyze rare earth complexes with amino acids [3–13]. Among them, the studies of complexes of rare earth bromides with amino acids are rare [12–13]. In pre-

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

vious work, we have prepared and characterized these complexes $REBr_3 \cdot 3Ala \cdot 3H_2O$ (*RE*=La and Nd, *Ala*=alanine) [12]. In this work, we prepared and characterized eight complexes, $REBr_3 \cdot 3Ala \cdot nH_2O$ (*RE*=Ce, Pr, Sm, Eu, Gd and Tb, n=3; *RE*=Dy and Y, n=2.5; *Ala*=alanine). The thermal decomposition of these complexes was studied under non-isothermal conditions by means of TG-DTG techniques.

Experimental

Purity of reagents and preparation of the complexes

The purities of the rare earth oxides were better than 99.9 per cent. Alanine was purified by recrystallization. The purified alanine was kept in a desiccator over $CaCl_2$ until its mass became constant.

$REBr_3 \cdot nH_2O$ (n=6 or 7) were prepared as described by Mayer *et al.* [14]. To prepare $REB_3 \cdot 3Ala \cdot nH_2O$ (n=3 or 2.5), $REBr_3 \cdot nH_2O$ and alanine (in a molar ratio of 1:3) were dissolved in distilled water, and the solution concentrated at a constant temperature of 50°C. The crystals obtained were filtered off, washed with ether and then acetone, dried over 50% H_2SO_4 to constant mass. The resulting complexes were $REBr_3 \cdot 3Ala \cdot nH_2O$ (n=3 or 2.5).

Analysis of the complexes

The rare earth contents of the complexes were determined by EDTA titration, and the Br^- contents were determined by means of the Volhard method. C, H and N contents were determined with a Perkin-Elmer 240°C Elemental Analyzer.

Physical measurements

The IR spectra of the complexes were recorded with a Nicolet Model FTIR5DX Spectrophotometer. The samples were mounted as mulls in KBr discs and examined between 4000 and 400 cm^{-1}.

The X-ray powder diffraction patterns of the complexes were obtained with a X-ray Diffractometer (D/Max-rA, Rigaku, Japan) using copper radiation and a nickel filter.

The molar conductances were determined with a DDS-11A Model Conductometer (made in China) at 25°C.

TG-DTG experimental equipment and conditions

TG-DTG experiments were carried out on a Perkin-Elmer TGA 7 Thermogravimetric Analyzer, in a N_2 atmosphere (40 ml min^{-1}) and a heating rate of 10°C min^{-1}. The sample mass was between 4–9 mg.

Table 1 Results of analysis and molar conductances of the complexes (theoretical values in parentheses)

[a]Complex	RE%	Br%	C%	H%	N%	Molar cond./ Ω^{-1} cm^2 mol^{-1}
$CeBr_3 \cdot 3L \cdot 3H_2O$	19.73(19.98)	33.75(34.19)	15.11(15.42)	3.73(3.88)	5.77(5.99)	369.6
$PrBr_3 \cdot 3L \cdot 3H_2O$	20.06(20.07)	33.90(34.15)	15.42(15.40)	3.72(3.88)	6.03(5.99)	367.1
$SmBr_3 \cdot 3L \cdot 3H_2O$	21.04(21.14)	33.51(33.70)	15.06(15.20)	3.66(3.84)	6.01(5.91)	372.2
$EuBr_3 \cdot 3L \cdot 3H_2O$	21.37(21.31)	33.59(33.62)	15.14(15.16)	3.60(3.82)	5.81(5.89)	362.2
$GdBr_3 \cdot 3L \cdot 3H_2O$	21.64(21.89)	32.99(33.37)	15.28(15.05)	3.80(3.82)	5.70(5.85)	376.8
$TbBr_3 \cdot 3L \cdot 3H_2O$	21.61(22.07)	32.70(33.29)	14.98(15.01)	3.75(3.78)	5.60(5.84)	384.6
$DyBr_3 \cdot 3L \cdot 2.5H_2O$	22.62(22.74)	33.13(33.55)	14.78(15.13)	3.50(3.64)	6.00(5.88)	379.9
$YBr_3 \cdot 3L \cdot 2.5H_2O$	13.53(13.87)	36.35(37.40)	16.76(16.86)	4.14(4.06)	6.46(6.55)	359.6

[a]*L*=alanine

Table 2 Wavenumbers (cm^{-1}) of some group vibrations of the complexes

Approximate description of mode	Vibrations of NH_3^+ group of Ala			rock	Vibration of $-COO^-$ group Ala				Vibration of $-CH_3$ group of Ala			Vibration of –OH group of water
	stretch	asymmetric bend	symmetric bend		asymmetric stretch	symmetric stretch	bend	rock	asymmetric bend	symmetric bend	stretch	stretch
Ala	3087.3mb[b]	1623.8s	1528.3s	1236.8m 1114.6s	1593.3s	1409.8s	770.5m	646.4m	1452.8s	1354.8s	2922.9m	–
$CeBr_3{\cdot}3L^a{\cdot}3H_2O$	–	1615.8s	–	1203.1m 1107.7m	1562.2s	1433.0s	767.8m	657.2m	1467.4s	1355.4s	2984.3mb	3364.8mb
$PrBr_3{\cdot}3L{\cdot}3H_2O$	3072.0m	1615.9s	–	1202.8m 1107.2m	1564.0s	1432.6s	767.6m	656.5m	1467.0s	1355.0s	2984.7mb	3373.7mb
$SmBr_3{\cdot}3L{\cdot}3H_2O$	3012.7s	1677.1s	–	1203.5m 1118.8m	1593.7s	1428.6s	767.0m	655.4m	1479.8s	1349.4s	–	3420.4sb
$EuBr_3{\cdot}3L{\cdot}3H_2O$	3000.8s	1682.7s	–	1200.1m 1115.0m	1597.6s	1427.7s	766.7m	653.0m	1476.9s	1348.3s	–	3420.3sb
$GdBr_3{\cdot}3L{\cdot}3H_2O$	3006.3s	1688.1s	–	1199.0m 1115.6m	1604.0s	1426.0s	765.4m	–	1477.3s	1349.0s	2943.8s	3405.6sb
$TbBr_3{\cdot}3L{\cdot}3H_2O$	3003.5s	1690.4s	–	1198.6m 1115.4m	1604.4s	1425.7s	765.1m	–	1476.7s	1350.1s	2940.8s	3406.9sb
$DyBr_3{\cdot}3L{\cdot}2.5H_2O$	3001.2mb	1690.8m	–	1197.3m 1117.0m	1608.6s	1427.5s	765.6m	–	1476.9s	1347.5m	2939.7m	3408.2mb
$YBr_3{\cdot}3L{\cdot}2.5H_2O$	3003.2mb	1694.6m	–	1198.2m 1116.5m	1611.1s	1428.9s	766.3m	642.9m	1477.3s	1354.6m	2938.8m	3406.6mb

[a] L=alanine

[b] Intensity of peaks: s-strong, m-medium; sb-strong, broad; mb-medium, broad

Results and discussion

Analysis of the complexes

The results of analysis and molar conductance values of the complexes are given in Table 1. The formula masses of the complexes of Ce, Pr, Sm, Eu, Gd and Tb agree with the general formula $REBr_3 \cdot 3Ala \cdot 3H_2O$, but for the complexes of Dy and Y agree with the general formula $REBr_3 \cdot 3Ala \cdot 2.5H_2O$.

Physical measurements

The IR wavenumbers of some group vibrations of the complexes are listed in Table 2.

The results indicate that alanine retains its zwitterionic structure in its rare earth complexes (since the peak of symmetric bond vibration of the NH_3^+ group of alanine is weak, very often it does not appear [5]). This excludes the possibility of the coordination of nitrogen to the rare earth ions. There remains the possibility of attachment of the carboxylic group of alanine to the rare earth ions. In

Table 3 X-ray diffraction data of $PrBr_3 \cdot 3Ala \cdot 3H_2O$, $PrBr_3 \cdot 6H_2O$ and alanine

$PrBr_3 \cdot 3Ala \cdot 3H_2O$		$PrBr_3 \cdot 6H_2O$		Alanine	
2θ / °	I/I_0	2θ / °	I/I_0	2θ / °	I/I_0
5.454	11.15	10.273	54.5	14.630	4.8
8.189	100.0	12.604	32.7	16.347	9.9
11.082	35.0	13.070	15.6	20.779	100.0
12.191	34.0	16.207	18.9	29.609	11.6
17.830	35.0	19.294	26.4	30.666	6.5
19.254	32.7	20.174	74.9	33.155	13.7
20.813	16.1	21.442	100.0	34.870	4.3
21.594	20.6	22.320	15.0	37.237	2.7
22.819	26.7	25.810	14.1	43.726	1.6
23.233	13.0	27.439	27.1	45.205	1.3
25.647	21.9	28.209	42.1		
29.270	14.3	31.836	25.4		
30.884	10.0	33.116	18.3		
33.871	16.4	35.513	34.6		
34.382	6.9	40.007	16.8		
		45.506	10.8		

the complexes of Ce and Pr the asymmetric bends show a red shift, but in the complexes of Sm, Eu, Gd, Tb, Dy and Y, the asymmetric bends exhibit an ultraviolet shift. This indicates that in the complexes the effects of hydrogen bond formation are different [5].

In free alanine, $\Delta\nu(COO^-)=\nu_{as}(COO^-)-\nu_s(COO^-)=d183.5\ cm^{-1}$; in complexes of alanine, $\Delta\nu=129.2–182.2\ cm^{-1}$. The decrease in $\Delta\nu(COO^-)$ indicates that in the

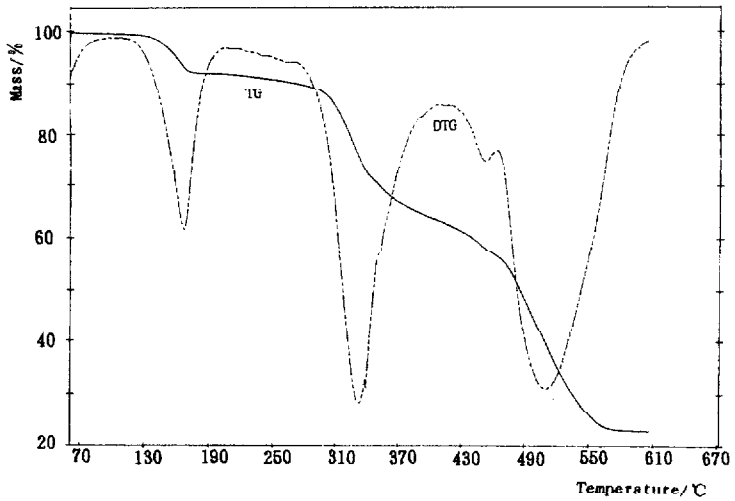

Fig. 1 TG-DTG curves of $CeBr_3{\cdot}3Ala{\cdot}3H_2O$

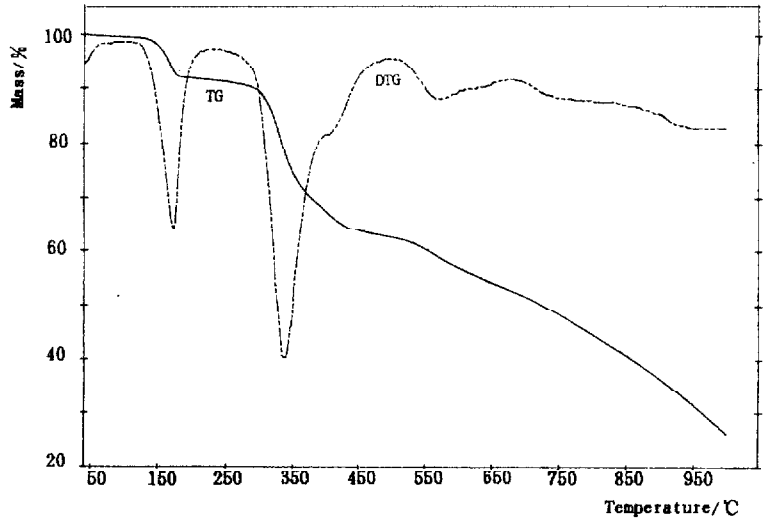

Fig. 2 TG DTG curves of $PrBr_3{\cdot}3Ala{\cdot}3H_2O$

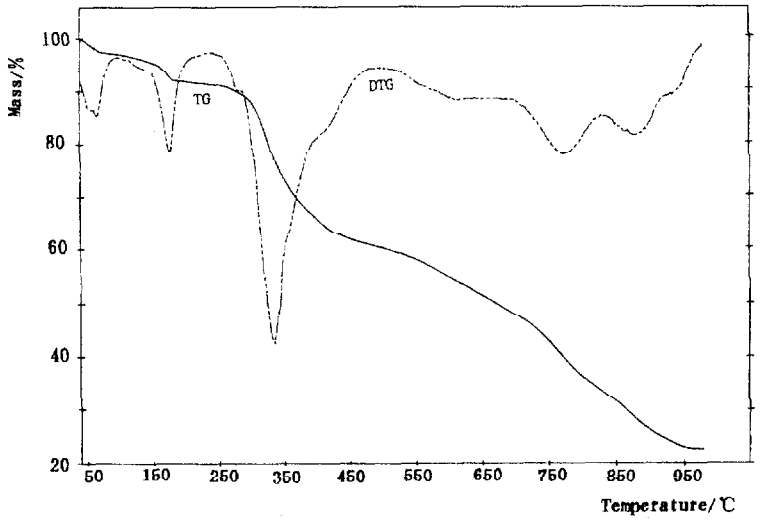

Fig. 3 TG-DTG curves of $SmBr_3 \cdot 3Ala \cdot 3H_2O$

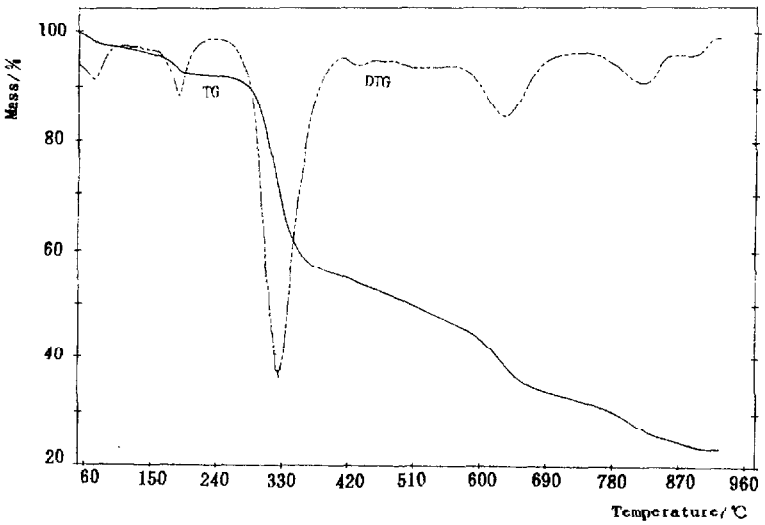

Fig. 4 TG-DTG curves of $EuBr_3 \cdot 3Ala \cdot 3H_2O$

complexes the two oxygens of $-COO^-$ have higher symmetry and the two oxygens are coordinated to the rare earth ions.

The stretch of NH_3^+ in the alanine complexes has a red shift. In free alanine, ν_{NH}=3087.3 cm^{-1}; in complexes of alanine, ν_{NH}=3072.0–3000.8 cm^{-1}. The smaller shifts (15.3 cm^{-1}–86.5 cm^{-1}) in the complexes of alanine may be due to the formation of hydrogen bonds between alanine and water in the complexes [5, 15].

The O–H stretch of the water molecules in these complexes is observed at 3364.8–3420.4 cm^{-1}. This shows that these water molecules are hydrogen-bonded [5].

As an example, the X-ray diffraction data of $PrBr_3 \cdot 3Ala \cdot 3H_2O$, alanine, and $PrBr_3 \cdot 6H_2O$ are listed in Table 3. The X-ray diffraction results show that these complexes of rare earth bromides with alanine can be divided into two groups ac-

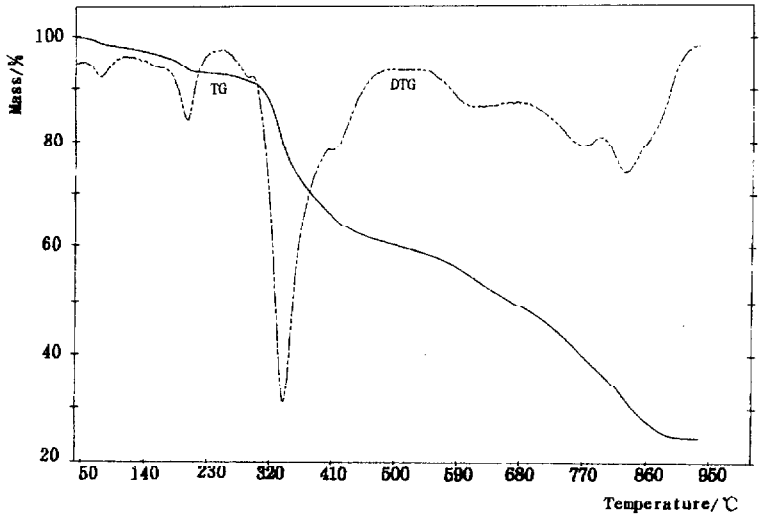

Fig. 5 TG-DTG curves of $GdBr_3 \cdot 3Ala \cdot 3H_2O$

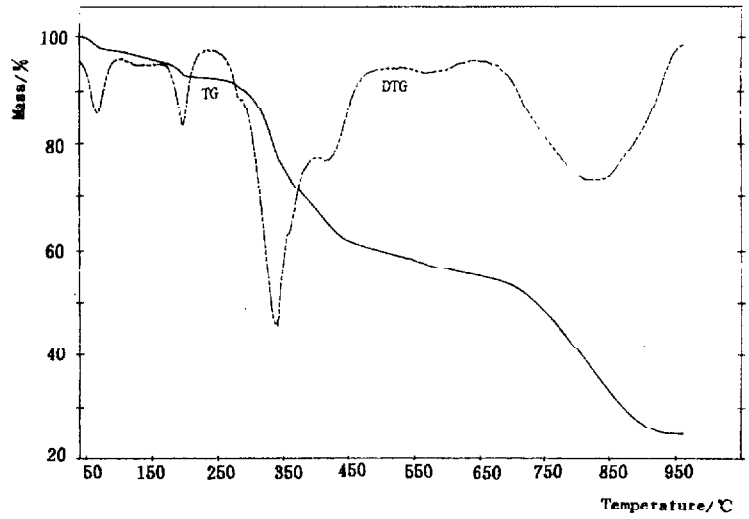

Fig. 6 TG-DTG curves of $TbBr_3 \cdot 3Ala \cdot 3H_2O$

cording to their structures. The first group includes the complexes of Ce, Pr, Sm and Eu, the second group those of Gd, Td, Dy and Y. The results also indicate that the prepared complexes $REBr_3 \cdot 3Ala \cdot nH_2O$ are not simple mixtures of $REBr_3 \cdot nH_2O$ and alanine, but new substances.

The molar conductance values of aqueous solutions (10^{-3} M) of the ten complexes were observed in the range of 359.6–384.6 Ω^{-1} cm^2 mol^{-1}, which indicates

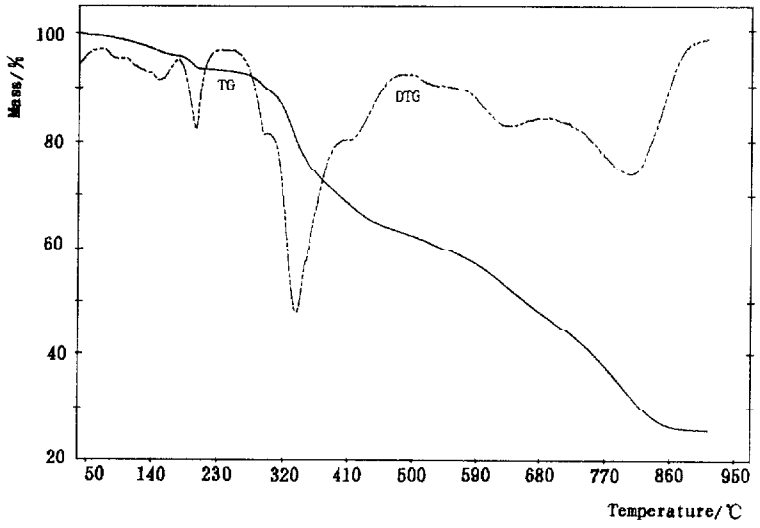

Fig. 7 TG-DTG curves of $DyBr_3$ 3Ala 2.5H_2O

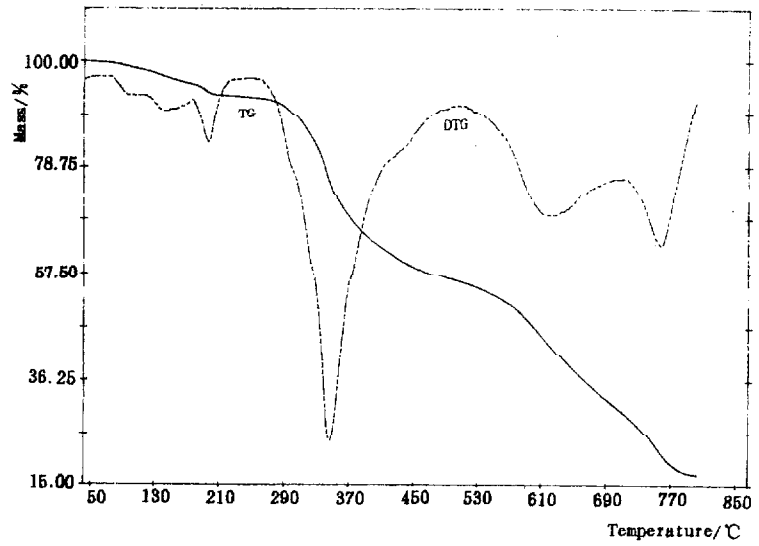

Fig. 8 TG-DTG curves of $YBr_3 \cdot 3Ala \cdot 2.5H_2O$

Table 4 Thermal decomposition data of $REBr_3 \cdot 3Ala \cdot nH_2O$[a]

Decomp. step of complex		T_{range}/°C	Mass loss/%	
			calcd.	found
$CeBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow CeBr_3 \cdot 3L$	104–209	7.71	7.80
$CeBr_3 \cdot 3L$	$\rightarrow CeBr_3 \cdot 0.5L$	209–422	31.76	29.74
$CeBr_3 \cdot 0.5L$	$\rightarrow CeO_2$	422–578	35.98	38.97
$PrBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow PrBr_3 \cdot 3L$	86–216	7.70	7.96
$PrBr_3 \cdot 3L$	$\rightarrow PrBr_3 \cdot 0.5L$	216–505	31.73	29.39
$PrBr_3 \cdot 0.5L$	$\rightarrow Pr_6O_{11}$	505–998	36.33	36.16
$SmBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow SmBr_3 \cdot 3L \cdot 2H_2O$	41–101	2.53	2.95
$SmBr_3 \cdot 3L \cdot 2H_2O$	$\rightarrow SmBr_3 \cdot 3L$	101–229	5.07	5.66
$SmBr_3 \cdot 3L$	$\rightarrow SmBr_3 \cdot 0.5L$	229–499	31.31	31.26
$SmBr_3 \cdot 0.5L$	$\rightarrow Sm_2O_3$	499–958	36.58	37.74
$EuBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow EuBr_3 \cdot 3L \cdot 3H_2O$	51–106	2.53	2.79
$EuBr_3 \cdot 3L \cdot 2H_2O$	$\rightarrow EuBr_3 \cdot 3L$	106–233	5.07	5.09
$EuBr_3 \cdot 3L$	$\rightarrow EuBr_3$	233–415	37.49	36.87
$EuBr_3$	$\rightarrow EuOBr$	415–730	20.17	22.64
$EuOBr$	$\rightarrow Eu_2O_3$	730–906	10.09	9.11
$GdBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow GdBr_3 \cdot 3L \cdot 2H_2O$	41–115	2.51	2.21
$GdBr_3 \cdot 3L \cdot 2H_2O$	$\rightarrow GdBr_3 \cdot 3L$	115–245	5.02	5.04
$GdBr_3 \cdot 3L$	$\rightarrow GdBr_3 \cdot 0.5L$	245–482	31.01	31.92
$GdBr_3 \cdot 0.5L$	$\rightarrow Gd_2O_3$	482–908	36.23	36.04
$TbBr_3 \cdot 3L \cdot 3H_2O$	$\rightarrow TbBr_3 \cdot 3L \cdot 2H_2O$	41–100	2.50	2.75
$TbBr_3 \cdot 3L \cdot 2H_2O$	$\rightarrow TbBr_3 \cdot 3L$	100–236	5.01	4.87
$TbBr_3 \cdot 3L$	$\rightarrow TbBr_3 \cdot 0.5L$	236–497	30.94	32.49
$TbBr_3 \cdot 0.5L$	$\rightarrow Tb_4O_7$	497–938	35.59	35.09
$DyBr_3 \cdot 3L \cdot 2.5H_2O$	$\rightarrow DyBr_3 \cdot 3L \cdot H_2O$	43–179	3.78	4.12
$DyBr_3 \cdot 3L \cdot H_2O$	$\rightarrow DyBr_3 \cdot 3L$	179–238	2.52	2.68
$DyBr_3 \cdot 3L$	$\rightarrow DyBr_3 \cdot 0.5L$	238–492	31.17	30.46
$DyBr_3 \cdot 0.5L$	$\rightarrow Dy_2O_3$	492–883	36.43	36.95
$YBr_3 \cdot 3L \cdot 2.5H_2O$	$\rightarrow YBr_3 \cdot 3L$	46–246	7.03	7.03
$YBr_3 \cdot 3L$	$\rightarrow YBr_3 \cdot 0.5L$	246–482	34.75	36.07
$YBr_3 \cdot 0.5L$	$\rightarrow Y_2O_3$	482–793	40.6	39.58

[a] *RE*=Ce, Pr, Sm, Eu, Gd, Tb, Dy and Y; *L*=alanine

that these complexes are electrolytes of the 1:3 type and all bromide ions are situated in the outer sphere.

Thermal decomposition processes

The TG-DTG curves of the $REBr_3 \cdot 3Ala \cdot nH_2O$ complexes are shown in Figs 1–8. The thermal decomposition data of these complexes are listed in Table 4. The thermal decomposition processes of the complexes derived from the TG-DTG curves in the given temperature range may be described by the following sequences:

$$REBr_3 \cdot 3Ala \cdot 3H_2O \xrightarrow[-3H_2O]{I} REBr_3 \cdot 3Ala \xrightarrow[-2.5Ala]{II} REBr_3 \cdot 0.5Ala \xrightarrow{III} \begin{matrix} REO_2 \ (RE{=}Ce) \\ RE_6O_{11} \ (RE{-}Pr) \end{matrix} \quad (1)$$

$$REBr_3 \cdot 3Ala \cdot 3H_2O \xrightarrow[-H_2O]{I} REBr_3 \cdot 3Ala \cdot 2H_2O \xrightarrow[-2H_2O]{II} REBr_3 \cdot 3Ala \xrightarrow[-2.5Ala]{III} REBr_3 \cdot 0.5Ala \xrightarrow{IV} \begin{matrix} RE_2O_3 \ (RE{=}Sm, Gd) \\ RE_4O_7 \ (RE{=}Tb) \end{matrix} \quad (2)$$

$$EuBr_3 \cdot 3Ala \cdot 3H_2O \xrightarrow[-H_2O]{I} EuBr_3 \cdot 3Ala \cdot 2H_2O \xrightarrow[-2H_2O]{II} EuBr_3 \cdot 3Ala \xrightarrow[-3Ala]{III} EuBr_3 \xrightarrow{IV} EuOBr \xrightarrow{V} Eu_2O_3 \quad (3)$$

$$DyBr_3 \cdot 3Ala \cdot 2.5H_2O \xrightarrow[-1.5H_2O]{I} DyBr_3 \cdot 3Ala \cdot H_2O \xrightarrow[-H_2O]{II} DyBr_3 \cdot 3Ala \xrightarrow[-2.5Ala]{III} DyBr_3 \cdot 0.5Ala \xrightarrow{IV} Dy_2O_3 \quad (4)$$

$$YBr_3 \cdot 3Ala \cdot 2.5H_2O \xrightarrow[-2.5H_2O]{I} YBr_3 \cdot 3Ala \xrightarrow[-2.5Ala]{II} YBr_3 \cdot 0.5Ala \xrightarrow{III} Y_2O_3 \quad (5)$$

Among these complexes apparently only the complexes of La and Eu go through the intermediate EuOBr or LaOBr.

Some of these complexes lose water molecules in one step, others in two steps. This may be due to the different effects of hydrogen bonding in these complexes. Alanine in the complexes decomposes in different steps except for the complex of Eu. This indicates that the coordinated states of alanine are different in the complexes [15].

References

1 Fang Jian-Yun, Jin Tian-Zhu, Xu Guang-Xian and Xie Jun, J. Chinese Rare Earth Society, 4 (1983) 18.
2 J. Reuben, Handbook on the Physics and Chemistry of Rare Earth, Elsevier, Amsterdam 3 (1979) 515.
3 B. S. Mathur and T. S. Srivastava, J. Inorg. Nucl. Chem., 32 (1970) 3277.
4 Wu Bo-Neng, Zhu Jia-Quing and Yang Yan-Sheng, J. Zhongshan Univ. Natural Sciences Edn. (P. R. China), 29 (1990) 199.
5 Wu Jigui, Deng Ruwen, Wang Liufang and Yu Ming, J. Lanzhou Univ. Natural Sciences Edn. (P. R. China), 20 (1984) 69.
6 Chao Jin-Rong, Wang Zhe-Ming and Fu Chu-Jing, J. Chinese Rare Earth Society, 6 (1988) 19.
7 Shong Di-Sheng, Fu Cao-Ran and Liu Yi-Lun, J. Northwest Univ. Natural Sciences Edn. (P.R. China), 20 (1990) 51.
8 Jin Tian-Zhu, Sun Xiao-Dong and Xu Guang-Xian, J. Chinese Rare Earth Society, 8 (1990) 193.
9 Jin Tian-Zhu, Yang Chang-Quing, Yang Quing-Chuan, Wu Jing-Guang and Xu Guang-Xian, Chem. J. Chinese Univ., 10 (1989) 118.
10 Jin Tian-Zhu, Gao-Shong, Huang Chun-Hui, Han Yu-Zheng and Xu Guang-Xian, J. Chinese Rare Earth Society, 5 (1987) 1.
11 J. Legendziewicz, E. Huskowska, G. Argay and A. Waskowska, Inorg. Chim. Acta, 95 (1984) 57.
12 Tongshan Sun, Yuting Zhao, Jiahui Jin and Daquing Wang, J. Thermal Anal., 45 (1995) 317.
13 M. C. Lavin Guemes, M. C. Lequerica Gomez, J. G. Ribas Bernat and F. J. Garay Sanchez, Anales Quim., 73 (1977) 1292.
14 I. Mayer and S. Zolotov, J. Inorg. Nucl. Chem., 27 (1965) 1905.
15 Ma Ai-Zheng, Li Lai-Ming and Xi Shi-Quan, Chinese J. Anal. Chem., 21 (1993) 105.