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THE SYNTHESIS AND THERMAL DECOMPOSITION OF COMPLEX SALTS OF LANTHANIDE BROMIDES WITH HEXAMETHYLENETETRAMINE

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ABSTRACT

New complex salts of lanthanide bromides with hexamethylenetetramine of general formula $LnBr_3 \cdot 2HMTA \cdot nH_2O$ (where Ln ≡ La, Nd, Gd, Dy, Er; HMTA ≡ hexamethylenetetramine ($N_4(CH_2)_6$); $n = 0–12$) have been obtained by crystallization and thermal decomposition. The stoichiometric compositions of the salts have been determined. On the basis of analysis of thermal curves, diffractograms and quantitative analysis of solid thermal decomposition products, the mechanism of the thermal dehydration reaction and further thermal decomposition has been established.

INTRODUCTION

In a previous study [1], chloride salts of lanthanum, praseodymium, neodymium, gadolinium, dysprosium and erbium with hexamethylene-tetramine (HMTA) of various degrees of dehydration were obtained. The thermal dehydration reactions of the chloride 12-, 10- and 8-hydrous salts of the lanthanides under investigation were determined from the findings of a thermal decomposition study [2], and changes occurring in the structure of the coordination sphere along with the dehydration process were determined on the basis of IR spectra (4000–200 cm^{-1}) and Raman spectra (3000–300 cm^{-1}) [1].

The present paper describes the synthesis of bromide 12-, 10- and 8-hydrous salts of lanthanum, neodymium, gadolinium, dysprosium and erbium with HMTA, and the conditions of formation of salts of lower hydration degree obtained by the thermal method. An analysis of the thermal curves of the salts obtained, heated up to 1000 °C, is reported, and a mechanism is proposed for the thermal dehydration reaction and further decomposition of the salts, on the basis of thermal studies, diffractograms and quantitative analysis.

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EXPERIMENTAL

Thermal curves were obtained using a MOM Budapest type OD-102 derivatograph. The compounds were heated over the temperature range 20–1000 °C in air, in the presence of α-Al_2O_3 as reference material. The heating rate was 5 °C min^{-1}, TG sensitivity was 100 mg, DTA and DTG sensitivity was 0.1, and the weighed samples were of 100 mg each. The diffractograms for $2\theta = 2–70°$ were obtained using a Russian DRON-1 diffractograph with a nickel filter and Cu $K\alpha$ radiation.

For synthesis, we used: HMTA ($N_4(CH_2)_6$), analytically pure, from P.O.Ch., Gliwice; lanthanide oxides (La_2O_3, Nd_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3), 99.9% pure, from Koch-Light Laboratory and Fluka A.G.; anhydrous alcohol and an 80% alcohol–water solution (v/v); hydrobromic acid solution HBr(2 + 1).

Preparation

Bromide salts of lanthanides with HMTA of varying degrees of hydration were obtained by crystallization from water solutions or alcohol solutions and by thermal dehydration.

Crystallization from water solutions

Solutions of lanthanide bromides were obtained by dissolving in HBr(2 + 1) the following quantities (in g) of lanthanide oxides at high temperatures: La_2O_3, 1.62; Nd_2O_3, 1.68; Gd_2O_3, 1.81; Dy_2O_3, 1.86; Er_2O_3, 1.91. HBr(2 + 1) solution was added dropwise so that after dissolution of the lanthanide bromides the pH of the solution was 6. The lanthanide bromide solutions were then poured into saturated water solutions containing 2.8 g of HMTA each. During the intensive mixing and cooling of the samples (in a stream of cold water), precipitates were formed. These precipitates were separated from the solutions by filtering through filter paper and then dried in air at room temperature. The analysis results, which were used to determine the stoichiometric composition of the compounds obtained, are presented in Tables 1 and 2.

Crystallization from ethyl alcohol

Solutions of lanthanide bromides were prepared as above, and to these were added solutions containing 2.8 g of HMTA each, dissolved in the mixture of rectified alcohol (16 ml) and water (4 ml). During the cooling and intensive mixing, precipitates were formed, which were filtered through filter paper and dried at room temperature.

The analysis results for the compounds obtained in this way are presented in Tables 1 and 2.

TABLE 1

Analytical data for the lanthanide bromides obtained

Compound	Ln	Temperature (°C)	Metal (%)		Br (%)	
			Calc.	Found	Calc.	Found
$LnBr_3 \cdot 2HMTA \cdot 12H_2O$	La	198	15.88	15.73	27.41	27.67
	Nd	205	16.39	16.93	27.24	28.35
	Gd	201	17.62	17.76	26.84	25.34
	Dy	189	18.09	17.75	26.69	26.68
	Er	196	18.53	18.56	26.55	27.44
$LnBr_3 \cdot 2HMTA \cdot 10H_2O$	La	192	16.56	16.74	28.58	28.79
	Nd	213	17.09	17.28	28.40	28.69
	Gd	206	18.36	18.19	27.97	28.63
	Dy	195	18.85	18.64	27.80	29.98
$LnBr_3 \cdot 2HMTA \cdot 8H_2O$	La	204	17.31	16.96	29.87	30.17
	Nd	218	17.85	17.31	29.67	30.51
	Gd	208	19.16	18.77	29.20	29.30
	Dy	198	19.67	18.89	29.01	29.77

If solutions containing 2.8 g of HMTA in the mixture of anhydrous alcohol (16 ml) and water (4 ml) were added to the lanthanide bromide solutions (obtained in the manner described above), the compositions of the salts obtained were as reported in Tables 1 and 2.

TABLE 2

Analytical carbon, hydrogen, nitrogen data for the lanthanide bromides obtained

Compound	Ln	C (%)		H (%)		N (%)	
		Calc.	Found	Calc.	Found	Calc.	Found
$LnBr_3 \cdot 2HMTA \cdot 12H_2O$	La	16.47	17.67	5.49	5.90	12.81	12.94
	Nd	16.37	17.08	5.46	5.46	12.73	12.80
	Gd	16.13	16.76	5.38	5.41	12.54	12.68
	Dy	16.03	16.08	5.34	5.65	12.47	12.68
	Er	15.95	16.20	5.32	5.31	12.40	11.87
$LnBr_3 \cdot 2HMTA \cdot 10H_2O$	La	17.17	17.56	5.25	5.58	13.36	13.12
	Nd	17.06	17.08	5.21	5.44	13.27	12.90
	Gd	16.80	17.68	5.13	5.34	13.07	12.90
	Dy	16.70	17.40	5.10	5.63	12.99	12.64
$LnBr_3 \cdot 2HMTA \cdot 8H_2O$	La	17.94	17.09	4.98	5.06	13.96	12.99
	Nd	17.82	17.22	4.95	5.12	13.86	12.80
	Gd	17.54	17.56	4.87	4.90	13.64	13.36
	Dy	17.43	17.58	4.84	4.89	13.57	13.05

TABLE 3

Analytical data for the compounds obtained by thermal dehydration

Compound	Temperature (°C)	Ln (%) Calc. (Found)	Br (%) Calc. (Found)	C (%) Calc. (Found)	N (%) Calc. (Found)	H (%) Calc. (Found)
$LaBr_3 \cdot 2HMTA \cdot 2H_2O$	130	20.00 (19.22)	34.51 (35.41)	20.73 (20.78)	16.12 (16.36)	4.03 (4.07)
$LaBr_3 \cdot 2HMTA \cdot H_2O$	110	20.53 (18.42)	35.43 (32.22)	21.28 (21.09)	16.55 (16.48)	3.55 (3.95)
$NdBr_3 \cdot 2HMTA \cdot 4H_2O$	130	19.60 (19.12)	32.57 (32.17)	19.56 (19.75)	15.21 (14.41)	4.34 (4.28)
$NdBr_3 \cdot 2HMTA \cdot 2H_2O$	140	20.61 (21.43)	34.25 (33.23)	20.57 (20.73)	16.00 (14.25)	4.00 (4.02)
$NdBr_3 \cdot 2HMTA \cdot H_2O$	180	21.15 (22.35)	35.15 (32.86)	21.12 (29.30)	16.43 (16.24)	3.52 (3.71)

Thermal method

Salts of intermediate degrees of hydration were obtained by the thermal method. The 12-, 10- and 8-hydrous compounds were heated in a drier to the

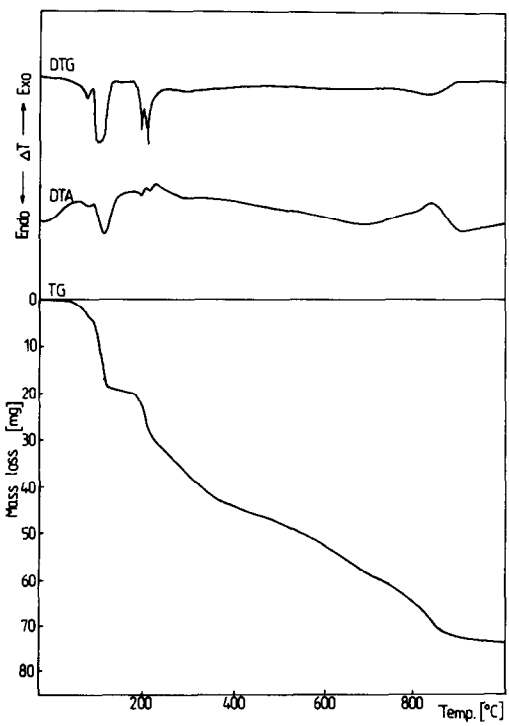

Fig. 1. Thermal curves of $LaBr_3 \cdot 2HMTA \cdot 12H_2O$ salt.

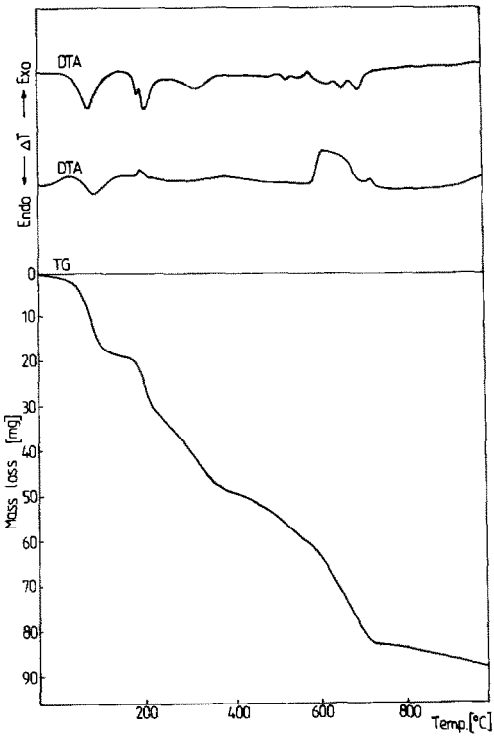

Fig. 2. Thermal curves of $ErBr_3 \cdot 2HMTA \cdot 12H_2O$ salt.

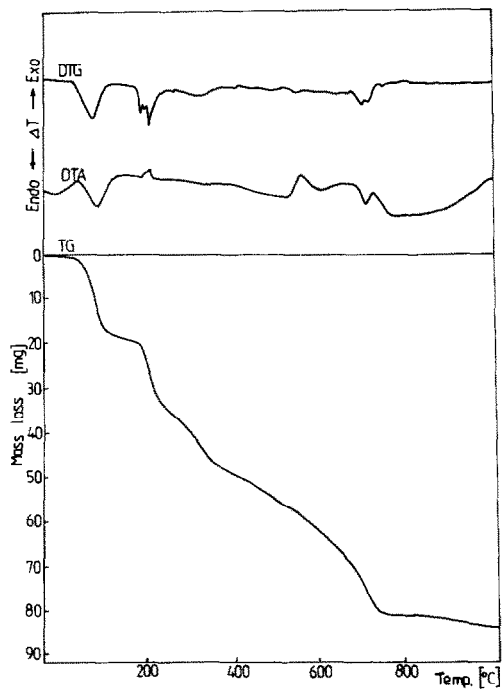

Fig. 3. Thermal curves of $DyBr_3 \cdot 2HMTA \cdot 10H_2O$ salt.

temperatures that had been determined from the thermal curves (up to the temperatures corresponding to particular stages of thermal dehydration). The temperatures of formation of particular salts are given in Tables 4, 6 and 8. Analysis results for the lanthanum and neodymium salts obtained by thermal dehydration are summarized in Table 3.

Chemical analysis

Quantitative analysis of the compounds obtained was carried out by various methods: lanthanides were determined by complexometry with ascorbic acid in the presence of xylene orange [3], bromides by the Mohr method, and nitrogen, carbon and hydrogen by elemental analysis.

Thermal studies

Thermal curves were obtained for all the salts over the temperature range 20–1000 °C . Figure 1 shows thermal curves for $LaBr_3 \cdot 2HMTA \cdot 12H_2O$.

TABLE 4

Determined and calculated mass losses for the thermal decomposition reactions of $LnBr_3 \cdot 2HMTA \cdot 12H_2O$ (Ln ≡ La, Nd, Gd, Dy, Er)

Compound	Temperature (°C)	Mass loss (%)			Compounds obtained (Z ≡ $LnBr_3 \cdot 2HMTA$) [a]
		Determined		Calc.	
		TG	Decomp.		
$LaBr_3 \cdot 2HMTA \cdot 12H_2O$	90	4.5	–	4.12	$Z \cdot 10H_2O$
	130	21.0	20.63	10.58	$Z \cdot 2H_2O$
	180	25.0	–	24.70	Z *
	900	81.0	77.17	81.37	La_2O_3
$NdBr_3 \cdot 2HMTA \cdot 12H_2O$	130	16.3	16.38	16.36	$Z \cdot 4H_2O$
	180	18.0	18.90	18.41	$Z \cdot 3H_2O$
	220	24.55	–	24.50	Z *
	950	81.56	80.05	80.80	Nd_2O_3
$GdBr_3 \cdot 2HMTA \cdot 12H_2O$	160	16.0	16.55	18.14	$Z \cdot 3H_2O$
	218	24.0	–	24.19	Z *
	900	87.0	78.44	79.70	Gd_2O_3
$DyBr_3 \cdot 2HMTA \cdot 12H_2O$	140	18.5	18.20	18.03	$Z \cdot 3H_2O$
	190	24.0	–	24.05	Z *
	850	84	78.93	79.24	Dy_2O_3
$ErBr_3 \cdot 2HMTA \cdot 12H_2O$	160	18.0	17.95	17.94	$Z \cdot 3H_2O$
	195	24.0	–	23.92	Z *
	800	82	78.41	78.82	Er_2O_3

[a] Z *: This compound was not isolated, but a mass loss corresponding to the loss of a definite amount of H_2O was calculated from the TG curve.

At 80–90 °C, the DTA and DTG curves for lanthanum salts show a weak endothermic peak overlapped by another distinct peak visible on both the DTA (110 °C) and DTG (100 °C) curves. These transformations are accompanied by a mass loss (calculated from the TG curve) amounting to 21% at 130 °C. The next peaks on the DTA and DTG curves at 180 °C correspond to a mass loss of 3.5%, as determined from the TG curve. Another decomposition process overlaps this reaction, with peaks on both the DTA (198 °C) and DTG (195 °C) curves. At 205 °C, an exothermic peak appears on the DTA curve. At 720 °C, there is a broad peak on the DTA curve (with a maximum at 860 °C), indicating the occurrence of an exothermic reaction.

The TG curve shows continuous mass loss over the temperature range 180–900 °C.

TABLE 5

Thermal analysis data for the decomposition of the 12-hydrous salts

Compound	Peak	Temperature (°C)	
		DTA curve	DTG curve
$LaBr_3 \cdot 2HMTA \cdot 12H_2O$	Endo	90	90
	Endo	105	100
	Endo	180	185
	Endo	198	195
	Exo	205	200
	Exo	860	210
$NdBr_3 \cdot 2HMTA \cdot 12H_2O$	Endo	120	110
	Endo	160	160
	Endo	200	200
	Endo	230	230
	Exo	785	785
$GdBr_3 \cdot 2HMTA \cdot 12H_2O$	Endo	110	100
	Endo	200	205
	Exo	210	218
	Endo	230	230
	Exo	580	785
	Exo	785	
	Endo	900	
$DyBr_3 \cdot 2HMTA \cdot 12H_2O$	Endo	95	95
	Endo	175	170
	Exo	195	190
	Exo	580	
$ErBr_3 \cdot 2HMTA \cdot 12H_2O$	Endo	90	90
	Endo	180	180
	Exo	190	190
	Exo	610	610
	Exo	720	700

TABLE 6

Determined and calculated mass losses for the thermal decomposition reactions of $LnBr_3 \cdot 2HMTA \cdot 10H_2O$ (Ln ≡ La, Nd, Gd, Dy)

Compound	Temperature (°C)	Mass loss (%)			Compounds obtained (Z ≡ $LnBr_3 \cdot 2HMTA$)
		Determined		Calc.	
		TG	Decomp.		
$LaBr_3 \cdot 2HMTA \cdot 10H_2O$	110	19.0	18.93	19.38	$Z \cdot H_2O$
	185	22.5	–	21.46	Z *
	900	–	85.36	81.37	La_2O_3
$NdBr_3 \cdot 2HMTA \cdot 10H_2O$	140	17.0	16.80	17.06	$Z \cdot 2H_2O$
	180	19.0	19.2	19.19	$Z \cdot H_2O$
	900	81.0	79.11	80.06	Nd_2O_3
$GdBr_3 \cdot 2HMTA \cdot 10H_2O$	160	17.0	15.83	16.80	$Z \cdot 2H_2O$
	220	21.0	–	21.0	Z *
	900	78.0	78.63	78.85	Gd_2O_3
$DyBr_3 \cdot 2HMTA \cdot 10H_2O$	150	18.0	17.89	18.79	$Z \cdot H_2O$
	190	20.0	–	20.88	Z *
	900	80.5	78.61	78.36	Dy_2O_3

TABLE 7

Thermal analysis data for the decomposition of the 10-hydrous salts

Compound	Peak	Temperature (°C)	
		DTA curve	DTG curve
$LaBr_3 \cdot 2HMTA \cdot 10H_2O$	Endo	115	
	Endo	185	
	Exo	200	
	Endo	210	
$NdBr_3 \cdot 2HMTA \cdot 10H_2O$	Endo	105	105
	Endo	158	158
	Endo	200	200
	Exo	220	220
	Exo	750	750
$GdBr_3 \cdot 2HMTA \cdot 10H_2O$	Endo	120	110
	Endo	210	120
	Exo	220	
	Exo	780	
	Exo	860	
$DyBr_3 \cdot 2HMTA \cdot 10H_2O$	Endo	98	95
	Endo	195	190
	Exo	205	200
	Exo	550	205
	Endo	700	320
	Endo	760	

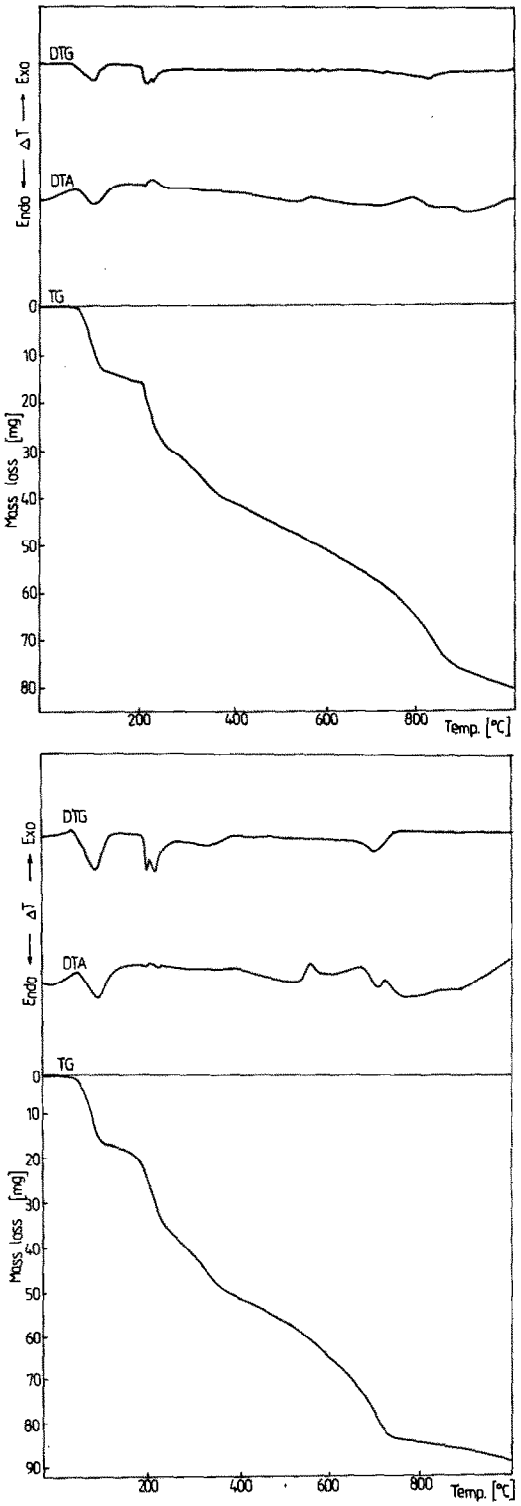

Fig. 4. Thermal curves of (a) $GdBr_3 \cdot 2HMTA \cdot 8H_2O$ and (b) $DyBr_3 \cdot 2HMTA \cdot 8H_2O$ salts.

TABLE 8

Determined and calculated mass losses for the thermal decomposition reactions of $LnBr_3 \cdot 2HMTA \cdot 8H_2O$ (Ln ≡ La, Nd, Gd, Dy)

Compound	Temperature (°C)	Mass loss (%)			Compounds obtained (Z ≡ $LnBr_3 \cdot 2HMTA$)
		Determined		Calc.	
		TG	Decomp.		
$LaBr_3 \cdot 2HMTA \cdot 8H_2O$	105	14.5	14.44	15.70	$Z \cdot H_2O$
	180	18.0	17.85	17.98	Z *
	900	80.0	79.65	79.70	La_2O_3
$NdBr_3 \cdot 2HMTA \cdot 8H_2O$	120	15.5	15.31	15.60	$Z \cdot H_2O$
	160	17.5	17.76	17.82	Z
	800	77.0	78.71	79.18	Nd_2O_3
$GdBr_3 \cdot 2HMTA \cdot 8H_2O$	160	15.0	15.71	15.35	$Z \cdot H_2O$
	210	17.0	–	17.54	Z *
	950	79.0	78.95	77.92	Gd_2O_3
$DyBr_3 \cdot 2HMTA \cdot 8H_2O$	140	17.0	17.13	17.43	Z
	900	81.0	78.90	77.42	Dy_2O_3

TABLE 9

Thermal analysis data for the decomposition of the 8-hydrous salts

Compound	Peak	Temperature (°C)	
		DTA curve	DTG curve
$LaBr_3 \cdot 2HMTA \cdot 8H_2O$	Endo	110	85
	Endo	180	105
	Endo	200	180
	Exo	215	190
	Exo	870	
$NdBr_3 \cdot 2HMTA \cdot 8H_2O$	Endo	95	80
	Endo	140	140
	Exo	180	
	Exo	195	180
	Exo	205	200
	Exo	730	720
$GdBr_3 \cdot 2HMTA \cdot 8H_2O$	Endo	110	110
	Endo	205	205
	Exo	218	218
	Exo	220	705
	Exo	550	
	Exo	790	
$DyBr_3 \cdot 2HMTA \cdot 8H_2O$	Endo	98	95
	Endo	190	190
	Endo	210	210
	Exo	560	705
	Endo	710	
	Endo	780	

TABLE 10

Analytical data for La and Nd compounds heated to 600 °C

Compound	Composition found (%)				
	Metal	Br	C	N	H
$LaBr_3 \cdot 2HMTA \cdot 12H_2O$	34.73	23.77	11.28	3.92	4.07
$NdBr_3 \cdot 2HMTA \cdot 12H_2O$	41.39	26.14	11.43	3.30	3.96
$NdBr_3 \cdot 2HMTA \cdot 10H_2O$	41.82	27.24	11.80	3.74	2.75
$NdBr_3 \cdot 2HMTA \cdot 8H_2O$	41.59	33.89	14.14	4.16	2.17

The 12-hydrous salts of neodymium and gadolinium undergo similar thermal changes, while the salts of dysprosium and erbium show two reaction stages, corresponding to water loss (Stage I at 95 (Dy) and 90 °C (Er); Stage II at 170 (Dy) and 180 °C (Er)). The second decomposition stage is overlapped by peaks indicating an exothermic process (195 °C for Dy and 190 °C for Er). The Tg curves show continuous mass loss.

In the case of the erbium salts (Fig. 2), there are two exothermic peaks on the DTA curve, with maxima at 610 and 720 °C, respectively, associated with mass loss which stabilizes at 800 °C. Data on the thermal changes of 12-hydrous salts are presented in Tables 4 and 5.

The 10-hydrous compounds show similar thermal curves for the dehydration reaction, which takes place in two stages (Stage I at 115 (La), 105 (Nd), 120 (Gd) and 98 °C (Dy); Stage II at 185 (La), 158 (Nd), 210 (Gd) and

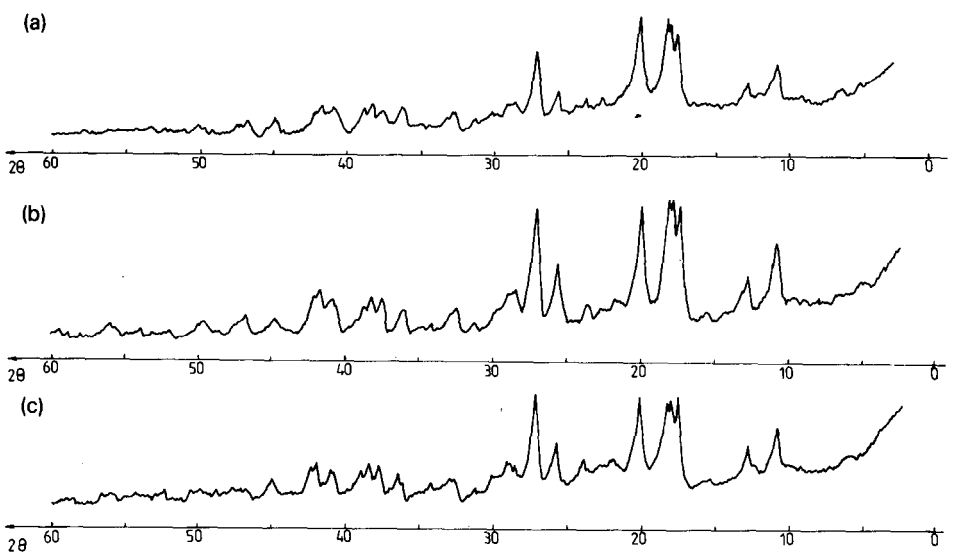

Fig. 5. Diffractograms of (a) $NdBr_3 \cdot 2HMTA \cdot 12H_2O$, (b) $NdBr_3 \cdot 2HMTA \cdot 10H_2O$ and (c) $NdBr_3 \cdot 2HMTA \cdot 8H_2O$ salts.

195 °C (Dy)). The second stage is overlapped by melting of the salts and further decomposition associated with a continuous mass loss up to 900 °C.

In the case of the 10-hydrous salt of dysprosium (Fig. 3), an exothermic peak is observed on the DTA curve (maximum at 550 °C), and two endothermic peaks (700 and 760 °C) on the DTA and DTG curves.

The temperatures of the transformations of the 10-hydrous salts, and associated mass losses, are presented in Tables 6 and 7.

The 8-hydrous salts undergo a one-stage dehydration reaction. The DTA and DTG curves show endothermic peaks at 100–110 °C, and further decomposition occurs from 200 °C, accompanied by a continuous mass loss. The DTA curves for the 8-hydrous salts show peaks indicating exothermic processes, with maxima at 870 (La), 730 (Nd), 550 (Gd) and 560 °C (Dy).

The gadolinium and dysprosium salts (Fig. 4) show DTA and DTG peaks at 790 (Gd) and 710, 780 °C (Dy).

The transformation temperatures for the 8-hydrous compounds, and associated mass losses, are listed in Tables 8 and 9.

As the decomposition of the salts is associated with continuous mass loss from 200 °C, the decomposition products were determined by analysis after the salts had been heated in a muffle furnace to the temperatures at which the exothermic process begins (temperatures taken from DTA curves for particular compounds). Lanthanides were determined by complexometry in the filtrate, after leaching with water with the addition of a few drops of

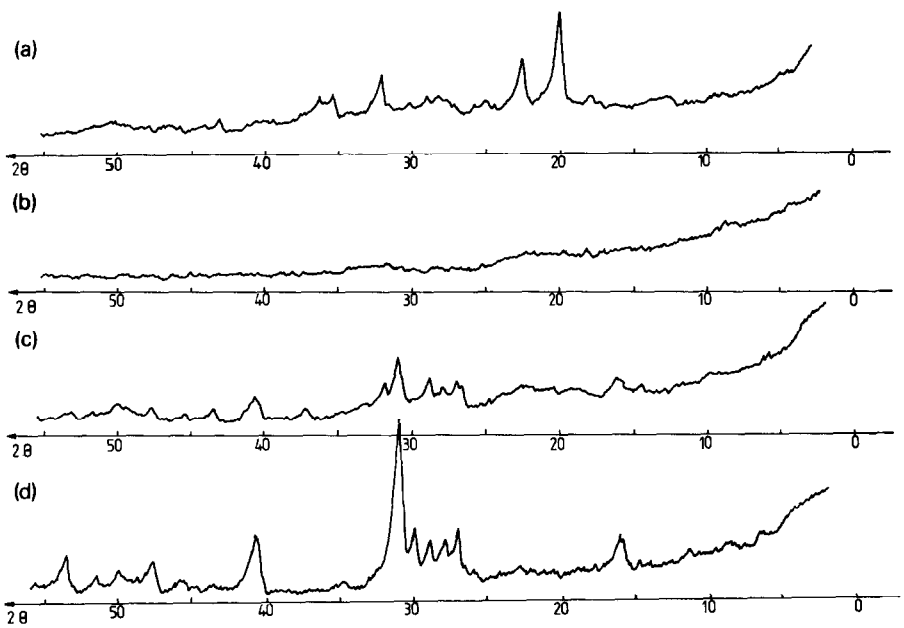

Fig. 6. Diffractograms of $NdBr_3 \cdot 2HMTA \cdot 12H_2O$ salt heated to (a) 140, (b) 600 and (c) 900 °C; and (d) diffractogram of Nd_2O_3.

HNO_3 (earlier tests having shown that the total amount of lanthanide from the sinters passes into solution). Carbon, nitrogen, hydrogen and bromides in some salts were determined by elemental analysis. The results of these determinations are listed in Table 10.

X-ray analysis

Diffractograms were obtained for $NdBr_3 \cdot 2HMTA \cdot 12H_2O$, $NdBr_3 \cdot 2HMTA \cdot 10H_2O$ and $NdBr_3 \cdot 2HMTA \cdot 8H_2O$ (Fig. 5); for the compounds obtained by thermal decomposition (i.e. $NdBr_3 \cdot 2HMTA \cdot 12H_2O$ heated to 140, 600 and 900 °C) and Nd_2O_3 (Fig. 6); and for the $DyBr_3 \cdot 2HMTA \cdot 12H_2O$ salt and the compounds obtained by thermal decomposition (i.e. $DyBr_3 \cdot 2HMTA \cdot 12H_2O$ heated to 160, 600 and 900 °C).

DISCUSSION AND CONCLUSIONS

From analysis of the thermal curves and the sinters (i.e. the products of thermal dehydration and subsequent further decomposition), the following thermal decomposition reactions were established.

12-Hydrous compounds

$$LaBr_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{90\,^\circ C} LaBr_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{130\,^\circ C}$$

$$LaBr_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{180\,^\circ C} La_1Br_{1.19}C_{3.37}N_{1.12}H_{16.28}O_{5.55} \xrightarrow{900\,^\circ C}$$

$$\tfrac{1}{2}La_2O_3$$

$$NdBr_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{130\,^\circ C} NdBr_3 \cdot 2HMTA \cdot 4H_2O \xrightarrow{180\,^\circ C}$$

$$NdBr_3 \cdot 2HMTA \cdot 3H_2O \xrightarrow{220\,^\circ C} Nd_1Br_{1.14}C_{3.32}N_{0.82}H_{13.78}O_{2.96} \xrightarrow{950\,^\circ C}$$

$$\tfrac{1}{2}Nd_2O_3$$

$$LnBr_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{(1)} LnBr_3 \cdot 2HMTA \cdot 3H_2O \xrightarrow{(2)}$$

$$Ln_1Br_xC_yN_zH_pO_q \xrightarrow{(3)} \tfrac{1}{2}Ln_2O_3$$

	(1)	(2)	(3)
Gd	160 °C	218 °C	900 °C
Dy	140 °C	190 °C	850 °C
Er	160 °C	195 °C	800 °C

10-Hydrous compounds

$LaBr_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{110\,^\circ C} LaBr_3 \cdot 2HMTA \cdot H_2O \xrightarrow{185\,^\circ C}$

$La_1Br_xC_yN_zH_pO_q \xrightarrow{900\,^\circ C} \frac{1}{2}La_2O_3$

$NdBr_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{140\,^\circ C} NdBr_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{180\,^\circ C}$

$NdBr_3 \cdot 2HMTA \cdot H_2O \xrightarrow{200\,^\circ C} Nd_1Br_{1.69}C_{3.39}N_{0.86}H_{9.48}O_{2.72} \xrightarrow{900\,^\circ C}$

$\frac{1}{2}Nd_2O_3$

$GdBr_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{160\,^\circ C} GdBr_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{220\,^\circ C}$

$Gd_1Br_xC_yN_zH_pO_q \xrightarrow{900\,^\circ C} \frac{1}{2}Gd_2O_3$

$DyBr_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{150\,^\circ C} DyBr_3 \cdot 2HMTA \cdot H_2O \xrightarrow{190\,^\circ C}$

$Dy_1Br_xC_yN_zH_pO_q \xrightarrow{900\,^\circ C} \frac{1}{2}Dy_2O_3$

8-Hydrous compounds

$LnBr_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{(1)} LnBr_3 \cdot 2HMTA \cdot H_2O \xrightarrow{(2)}$

$Ln_1Br_xC_yN_zH_pO_q \xrightarrow{(3)} \frac{1}{2}Ln_2O_3$

	(1)	(2)	(3)
La	110 °C	180 °C	900 °C
Gd	160 °C	210 °C	950 °C

$NdBr_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{120\,^\circ C} NdBr_3 \cdot 2HMTA \cdot H_2O \xrightarrow{160\,^\circ C}$

$Nd_1Br_{1.57}C_{3.57}N_{0.90}H_{6.54}O_{0.76} \xrightarrow{800\,^\circ C} \frac{1}{2}Nd_2O_3$

$DyBr_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{140\,^\circ C} DyBr_3 \cdot 2HMTA \xrightarrow{150\,^\circ C} Dy_1Br_xC_yN_zH_pO_q$

$\xrightarrow{900\,^\circ C} \frac{1}{2}Dy_2O_3$

The changes occurring at 200–800 °C are the stage of the decomposition reaction that is most difficult to establish. Over this range there is continuous mass loss, indicating variable composition of the substance being heated. Elemental analysis of the substances produced at the temperatures at which exothermic peaks begin on the DTG curves shows the presence of carbon, nitrogen, hydrogen and bromine. The elemental analysis, lanthanide analysis and mass loss findings point to the presence of the form $Ln_1Br_xC_yN_zH_pO_q$.

TABLE 11

Summary of results

From	Obtained
12-hydrous lanthanum salt	2-hydrous salt
10-hydrous	1-hydrous salt
8-hydrous	1-hydrous salt
12-hydrous neodymium salt	4-hydrous salt
10-hydrous	2-hydrous salt
8-hydrous	1-hydrous and anhydrous salts
12-hydrous gadolinium salt	3-hydrous salt
10-hydrous	2-hydrous salt
8-hydrous	1-hydrous salt
12-hydrous dysprosium salt	3-hydrous salt
10-hydrous	1-hydrous salt
8-hydrous	anhydrous salt
12-hydrous erbium salt	3-hydrous salt

The exothermic peak indicates oxidation of this compound. The composition of the compounds (the amount of lanthanide) obtained at temperatures of approximately 900 °C, and the percentage mass loss, point to lanthanide oxides (Ln_2O_3) as the final decomposition products of the salts under investigation.

The presence of lanthanide oxides was also confirmed by X-ray studies performed for some compounds. The diffractogram obtained for 12-hydrous neodymium salt heated to 160 °C (corresponding to the 4-hydrous salt) differs from that of the initial salt (Figs. 5 and 6). The diffractogram of the same salt heated to 600 °C indicates the presence of an amorphous substance at this temperature, from which Nd_2O_3 is obtained on further heating.

To sum up the results of the thermal investigations, the thermal dehydration reactions and subsequent further decomposition of the salts resulted in compounds of lower degrees of hydration than those obtained by crystallization.

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