

## Preparation and thermal decomposition of solid state lanthanide(III) and yttrium(III) chelates of ethylenediaminetetraacetic acid

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### Abstract

Solid state chelates of general formula  $H[Ln(EDTA)] \cdot nH_2O$  ( $Ln$  = trivalent lanthanide (except for promethium) or yttrium; EDTA = ethylenediaminetetraacetate) were prepared. Thermogravimetry, differential thermal analysis, X-ray diffraction and complexometry were used to characterize and study the thermal stability and thermal decomposition of these compounds.

### INTRODUCTION

Since the introduction of EDTA as a chelating agent [1], literature information upon lanthanide(III) and yttrium(III) chelates has been concerned with their properties in aqueous solution. Studies of the solid state compounds have been investigated by Brintzinger et al., who have reported the preparation of the chelates  $H[La(EDTA)]$ ,  $H[Nd(EDTA)]$  and  $Y[Y(EDTA)]_3$  [2, 3]. Moeller et al. have reported the nature of solid state chelates of the type  $H[Ln(EDTA)]$  and their sodium salts, using IR spectroscopy, differential thermal analysis (DTA), X-ray diffraction and light rotation measurements, in an attempt to characterize these compounds [4]. Kolat and Powell have extended this work on the series of lanthanide chelates, using several techniques including thermogravimetry (TG), but have only mentioned a brief study of the dehydration of these compounds by analyzing TG curves [5]. The complexes  $H[Nd(EDTA)] \cdot H_2O$  and  $M[Nd(EDTA)] \cdot nH_2O$  ( $M = Li, Na, K, Rb$  or  $Cs$ ) have been investigated by means of TG, DTA and thermomanometric analysis under a stream of argon [6]. Bhat and Krishna Iyer have described the thermal

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behavior under air or nitrogen of several metal–EDTA complexes, including the dysprosium chelate [7]. Studies of the thermal properties of a number of EDTA complexes have been described by Wendlandt and co-workers [8–10].

Lanthanide(III) and yttrium(III) EDTA chelates were prepared, characterized and studied by using complexometric analysis, TG, DTA and X-ray diffraction techniques. The present paper is primarily an extension of the work of refs. 4 and 5, including TG and DTA studies up to 800°C.

## EXPERIMENTAL

Hydrated basic carbonates of all lanthanides and yttrium were prepared following well-known procedures [11]. The lanthanide and yttrium chelates were prepared by neutralizing the corresponding aqueous suspensions of the hydrated basic carbonates with equimolar amounts of EDTA. The solid compounds were filtered using a sintered glass crucible. The solutions were dried in a water bath and kept in a desiccator over anhydrous calcium chloride.

Lanthanide(III) and yttrium(III) ions, after igniting the compounds to their respective oxides, were determined by complexometric titration with standard EDTA solutions using xylenol orange as indicator [12], and TG curves. The total amount of water plus EDTA for the lighter lanthanides (La–Sm) and the water and EDTA for the heavier lanthanides and yttrium were determined by TG curves.

The TG curves were recorded on a Perkin-Elmer TGS-2, thermogravimetric system. A sample of about 7 mg of each material was put in a platinum crucible and heated at a rate of 20°C min<sup>-1</sup> in air (flow ≈5 ml min<sup>-1</sup>) at atmospheric pressure.

DTA curves were recorded on a Perkin-Elmer DTA-1700 apparatus and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference material. Samples of about 7 mg were put in alumina crucibles and heated at a rate of 20°C min<sup>-1</sup> in air (flow ≈30 ml min<sup>-1</sup>) at atmospheric pressure.

Diffraction patterns were obtained as previously described [13].

## RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical data for the compounds. These results establish the general formula H[Ln(EDTA)] · *n*H<sub>2</sub>O (Ln = lanthanide or yttrium; EDTA = ethylenediaminetetraacetate; *n* = 1 (La–Nd), *n* = 2 (Sm–Ho, Tm), *n* = 2.5 (Er, Lu, Y) and *n* = 3 (Yb)).

X-ray diffraction patterns of the entire Ln series, suggest that the crystalline solids exist in two isomorphous series. In the first series are the chelates of lanthanum to samarium. The chelates of europium to lutetium and yttrium belong to the second isomorphous series. These results are in good agreement with the series proposed by Kolat and Powell [5]. The

TABLE 1  
Analytical and thermoanalytical (TG) results

Compound	Lanthanide (wt.%)			Ligand + water (wt.%)		Ligand (wt.%)		Water (wt.%)	
	Theor.	TG	EDTA	Theor.	TG	Theor.	TG	Theor.	TG
H[La(EDTA)] · H <sub>2</sub> O	31.13	31.1	30.96	63.49	63.6	–	–	–	–
H[Ce(EDTA)] · H <sub>2</sub> O	31.32	30.7	30.58	61.53	62.3	–	–	–	–
H[Pr(EDTA)] · H <sub>2</sub> O	31.44	31.9	32.10	62.02	61.4	–	–	–	–
H[Nd(EDTA)] · H <sub>2</sub> O	31.95	31.4	31.41	62.74	63.4	–	–	–	–
H[Sm(EDTA)] · 2H <sub>2</sub> O	31.62	30.9	30.98	62.34	64.2	–	–	–	–
H[Eu(EDTA)] · 2H <sub>2</sub> O	31.84	31.4	31.11	63.33	63.6	55.58	55.8	7.75	7.8
H[Gd(EDTA)] · 2H <sub>2</sub> O	32.59	32.9	32.28	62.44	62.2	54.97	54.6	7.47	7.6
H[Tb(EDTA)] · 2H <sub>2</sub> O	32.82	32.5	32.31	61.40	61.8	53.96	54.5	7.44	7.3
H[Dy(EDTA)] · 2H <sub>2</sub> O	33.31	33.3	33.26	61.77	61.8	54.38	54.2	7.39	7.6
H[Ho(EDTA)] · 2H <sub>2</sub> O	33.64	33.7	33.37	61.46	61.9	54.11	54.4	7.35	7.5
H[Er(EDTA)] · 2.5H <sub>2</sub> O	33.35	33.4	33.43	61.86	61.8	52.88	52.7	8.98	9.1
H[Tm(EDTA)] · 2H <sub>2</sub> O	34.18	34.6	34.72	60.96	60.5	53.66	53.3	7.28	7.2
H[Yb(EDTA)] · 3H <sub>2</sub> O	33.51	33.1	33.26	61.84	62.4	51.37	52.1	10.47	10.3
H[Lu(EDTA)] · 2.5H <sub>2</sub> O	34.35	34.81	34.54	60.93	60.4	52.08	51.4	8.85	9.0
H[T(EDTA)] · 2.5H <sub>2</sub> O	21.01	21.2	20.86	73.32	73.1	62.68	62.2	10.64	10.9

more characteristic lines obtained by the powder diffraction method are shown in Tables 2 and 3.

The TG–DTG curves for the compounds are shown in Fig. 1. These curves show mass losses in steps between 40 and 740°C. For the heavier lanthanide chelates (Eu–Lu, Y), the TG curves show a great similarity. However, for the lighter lanthanide chelates similar curves are observed only in the first step of the thermal decomposition.

For compounds of lanthanum to samarium, the TG curves show that water is not released until the chelate itself decomposes. For the heavier lanthanide and yttrium chelates, dehydration occurs before thermal decomposition, as observed by Kolat and Powell [5]. Only terbium,

TABLE 2  
X-ray powder patterns of the compound H[Ln(EDTA)] · nH<sub>2</sub>O

La		Ce		Pr		Nd		Sm	
<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> (Å)
100	13.05	100	12.99	46	13.10	100	12.99	100	12.99
26	7.37	23	7.37	20	11.04	33	7.37	29	7.31
52	6.55	58	6.55	46	7.69	75	6.46	76	6.46
45	5.98	61	6.00	100	5.90	92	5.94	88	5.86
19	4.34	27	4.34	20	4.46	40	4.31	41	4.31
16	3.97	19	3.95	25	3.91	42	3.93	34	3.93
21	3.75	36	3.75	27	3.96	50	3.72	38	3.72

TABLE 3  
X-ray powder patterns of the compounds  $H[Lu(EDTA)] \cdot nH_2O$

Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu		Y	
$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)
100	9.50	100	9.40	100	9.30	100	9.30	100	9.30	100	9.20	100	9.20	100	9.20	100	9.20	100	9.20
23	6.65	10	6.65	18	6.65	9	6.60	36	6.60	9	6.60	6	6.60	6	6.55	22	6.55	11	6.60
26	6.15	11	6.15	11	6.10	31	6.15	46	6.06	18	6.06	7	6.06	13	5.98	23	6.06	23	6.06
26	5.64	12	5.68	10	5.68	24	5.60	41	5.90	13	5.60	6	5.57	11	5.53	22	5.53	18	5.60
61	4.67	44	4.67	24	4.67	40	4.64	16	4.60	20	4.60	11	4.60	39	4.60	27	4.57	24	4.60
26	3.19	13	3.16	13	3.16	18	3.15	47	3.14	11	3.11	6	3.11	10	3.11	18	3.17	13	3.15
23	3.11	22	3.10	10	3.10	19	3.10	24	3.09	6	3.06	3	3.08	5	3.06	6	2.82	11	3.08

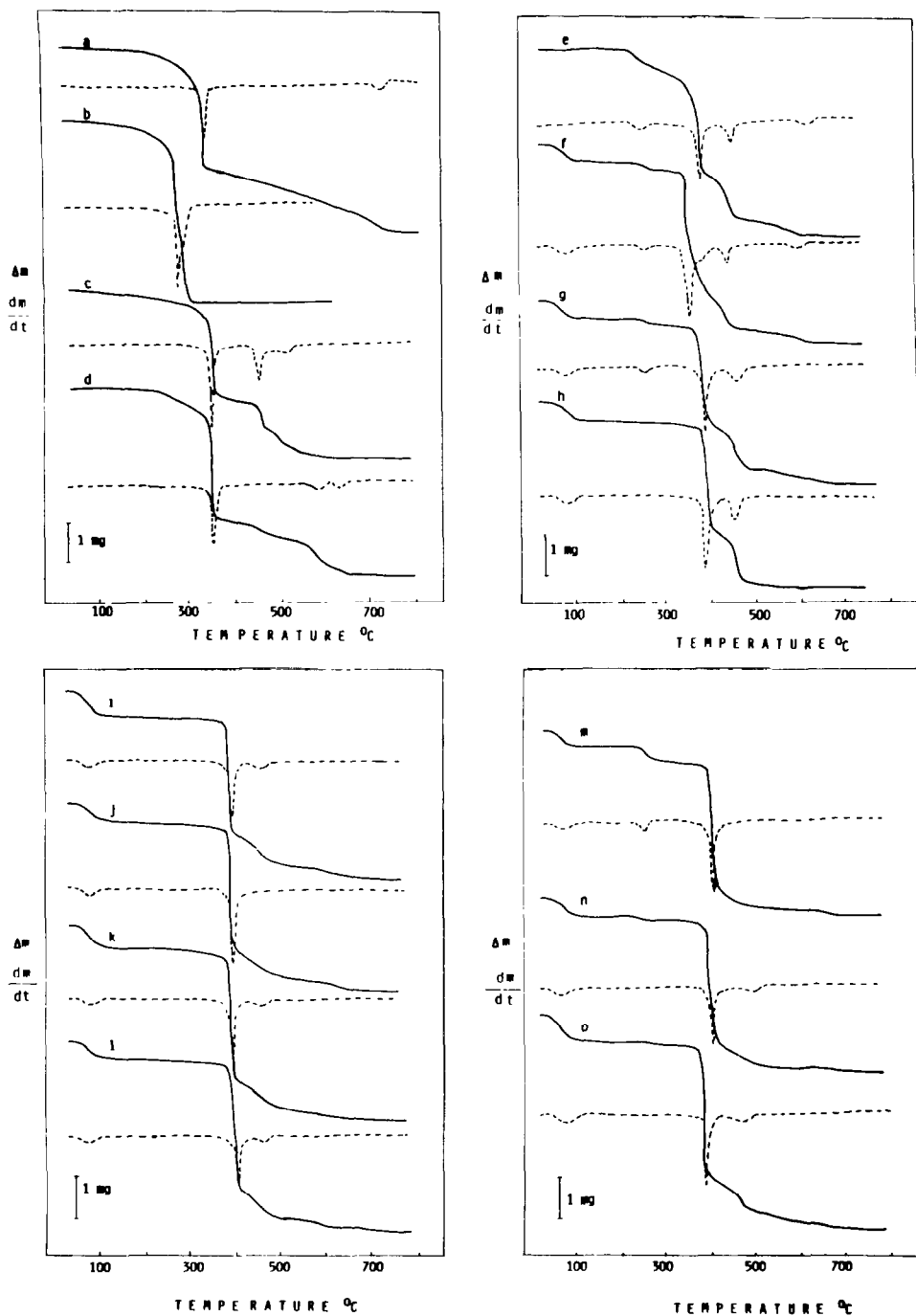


Fig. 1. TG-DTG curves of the compounds  $H[Ln(EDTA)] \cdot nH_2O$ : (a)  $La \cdot H_2O$  (7.00 mg); (b)  $Ce \cdot H_2O$  (7.14 mg); (c)  $Pr \cdot H_2O$  (7.00 mg); (d)  $Nd \cdot H_2O$  (7.33 mg); (e)  $Sm \cdot 2H_2O$  (7.17 mg); (f)  $Eu \cdot 2H_2O$  (7.70 mg); (g)  $Gd \cdot 2H_2O$  (7.24 mg); (h)  $Tb \cdot 2H_2O$  (7.53 mg); (i)  $Dy \cdot 2H_2O$  (7.20 mg); (j)  $Ho \cdot 2H_2O$  (7.30 mg); (k)  $Er \cdot 2.5H_2O$  (7.68 mg); (l)  $Tm \cdot 2H_2O$  (7.60 mg); (m)  $Yb \cdot 3H_2O$  (7.30 mg); (n)  $Lu \cdot 2.5H_2O$  (7.20 mg); (o)  $Y \cdot 2.5H_2O$  (7.32 mg).

dysprosium and thulium anhydrous chelates are obtained at temperatures up to 110°C. For the other heavier lanthanides dehydration occurs in two steps and anhydrous compounds are obtained only at temperatures up to 300°C. This result is in disagreement with the literature data [5].

For all chelates except the cerium compound, after the mass loss observed at temperatures up to  $\approx 400^\circ\text{C}$ , the TG curves suggest formation of carbonate as an intermediate product. Tests with hydrochloric acid on samples heated until the temperature indicated by the TG–DTG curves confirmed the presence of the carbonate anion accompanied by carbon residue. Some indication of the formation of the carbonate anion during the thermal decomposition of the dysprosium chelate has already been observed [7]. For the cerium chelate (probably due to low stability caused by an exothermic oxidation reaction of Ce(III) to Ce(IV)), carbonate as an intermediate product was not observed.

For the lanthanum chelate (the TG curve, Fig. 1a), the mass loss occurs in two steps between 120 and 740°C. The first mass loss (up to 350°C) begins with a slow process, followed by a fast process, which correspond respectively to dehydration and pyrolysis of the ligand, with formation of lanthanum carbonate and  $\approx 6.6\%$  of carbon residue (TG = 42.1%, calc. = 48.69%). The second mass loss (350–740°C) occurs through slow mass loss and is due to the carbon pyrolysis and the thermal decomposition of the carbonate to the lanthanum oxide  $\text{La}_2\text{O}_3$  (TG = 21.4%, calc. = 21.40%).

For the cerium chelate (Fig. 1b) the mass loss occurs in one step between 80 and 310°C and also begins with a slow mass followed by a fast process. These two processes are dehydration and total pyrolysis respectively of the ligand, with formation of the cerium oxide  $\text{CeO}_2$  (TG = 62.3%, calc. = 61.53%).

The praseodymium chelate (the TG curve, Fig. 1c), shows mass loss in four steps between 100 and 590°C. The first mass loss (up to 370°C) also begins with a slow process followed by a fast process, which correspond to dehydration and pyrolysis of the ligand respectively, with formation of praseodymium carbonate and  $\approx 6.1\%$  of carbon residue (TG = 42.4%, calc. = 48.47%). The second mass loss (370–470°C) corresponds to the thermal decomposition of the praseodymium carbonate to the dioxycarbonate  $\text{Pr}_2\text{O}_2\text{CO}_3$  (TG = 9.2%, calc. = 9.82%). The third mass loss (470–540°C) corresponds to the pyrolysis of the carbon ( $\approx 3.6\%$ ) and to the thermal decomposition of  $\text{Pr}_2\text{O}_2\text{CO}_3$  to  $\text{Pr}_2\text{O}_{2+x}(\text{CO}_3)_{0.5}$  (TG = 6.1%, calc. = 6.05%). The last step (540–590°C) is due to the pyrolysis of the carbon ( $\approx 2.5\%$ ) and to the thermal decomposition of the intermediate to the praseodymium oxide  $\text{Pr}_6\text{O}_{11}$  (TG = 3.7, calc. = 3.77%).

For the neodymium chelate (Fig. 1d), the mass losses occurs in four steps between 160 and 760°C. The first step (160–370°C) begins with a slow mass loss followed by a fast loss. These two processes correspond to dehydration

and pyrolysis of the ligand with formation of neodymium carbonate and  $\approx 4.5\%$  of carbon residue (TG = 43.6%, calc. = 48.12%). The second mass loss (370–580°C) is due to the thermal decomposition of neodymium carbonate to the intermediate  $\text{Nd}_2\text{O}_2\text{CO}_3$  (TG = 9.9%, calc. = 9.75%). The third mass loss (580–610°C) is due to the pyrolysis of the carbon ( $\approx 4.5\%$ ) and to the thermal decomposition of the oxycarbonate to  $\text{Nd}_2\text{O}_{2.5}(\text{CO}_3)_{0.5}$  (TG = 7.0%, calc. = 6.94%). The last step (610–670°C) is due to the final thermal decomposition of this intermediate to the neodymium oxide  $\text{Nd}_2\text{O}_3$  (TG = 2.9%, calc. = 2.44%).

For the samarium chelate (Fig. 1e), the mass loss occurs in four steps between 210 and 640°C. The first step (up to 260°C) is due to the partial dehydration with loss of  $1\text{H}_2\text{O}$  (TG = 3.5%, calc. = 3.79%). The second mass loss (260–410°C) is due to the final dehydration and to the pyrolysis of the ligand, with formation of samarium carbonate and  $\approx 6.2\%$  of carbon residue (TG = 39.5%, calc. = 45.68%). The third step (410–500°C) is due to the pyrolysis of carbon ( $\approx 6.2\%$ ) and to the thermal decomposition of samarium carbonate to the dioxycarbonate  $\text{Sm}_2\text{O}_2\text{CO}_3$  (TG = 15.9%, calc. = 15.45%). The last mass loss (500–640°C) is due to the thermal decomposition of the intermediate to the samarium oxide  $\text{Sm}_2\text{O}_3$  (TG = 4.7%, calc. = 4.62%).

For the europium, gadolinium and holmium chelates, (Figs. 1f, g and j) the mass losses occur in five steps between 40 and 680°C. The first mass loss (up to 100°C) is due to loss of  $1.5\text{H}_2\text{O}$  (Eu, TG = 5.8%, calc. = 5.66; Gd, TG = 5.5%, calc. = 5.60%; Ho, TG = 5.5%, calc. = 5.51). The second mass loss (Eu, 240–260°C; Gd, 230–280°C; Ho, 250–300°C) is due in every case to the loss of  $0.5\text{H}_2\text{O}$  (Eu, TG = 1.9%, calc. = 1.89%; Gd, TG = 2.1%, calc. = 1.87%; Ho, TG = 1.7%, calc. = 1.84%). The third step (Eu, 340–390°C; Gd, 350–410°C; Ho, 360–400°C) is due to ligand pyrolysis with formation of the lanthanide carbonate and carbon residue (Eu, 2.8%; Gd, 5.3%; Ho, small quantity) (Eu, TG = 39.0%, calc. = 41.75%; Gd, TG = 36.0%, calc. = 41.29%; Ho, TG = 40.9%, calc. = 40.64%). The fourth step (Eu, 390–450°C; Gd, 410–500°C; Ho, 360–400°C) is due to carbon pyrolysis and thermal decomposition of the carbonate to the dioxycarbonate  $\text{Ln}_2\text{O}_2\text{CO}_3$  (Eu, TG = 12.1%, calc. = 12.02%; Gd, TG = 14.0%, calc. = 14.42%; Ho, TG = 9.3%, calc. = 8.98%). The last step (Eu, 450–620°C; Gd, 480–680°C; Ho, 480–680°C) is due to the thermal decomposition of the last intermediate to the respective oxide  $\text{Ln}_2\text{O}_3$  (Eu, TG = 4.8%, calc. = 4.61%; Gd, TG = 4.6%, calc. = 4.56%; Ho, TG = 4.2%, calc. = 4.49%).

For the erbium, lutetium and yttrium chelates (Figs. 1k, 1n and 1o), the mass losses occur in five steps between 40 and 680°C. The first mass losses (up to 100°C) are due to loss of  $2\text{H}_2\text{O}$  (Er, TG = 7.2%, calc. = 7.19%; Lu, TG = 6.5%, calc. = 7.08%; Y, TG = 8.8%, calc. = 8.52%). The second mass losses (Er, 240–310°C; Lu, 220–250°C; Y, 260–300°C) are due to loss of

0.5H<sub>2</sub>O (Er, TG = 1.9%, calc. = 1.80%; Lu, TG = 1.8%, calc. = 1.77%; Y, TG = 1.8%, calc. = 2.12%). The third step (Er, 350–400°C; Lu, 350–410°C; Y, 350–400°C) is due to ligand pyrolysis with formation of lanthanide carbonate and a small amount of carbon residue (Er, TG = 39.7%, calc. = 39.72%; Lu, TG = 39.3%, calc. = 39.12%; Y, TG = 46.8%, calc. = 47.08%). The fourth step (Er, 400–490°C; Lu, 410–500°C; Y, 400–480°C) is due to carbon pyrolysis and thermal decomposition of the carbonate to the dioxycarbonate Ln<sub>2</sub>O<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> (Er, TG = 8.6%, calc. = 8.77%; Lu, TG = 8.7%, calc. = 8.64%; Y, TG = 10.5%, calc. = 10.40%). The last step (Er, 490–680°C; Lu, 500–670°C; Y, 480–680°C) is due to the thermal decomposition of the last intermediate to the respective oxide Ln<sub>2</sub>O<sub>3</sub> (Er, TG = 4.4%, calc. = 4.38%; Lu, TG = 4.1%, calc. = 4.32%; Y, TG = 5.3%, calc. = 5.20%).

For the terbium chelate (Fig. 1h), the mass loss occurs in three steps (40–630°C). The first mass loss (up to 100°C) is due to the total dehydration with the loss of 2H<sub>2</sub>O (TG = 7.4%, calc. = 7.44%). The second step (360–410°C) is due to the ligand pyrolysis, with the formation of terbium carbonate and ≈5% of carbon residue (TG = 35.7%, calc. = 41.15%). The last mass loss (420–630°C) is due to the thermal decomposition of the carbonate to the terbium oxide Tb<sub>4</sub>O<sub>7</sub> and to the pyrolysis of carbon (TG = 18.7%, calc. = 18.63%).

For the dysprosium and thulium chelates (Figs. 1i and 1l), the mass loss occurs in four steps (40–680°C). The first step (up to 100°C) is due to the total dehydration, with a loss of 2H<sub>2</sub>O (Dy, TG = 7.2%, calc. = 7.39%; Tm, TG = 6.7%, calc. = 7.29%). The second mass loss (350–400°C) is due to ligand pyrolysis with formation of carbonate and a small amount of carbon residue (Dy, TG = 40.8%, calc. = 40.84%; Tm, TG = 40.3%, calc. = 40.31%). The third step (400–470°C) is attributed to carbon pyrolysis and the thermal decomposition of the carbonate to the dioxycarbonate (Dy<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>; Tm<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>) (Dy, TG = 9.6%, calc. = 9.02%; Tm, TG = 9.0%, calc. = 8.90%).

For the ytterbium chelate (Fig. 1m) the mass loss occurs in four steps (40–680°C). The first mass loss (up to 100°C) and the second mass loss (250–280°C) are due to loss of 1.5H<sub>2</sub>O and 1.5H<sub>2</sub>O respectively (first mass loss, TG = 5.2%, calc. = 5.23%; second mass loss, TG = 5.23%). The third step (360–430°C) is due to ligand pyrolysis, with formation of the oxycarbonate intermediate Yb<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> (TG = 42.6%, calc. = 42.85%). The last step (430–680°C) is due to the thermal decomposition of the intermediate to the ytterbium oxide Yb<sub>2</sub>O<sub>3</sub> (TG = 9.3%, calc. = 8.25%).

The DTA curves are shown in Fig. 2. Cerium and praseodymium chelates show only exothermic peaks, whereas all other compounds show both endothermic and exothermic peaks, corresponding with the mass losses observed in the TG curves. For chelates of lanthanum to neodymium, endothermic peaks due to dehydration are not observed, which agrees with



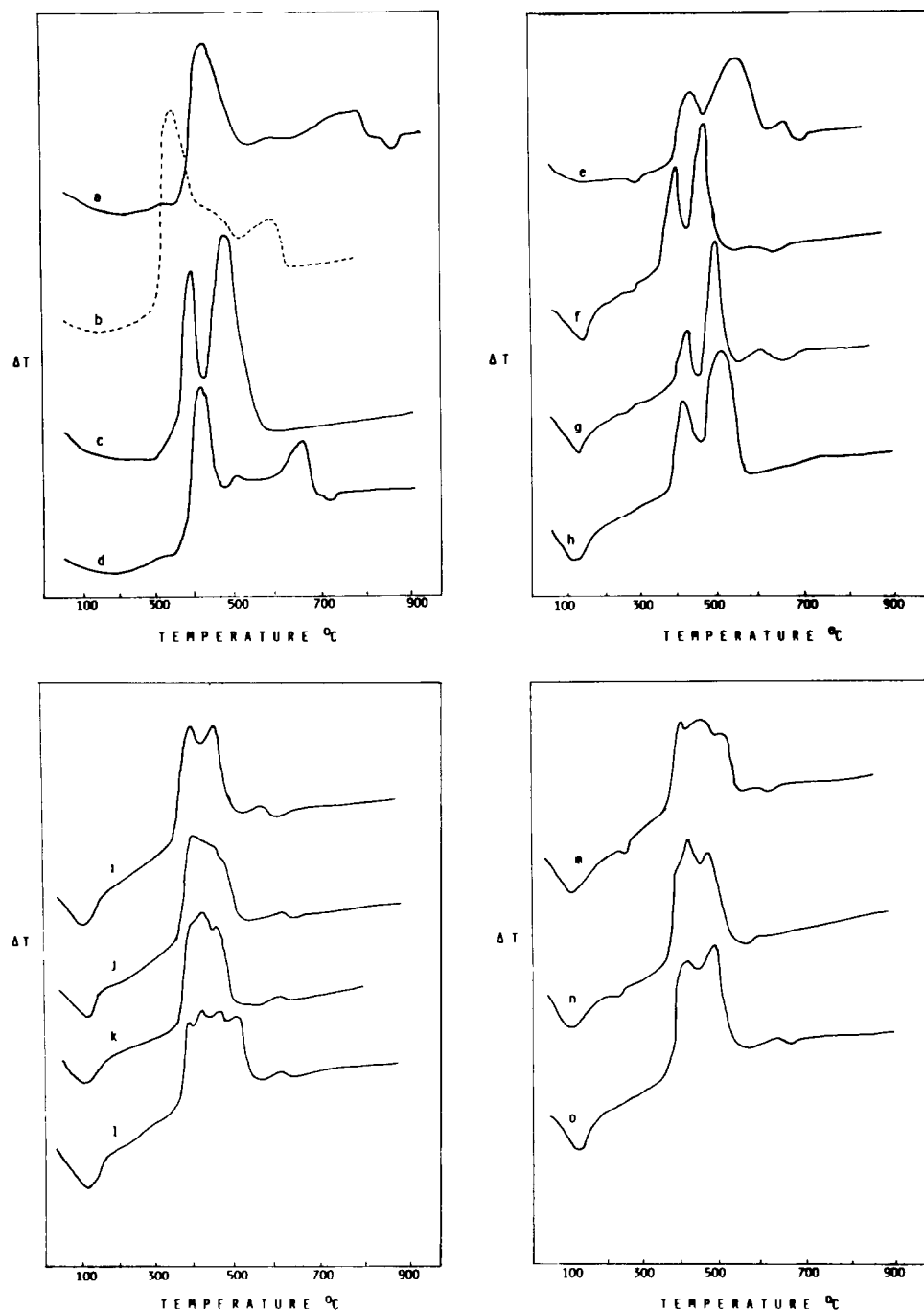


Fig. 2. DTA curves of the compounds  $H[Ln(EDTA)] \cdot nH_2O$ : (a)  $La \cdot H_2O$  (7.3 mg); (b)  $Ce \cdot H_2O$  (8.0 mg); (c)  $Pr \cdot H_2O$  (7.5 mg); (d)  $Nd \cdot H_2O$  (7.0 mg); (e)  $Sm \cdot 2H_2O$  (7.1 mg); (f)  $Eu \cdot 2H_2O$  (7.5 mg); (g)  $Gd \cdot 2H_2O$  (7.0 mg); (h)  $Tb \cdot 2H_2O$  (7.0 mg); (i)  $Dy \cdot 2H_2O$  (7.0 mg); (j)  $Ho \cdot 2H_2O$  (7.0 mg); (k)  $Er \cdot 2.5H_2O$  (7.0 mg); (l)  $Tm \cdot 2H_2O$  (7.8 mg); (m)  $Yb \cdot 3H_2O$  (7.2 mg); (n)  $Lu \cdot 2.5H_2O$  (7.0 mg); (o)  $Y \cdot 2.5H_2O$  (7.0 mg).

the TG data. The endothermic peak at 270°C for the samarium compound is due to the loss of 1H<sub>2</sub>O and the peak due to the loss of the second water molecule is not observed, because it is not released until the chelate itself decomposes.

For chelates of europium to lutetium and yttrium, the endothermic peak at ≈135°C is due to the weakly bound water. For all heavier lanthanide chelates, for which the TG curves show dehydration up to 310°C, only for europium, gadolinium, ytterbium and lutetium is a small endothermic peak observed (Eu, Gd, Yb, 270°C; Lu, 250°C). For chelates of holmium, erbium and yttrium, that peak is not observed, which is probably due to the absorbed heat in this step being insufficient to produce an endothermic peak.

The large exotherm, with the presence of one, two or three peaks (La, Nd, Eu, Gd, Dy, Ho, Er, Yb, Lu, Y, 350–550°C; Ce, 300–640°C; Pr, 310–600°C; Sm, 350–620°C; T, Tm, 350–580°C), are attributed to simultaneous dehydration and pyrolysis of the ligand in the lighter lanthanide chelates, and pyrolysis of the ligand in the heavier lanthanide chelates.

The large exotherm (La, 540–810°C; Nd, 550–700°C) with evidence of simultaneous reactions are due to the thermal decomposition of the carbonate to the dioxycarbonate and the pyrolysis of the carbon residue.

The small exothermic peak (Sm, 650°C; Eu, Gd, 610°C; Dy, 580°C; Ho, Er, Tm, 620°C; Lu, 600°C; Y, 640°C) suggests simultaneous thermal decomposition of the carbonate to the dioxycarbonate and carbon residue pyrolysis.

The last small endothermic peak (La, 850°C; Nd, 720°C; Sm, 700°C; Eu, Gd, Ho, Er, Tm, Y, 650°C; Dy, 610°C; Yb, 620°C) are due to the final thermal decomposition of the intermediate to the respective lanthanide oxide.

## CONCLUSIONS

The TG–DTG and DTA curves permit verification of the formation of lanthanide and yttrium carbonates and (di)oxycarbonates during the thermal decomposition of the EDTA complexes, and the formation of carbon residue during the pyrolysis of the ligand. The results also provide information about dehydration of the heavier lanthanide chelates.

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