Thermochimica Acta, 221 (1993) 53–62
Elsevier Science Publishers B.V., Amsterdam

The preparation and thermal decomposition of solid state compounds of 4-dimethylaminobenzylidenepyruvate and trivalent lanthanides and yttrium

M.H. Miyano, C.B. Melios, C.A. Ribeiro, H. Redigolo and M. Ionashiro *

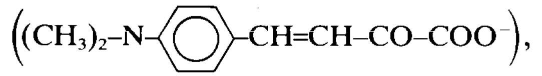
Instituto de Química, Universidade Estadual Paulista, Araraquara, São Paulo, C.P. 355, CEP 14800 (Brazil)

(Received 15 October 1992)

Abstract

Solid state Ln–DMBP compounds, where Ln represents trivalent lanthanides (except for promethium) and yttrium, and DMBP is 4-dimethylaminobenzylidenepyruvate, were prepared. Thermogravimetry (TG), differential thermal analysis (DTA), and other methods of analysis were used to characterize and to study the thermal stability and thermal decomposition of these compounds.

INTRODUCTION

The preparation and investigation of several metal-ion complexes with DMBP , have been studied in aqueous solutions [1–3]. As well as other studies, these papers report the thermodynamic stability (β_1) and spectroscopic parameters ($\varepsilon_{1,\max}$, $\lambda_{\max}$) of the 1:1 species.

Solid state compounds of Pb(II) and Cu(II) with DMBP have been isolated, and their analyses indicated a 1:2 metal:ligand relationship [4]. No reference has been found to the preparation of other solid-state metal–DMBP complexes.

In this study, solid-state compounds of lanthanide(III) and yttrium(III) with DMBP were prepared. These compounds were characterized and studied by complexometric titration, TG, DTA and X-ray powder diffractometry. The data obtained allowed us to acquire new information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

---

* Corresponding author.

EXPERIMENTAL

DMBP was prepared as previously described [1]. Lanthanide(III) and yttrium(III) chlorides were prepared in accordance with ref. 5.

The solid state complexes of trivalent lanthanides and yttrium with DMBP were prepared by mixing 100 ml solutions of the corresponding lanthanide and yttrium chlorides (6.9×10^{-3} mol l^{-1}) with ≈30 ml solutions of NaDMBP (1.2×10^{-1} mol l^{-1}), until total precipitation of the metal ions. The precipitates were washed until elimination of the chloride ions, filtered and dried in the Whatman no. 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In the solid state complexes, DMBP was determined from the TG curves, and the lanthanide(III) and yttrium(III) ions were determined by complexometric titrations with standard EDTA solutions, using xylenol orange as indicator [6].

TG curves were recorded on a Perkin-Elmer TGS-2 thermogravimetric system; samples of about 8 mg were used, in platinum crucibles, heated at a rate of 20°C min^{-1} in flowing air (≈5 ml min^{-1}) at ambient pressure.

DTA curves were recorded on a Perkin-Elmer DTA-1700 system, using α-Al_2O_3 as reference material. Samples of about 8 mg were used, in aluminium crucibles, heated at a rate of 20°C min^{-1} in flowing air (≈30 ml min^{-1}) at ambient pressure.

Diffraction patterns were obtained using an HGZ 4/B horizontal diffractometer (Germany), equipped with a proportional counter and pulse-height discriminator. The Bragg–Brentano arrangement was adopted, using Cu Kα radiation ($\lambda = 1.541$ Å) and settings of 38 kV and 20 mA.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data for the prepared compounds from which the general formula $Ln(DMBP)_3 \cdot nH_2O$ can be established, where Ln represents lanthanides and yttrium, DMBP is 4-dimethylaminobenzylidenepyruvate, and $n = 2$, except for Yb where $n = 3$.

The X-ray powder patterns showed that all the compounds are amorphous.

The thermal decomposition of these compounds, occurs in four, five or six consecutive steps between 50 and 900°C, with the lanthanum compound being the most stable, as can be seen in the TG–DTG curves, Fig. 1.

In all the curves, the first mass loss observed up to 170°C is due to the hydration water, and the final mass loss, above ≈570°C, except for the Ce, Pr, and Tb compounds, is due to the thermal decomposition of the intermediate dioxycarbonate, $Ln_2O_2CO_3$, to the corresponding oxide,

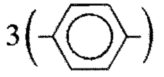
TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanide in %		DMBP[a] in %		Water in %	
	Theor.	EDTA	Theor.	TG	Theor.	TG
$La(DMBP)_3 \cdot 2H_2O$	16.74	16.99	78.91	78.9	4.34	4.6
$Ce(DMBP)_3 \cdot 2H_2O$	16.86	16.29	78.80	75.9	4.34	4.1
$Pr(DMBP)_3 \cdot 2H_2O$	16.94	16.85	78.72	77.9	4.33	3.6
$Nd(DMBP)_3 \cdot 2H_2O$	17.27	17.11	78.41	78.9	4.31	4.3
$Sm(DMBP)_3 \cdot 2H_2O$	17.87	17.72	77.84	77.7	4.28	4.2
$Eu(DMBP)_3 \cdot 2H_2O$	18.03	17.94	77.69	76.5	4.28	4.3
$Gd(DMBP)_3 \cdot 2H_2O$	18.54	18.47	77.21	77.1	4.25	4.4
$Tb(DMBP)_3 \cdot 2H_2O$	18.70	18.70	77.06	75.1	4.24	4.2
$Dy(DMBP)_3 \cdot 2H_2O$	19.04	19.01	76.73	76.8	4.22	4.3
$Ho(DMBP)_3 \cdot 2H_2O$	19.27	19.29	76.51	76.1	4.21	4.2
$Er(DMBP)_3 \cdot 2H_2O$	19.49	19.47	76.31	73.5	4.20	4.7
$Tm(DMBP)_3 \cdot 2H_2O$	19.65	19.70	76.16	76.3	4.19	4.0
$Yb(DMBP)_3 \cdot 3H_2O$	19.62	20.09	74.25	73.3	6.13	5.8
$Lu(DMBP)_3 \cdot 2H_2O$	20.21	20.25	75.63	74.25	4.16	4.2
$Y(DMBP)_3 \cdot 2H_2O$	11.40	11.89	83.97	81.7	4.62	4.9

[a] DMBP is 4-dimethylaminobenzylidenepyruvate.

Ln_2O_3. Tests with hydrochloric acid solution on samples heated up to the temperature of formation of the intermediate, as indicated by the TG–DTG curves, confirmed the elimination of CO_2. In the cerium, praseodymium and terbium compounds, the TG–DTG curves, Fig. 1(b), (c) and (h), show that this intermediate is not formed, probably because of the exothermic oxidation reaction that results in the formation of the respective oxides (CeO_2, Pr_6O_{11} and Tb_4O_7) at temperatures up to 580°C.

For the anhydrous lanthanum–samarium, terbium, thulium, ytterbium and lutecium compounds, the TG–DTG curves, Figs. 1(a)–(e), (h), (l), (m) and (n), show that the thermal decompositions occur in the same way. Calculations based on the mass losses observed in the TG curves are in agreement with the loss of $3(CH_3)_2N-$ (first step),  (second step), and the rest of the ligand (third step). For compounds that form the dioxycarbonate, only in the lanthanum compound are the mass-loss data in agreement with the elimination of $0.5CO_2$. In the other compounds, the TG curves show a decreasing mass losses in the last step, corresponding to the elimination of CO_2, with increasing atomic number of the lanthanide ions, suggesting that a mixture of intermediate and oxide is present in this step. A decreasing stability of these intermediates with increasing atomic number of the lanthanide ions has also been observed [7].

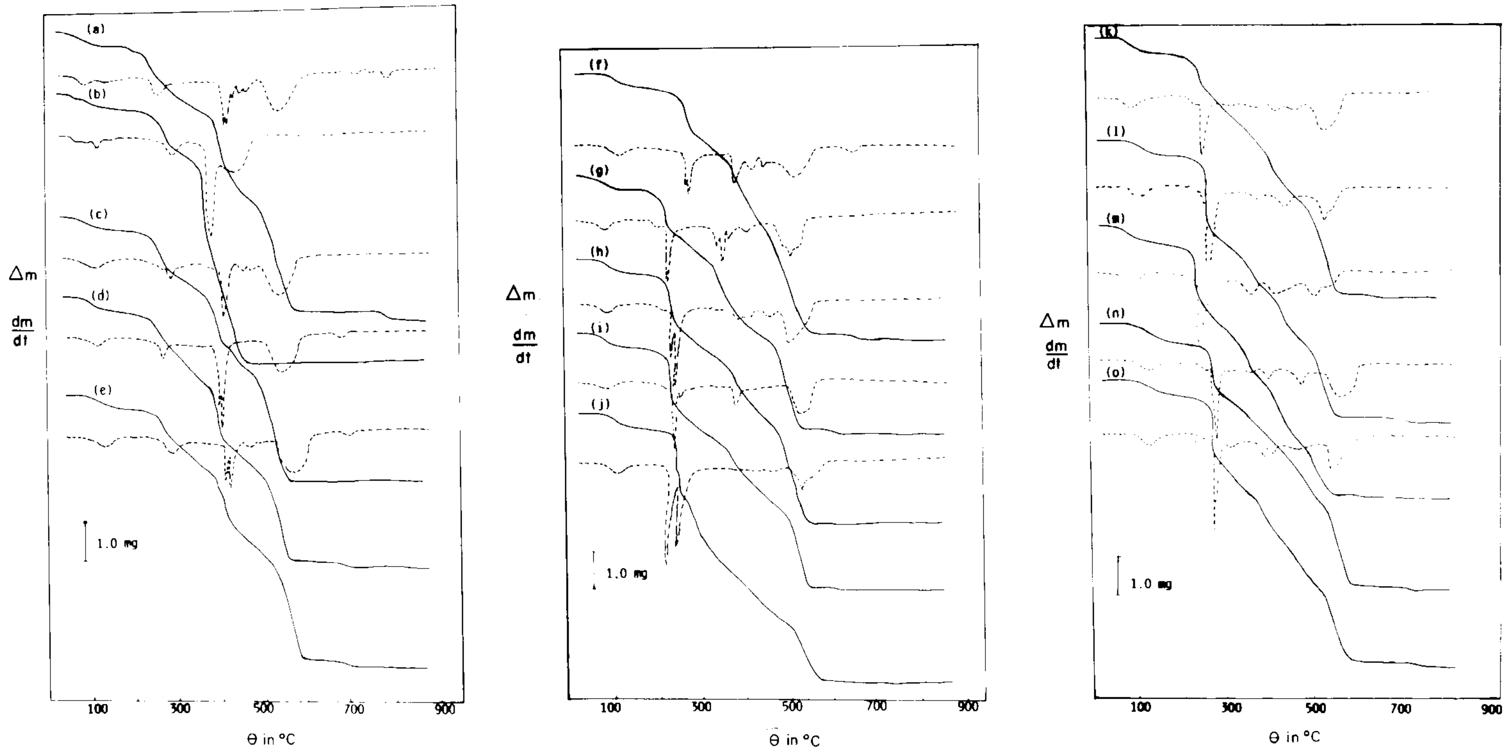


Fig. 1. TG–DTG curves of the compounds: (a) La(DMBP)$_3$ · 2H$_2$O (8.75 mg); (b) Ce(DMBP)$_3$ · 2H$_2$O (8.50 mg); (c) Pr(DMBP)$_3$ · 2H$_2$O (8.22 mg); (d) Nd(DMBP)$_3$ · 2H$_2$O (8.18 mg); (e) Sm(DMBP)$_3$ · 2H$_2$O (8.30 mg); (f) Eu(DMBP)$_3$ · 2H$_2$O (8.10 mg); (g) Gd(DMBP)$_3$ · 2H$_2$O (8.04 mg); (h) Tb(DMBP)$_3$ · 2H$_2$O (8.32 mg); (i) Dy(DMBP)$_3$ · 2H$_2$O (8.07 mg); (j) Ho(DMBP)$_3$ · 2H$_2$O (7.10 mg); (k) Er(DMBP)$_3$ · 2H$_2$O (8.43 mg); (l) Tm(DMBP)$_3$ · 2H$_2$O (8.65 mg); (m) Yb(DMBP)$_3$ · 3H$_2$O (8.73 mg); (n) Lu(DMBP)$_3$ · 2H$_2$O (8.35 mg); and (o) Y(DMBP)$_3$ · 2H$_2$O (8.20 mg). Heating rate, 20°C min^{-1}; flowing air, 5 ml min^{-1}.

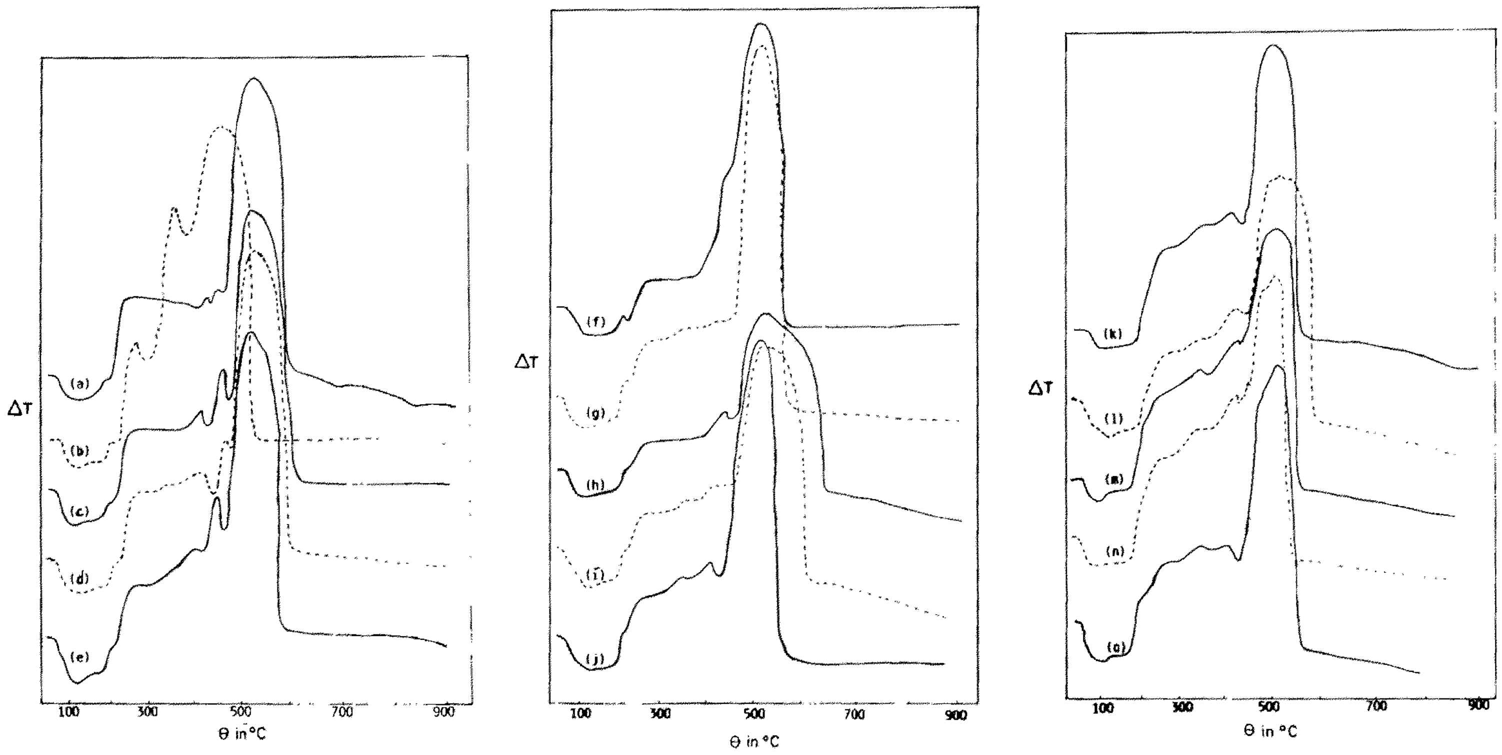


Fig. 2. DTA curves of the compounds: (a) La(DMBP)$_3$ · 2H$_2$O; (b) Ce(DMBP)$_3$ · 2H$_2$O; (c) Pr(DMBP)$_3$ · 2H$_2$O; (d) Nd(DMBP)$_3$ · 2H$_2$O; (e) Sm(DMBP)$_3$ · 2H$_2$O; (f) Eu(DMBP)$_3$ · 2H$_2$O; (g) Gd(DMBP)$_3$ · 2H$_2$O; (h) Tb(DMBP)$_3$ · 2H$_2$O; (i) Dy(DMBP)$_3$ · 2H$_2$O; (j) Ho(DMBP)$_3$ · 2H$_2$O; (k) Er(DMBP)$_3$ · 2H$_2$O; (l) Tm(DMBP)$_3$ · 2H$_2$O; (m) Yb(DMBP)$_3$ · 3H$_2$O; (n) Lu(DMBP)$_3$ · 2H$_2$O; and (o) Y(DMBP)$_3$ · 2H$_2$O. Heating rate, 20°C min^{-1}; flowing air, 30 ml min^{-1}; sample weight, ≈8 mg.

TABLE 2

Mass loss *m* and temperature range θ corresponding to the partial thermal decomposition of the compounds $Ln(DMBP)_3 \cdot nH_2O$, where Ln represents lanthanides and yttrium, and DMBP is 4-dimethylaminobenzylidenepyruvate

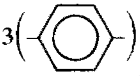
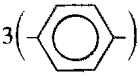
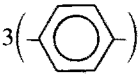
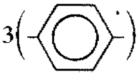
m/mg	θ/°C	Partial thermal decomposition	Loss in %	
			Theor.	Exp.
$La(DMBP)_3$				
0.40	50–170	$2H_2O$	4.34	4.6
1.40	170–330	$3(CH_3)_2N-$	15.94	16.0
2.45	330–480	3	27.52	28.0
2.85	480–700	Rest of the ligand with formation of dioxycarbonate	32.80	32.6
0.20	700–900	$0.5CO_2$	2.65	2.3
$Ce(DMBP)_3$				
0.35	50–170	$2H_2O$	4.34	4.1
1.35	170–340	$3(CH_3)_2N-$	15.92	15.9
2.30	340–380	3	27.48	27.1
2.80	380–460	Rest of the ligand	33.48	32.9
$Pr(DMBP)_3$				
0.30	50–170	$2H_2O$	4.33	3.6
1.30	170–330	$3(CH_3)_2N-$	15.90	15.8
2.30	330–490	3	27.45	28.0
2.80	490–580	Rest of the ligand	33.45	34.1
$Nd(DMBP)_3$				
0.35	50–170	$2H_2O$	4.31	4.3
1.35	170–330	$3(CH_3)_2N-$	15.84	16.5
2.20	330–430	3	27.34	26.9
2.70	430–560	Rest of the ligand with formation of dioxycarbonate	32.59	33.0
0.20	560–800	$0.5CO_2$	2.64	2.4
$Sm(DMBP)_3$				
0.35	50–170	$2H_2O$	4.28	4.2
1.25	170–320	$3(CH_3)_2N-$	15.73	15.1
2.20	320–460	3	27.14	26.5
2.80	360–580	Rest of the ligand with formation of dioxycarbonate	34.25	33.7
0.20	580–700	$0.5CO_2$	2.62	2.4

TABLE 2 (continued)

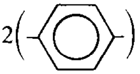
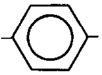
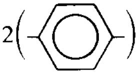
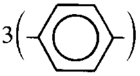
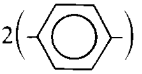
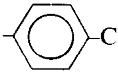
m/mg	θ/°C	Partial thermal decomposition	Loss in %	
			Theor.	Exp.
Eu(DMBP)$_3$				
0.35	50–170	2H_2O	4.28	4.3
0.80	170–250	2$(CH_3)_2N$–	10.46	9.9
1.10	250–360	$(CH_3)_2N$– 	14.26	13.6
1.40	360–440	2 	14.26	34.0
2.75	440–560	Rest of the ligand with partial formation of dioxycarbonate	34.19	34.0
0.15	560–660	0.5CO_2	2.61	1.8
Gd(DMBP)$_3$				
0.35	50–170	2H_2O	4.25	4.4
0.85	170–260	2$(CH_3)_2N$–	10.40	10.6
1.10	260–380	$(CH_3)_2N$– 	14.17	13.7
1.40	380–450	2 	17.95	17.4
2.70	450–580	Rest of the ligand with partial formation of dioxycarbonate	33.98	33.6
0.15	580–670	0.5CO_2	2.59	1.9
Tb(DMBP)$_3$				
0.35	50–170	2H_2O	4.24	4.2
1.30	170–250	2$(CH_3)_2N$–	15.57	15.9
2.25	250–460	3 	26.87	27.0
2.70	460–580	Rest of the ligand	32.74	32.5
Dy(DMBP)$_3$				
0.35	50–170	2H_2O	4.22	4.3
1.25	170–260	2$(CH_3)_2N$–	15.50	15.5
1.45	260–400	2 	17.84	18.0
1.60	400–530	 CH=CH–COCOO	20.41	19.8
1.75	530–580	Rest of the ligand with partial formation of dioxycarbonate	22.27	21.7
0.15	580–670	0.5CO_2	2.58	1.9

TABLE 2 (continued)

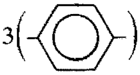
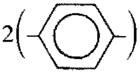
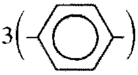
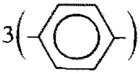
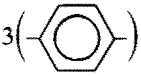
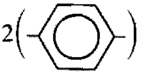
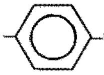
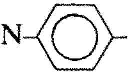
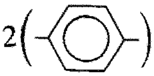
m/mg	θ/°C	Partial thermal decomposition	Loss in %	
			Theor.	Exp.
Ho(DMBP)$_3$				
0.30	50–170	$2H_2O$	4.21	4.2
0.75	170–250	$2(CH_3)_2N$–	10.30	10.6
0.35	250–270	$(CH_3)_2N$–	5.16	4.9
1.90	270–400	3	26.68	26.8
2.25	400–580	Rest of the ligand with partial formation of dioxycarbonate	31.72	31.7
0.15	580–700	$0.5CO_2$	2.57	2.1
Er(DMBP)$_3$				
0.40	50–170	$2H_2O$	4.20	4.7
0.80	170–260	$2(CH_3)_2N$–	10.28	9.5
1.20	260–370	$(CH_3)_2N$–	14.01	14.2
1.45	370–460	2	17.74	17.2
2.65	460–590	Rest of the ligand with partial formation of dioxycarbonate	31.72	31.4
0.10	590–700	$0.5CO_2$	2.56	1.2
Tm(DMBP)$_3$				
0.35	50–170	$2H_2O$	4.19	4.0
1.35	170–260	$3(CH_3)_2N$–	15.39	15.6
2.30	260–420	3	26.56	26.6
2.80	420–560	Rest of the ligand with partial formation of dioxycarbonate	31.66	32.4
0.15	560–700	$0.5CO_2$	2.56	1.7
Yb(DMBP)$_3$				
0.5	50–170	$3H_2O$	6.13	5.8
1.30	170–260	$2(CH_3)_2N$–	15.00	15.1
2.20	260–390	3	25.89	25.6
2.70	390–570	Rest of the ligand with partial formation of dioxycarbonate	30.86	31.4
0.2	570–760	$0.5CO_2$	2.50	2.3

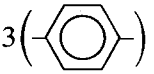
TABLE 2 (continued)

m/mg	θ/°C	Partial thermal decomposition	Loss in %	
			Theor.	Exp.
$Lu(DMBP)_3$				
0.35	50–170	$2H_2O$	4.16	4.2
1.25	170–270	$2(CH_3)_2N–$	15.28	15.0
2.15	270–460	3	26.37	25.7
2.80	460–600	Rest of the ligand with partial formation of dioxycarbonate	31.43	32.3
0.1	600–740	$0.5CO_2$	2.54	1.2
$Y(DMBP)_3$				
0.40	50–170	$2H_2O$	4.62	4.9
1.35	170–250	$2(CH_3)_2N–$	16.96	16.5
1.55	250–370	2	19.52	18.9
1.80	370–500	$-CH{=}CHCOCOO^-$	22.34	22.0
1.85	500–600	Rest of the ligand with partial formation of dioxycarbonate	22.33	22.6
0.15	600–740	$0.5CO_2$	2.82	1.8

For the anhydrous europium, gadolinium and erbium compounds, the TG–DTG curves, Fig. 1(f), (g) and (k), indicate that the thermal decomposition occurs in five steps, with the losses of $2(CH_3)_2N–$ (first step), $(CH_3)_2N$ (second step), 2 (third step), the rest of the ligand with partial formation of the dioxycarbonate (fourth step), and CO_2 elimination (last step).

For the anhydrous dysprosium and yttrium compounds, the TG–DTG curves, Fig. 1(i) and (o), also show mass losses in five steps with the losses of $3(CH_3)_2N–$ (first step), 2 (second step), $-CH{=}CH–CO–COO^-$ (third step), the rest of the ligand with partial formation of the dioxycarbonate (fourth step), and the elimination of CO_2 (last step).

Finally, for the anhydrous holmium compound, the TG curve, Fig. 1(j), shows that the thermal decomposition occurs in five steps with the losses of

$2(CH_3)_2N–$ (first step), $(CH_3)_2N–$ (second step), 3  (third step), the rest of the ligand with partial formation of the dioxycarbonate (fourth step), and the elimination of CO_2 (last step).

The mass losses and the corresponding temperature ranges for the partial thermal decompositions of all the compounds are shown in Table 2.

The DTA curves of these compounds, Fig. 2, show endothermic and exothermic peaks in correspondence with the mass losses observed in the TG curves. The broad endotherms that occur in all the compounds between 50 and ≈200°C, the peaks being at ≈100°C, are due to the loss of hydration water. The two or three broad exotherms observed after the dehydration between ≈250°C and ≈650°C are attributed to the pyrolysis of the ligand.

For the lanthanum compound only the DTA curve, Fig. 2(a), shows a small broad endothermic peak at 850°C, due to the thermal decomposition of the dioxycarbonate to lanthanum oxide. In all the other compounds where this intermediate is observed in the TG curves, no peak is observed in the DTA curves; this is probably due to the partial formation of the intermediates which accounts for a small amount of heat in the thermal decomposition.

CONCLUSIONS

From the TG–DTG curves, a general formula could be established for these compounds in the solid state, and also the partial losses of the ligand during the thermal decomposition could be suggested.

The TG–DTG and DTA curves, and the X-ray powder patterns provided previously unreported information about the thermal stability and thermal decomposition of these compounds.

ACKNOWLEDGEMENTS

The authors thank the FAPESP (Proc. 85/853-1) and the CNPq for financial support.

REFERENCES

1 C.B. Melios, V.R. Torres, M.H.A. Mota, J.O. Tognolli and M. Molina, Analyst, 109 (1984) 385.

2 C.B. Melios, J.T Souza Campos, M.A.C. Mazzeu, L.L. Campos, M. Molina and J.O. Tognolli, Inorg. Chim. Acta, 139 (1987) 163.

3 C.B. Melios, H. Redigolo and M. Molina, J. Inorg. Biochem., 36 (1989) 307.

4 C.B. Melios Ph.D. Thesis, F.F.C.L. Araraquara, SP, Brazil, 1973.

5 E. Giesbrecht, M. Perrier and W.W. Wendlandt, An. Acad. Bras. Cienc., 34 (1962) 37.

6 M. Ionashiro, C.A.F. Graner and J. Zuanon Netto, Ecl. Quím., 8 (1983) 29.

7 L. Moscardini D'Assunção, I. Giolito and M. Ionashiro, Thermochim. Acta, 137 (1989) 319.