Thermal Behaviour Studies of Solid State Lanthanide (III) and Yttrium (III) Compounds of Cinnamylidenepyruvic Acid in an Atmosphere of Air

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Compostos Ln-CP foram preparados no estado sólido, onde Ln representa os lantanídios trivalentes (exceto promécio) e ítrio e CP é o cinamalpiruvato. As técnicas termogravimetria (TG), calorimetria exploratória diferencial (DSC), difratometria de raios X e complexometria foram utilizadas para caracterizar e estudar o comportamento térmico destes compostos. Os resultados proporcionaram informações com respeito a desidratação, estabilidade e decomposição térmica.

Solid state Ln-CP compounds, where Ln represents trivalent lanthanides (except for promethium) and yttrium, and CP is cinnamylidenepyruvate, were prepared. Thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction powder patterns and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results provide information about dehydration, thermal stability and thermal decomposition.

Keywords: *lanthanides and yttrium, cinnamylidenepyruvate, thermal behaviour*

Introduction

The preparation and investigation of several metal ion complexes with 4-dimethylaminobenzylidenepyruvate (DMBP), 2-chloro-4-dimethylaminobenzylidene- pyruvate (DMBP), 2-chloro-4-dimethylaminobenzylidenepyruvate (2-Cl-DMBP), 4-methoxybenzylidenepyruvate (4-MeO-BP) and cinnamylidenepyruvate (CP) have been investigated in aqueous solution[1-5].

In the solid state, several metal-ion complexes with DMBP and 4-MeO-BP, have also been prepared and investigated using TG, DTG, DSC, DTA and X-ray powder diffractometry[6-9]. The establishment of the stoichiometry, thermal stability as well as the thermal decomposition have been the main purposes of the aforementioned studies.

As an extension of the works of Refs. 6-9, in the present paper, solid state compounds of lanthanides (III) (except promethium) and yttrium (III) with CP (◎-CH=CH-CH=CH-COCOO⁻) were prepared The compounds were characterized and studied by complexometric titration, TG, DTG, DSC and X-ray diffractometry. The data obtained allowed us to acquire new information concerning these compounds in the solid state, including the influence of the metal-ion and of the ligand on their thermal stability and thermal decomposition mechanism in comparison with DMBP and 4-MeO-BP.

Experimental

The HCP and NaCP were obtained as described in the literature[10]. Lanthanide (III) and yttrium (III) chlorides were prepared as previously described[11]. The solid state compounds of trivalent lanthanides and yttrium with CP

were prepared by reaction of aqueous solution of NaCP with equimolar amounts of an aqueous solution of the corresponding lanthanide or yttrium chloride. The precipitates obtained were washed until elimination of chloride ions, filtered and dried in Whatman n$^{\circ}$ 40 filter papers, and stored in a desiccator over anhydrous calcium chloride.

After igniting the compounds to the respective oxide and dissolving with hydrochloric acid, the lanthanide and yttrium ion contents were determined by complexometric titration with standard EDTA solution using xylenol orange as indicator[12], and from the TG curves. The water and the ligand contents were determined from the TG curves.

The TG, DTG and DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with an air flux of $\approx$ 150 mL min^{-1}, a heating rate of 20 °C min^{-1} and with samples weighing about 7-8 mg. A platinum crucible was used for TG, DTG curves and aluminium crucible with a perforated cover was used for the DSC curves.

X-ray powder patterns were obtained with an HGZ 4/B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator. The Bragg-Brentano arrangement was adopted using CuKα radiation (λ = 1.541 Å) and a setting 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(CP)$_3$.nH$_2$O can be established, where

Ln represents lanthanide or yttrium, CP is cinnamylidenepyruvate and n = 2, except for the praseodymium compound where n = 1.5.

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

The TG and DTG curves of the compounds are shown in Fig. 1. The thermal decomposition of these compounds occurs in three or four consecutive steps between 30 and 800 °C. The patterns of the TG and DTG curves show a great similarity, except for cerium and europium compounds.

In all TG and DTG curves, the first mass loss observed up to 140 °C is due to the hydration water, and between 140 and $\approx$ 750 °C, occurs the thermal decomposition of the anhydrous compounds to the corresponding oxide (Ln$_2$O$_3$, Pr$_6$O$_{11}$, Tb$_4$O$_7$), except for the cerium compound where the thermal decomposition of the anhydrous compound occurs between 140 and 390 °C with formation of cerium oxide, CeO$_2$.

The TG and DTG curves of the lanthanum, praseodymium-samarium, gadolinium-lutetium and yttrium compounds, Figs. 1(a), (c-e) (g-o), show that the thermal decomposition of the anhydrous compounds occurs in the same way. For the first step, the mass losses that occur through a slow process are in agreement with the losses of 3(—◯—) and 7CH$_2$. The temperature range and the loss in % for these steps are shown in Table 2. The following step that occurs by a fast process which corresponds to the final pyrolysis of the ligand with formation of lanthanide dioxy-

Table 1. Analytical and Thermoanalytical (TG) results.

| Compound	Metal (%)			CP* (%)		Water (%)	
	Theor.	TG	EDTA	Theor.	TG	Theor.	TG
La(CP)$_3$.2H$_2$O	17.84	17.77	18.19	74.47	74.74	4.63	4.42
Ce(CP)$_3$.2H$_2$O	17.97	17.71	18.00	73.31	73.80	4.62	4.44
Pr(CP)$_3$.1.5H$_2$O	17.45	17.81	18.29	75.57	75.01	3.35	3.47
Nd(CP)$_3$.2H$_2$O	18.40	17.45	17.59	75.09	75.12	4.40	4.54
Sm(CP)$_3$.2H$_2$O	18.20	18.18	19.28	74.53	74.75	4.36	4.17
Eu(CP)$_3$.2H$_2$O	18.36	18.26	19.52	74.39	74.60	4.35	4.26
Gd(CP)$_3$.2H$_2$O	18.88	19.25	20.02	73.91	73.67	4.33	4.15
Tb(CP)$_3$.2H$_2$O	19.04	19.19	20.25	73.29	73.15	4.32	4.28
Dy(CP)$_3$.2H$_2$O	19.39	19.71	20.49	73.45	73.23	4.30	4.15
Ho(CP)$_3$.2H$_2$O	19.62	19.57	20.43	73.24	73.26	4.29	4.32
Er(CP)$_3$.2H$_2$O	19.84	19.98	20.91	73.04	72.94	4.28	4.22
Tm(CP)$_3$.2H$_2$O	20.00	19.98	20.82	72.89	72.95	4.27	4.24
Yb(CP)$_3$.2H$_2$O	20.39	20.69	21.33	72.54	72.20	4.25	4.24
Lu(CP)$_3$.2H$_2$O	20.57	20.71	21.72	72.37	72.11	4.24	4.34
Y(CP)$_3$.2H$_2$O	11.63	11.51	12.23	80.52	80.68	4.71	4.70

* CP is cinnamylidenebenzalpyruvate.
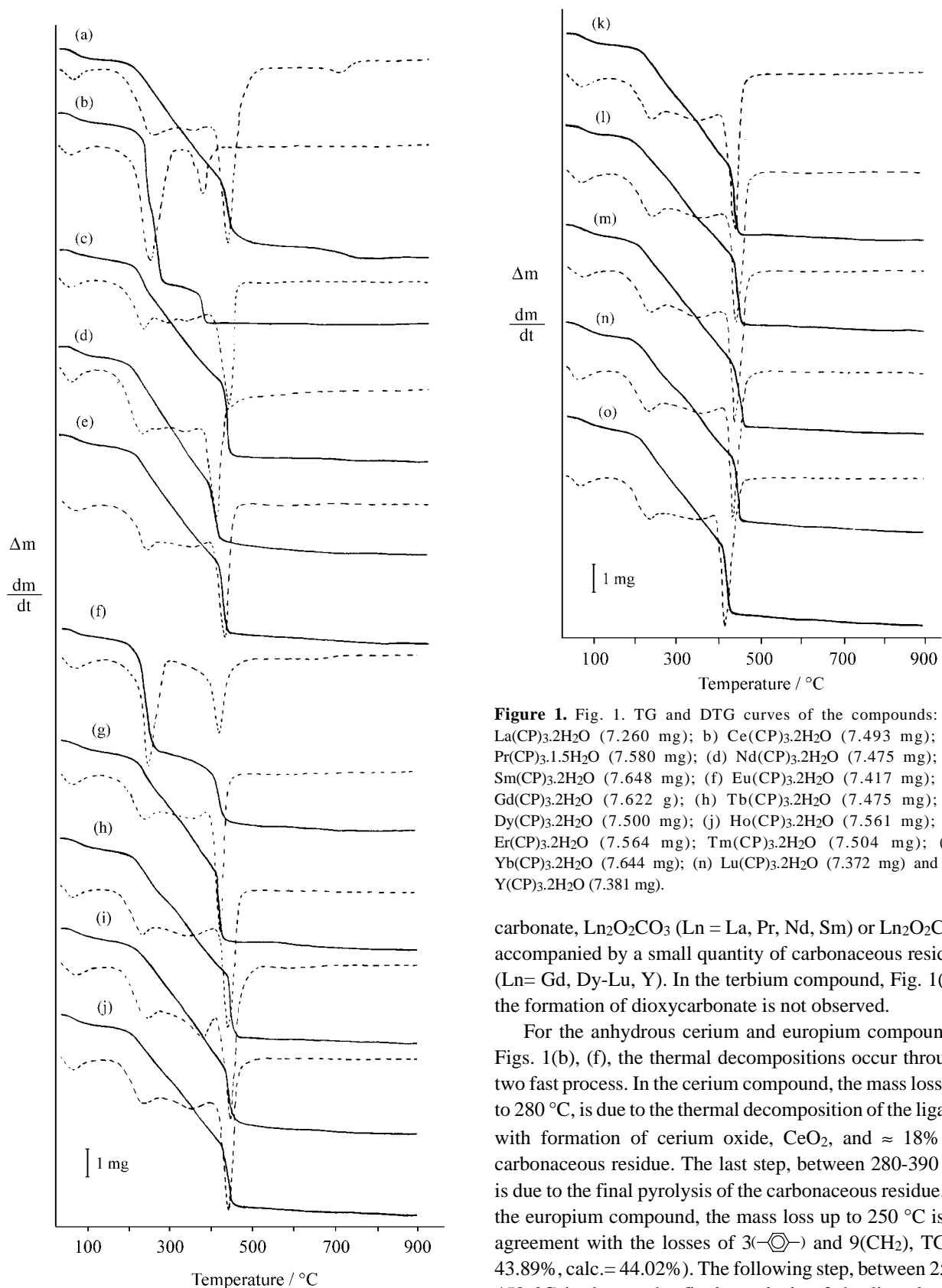
Figure 1. Fig. 1. TG and DTG curves of the compounds: (a) La(CP)$_3$.2H$_2$O (7.260 mg); b) Ce(CP)$_3$.2H$_2$O (7.493 mg); (c) Pr(CP)$_3$.1.5H$_2$O (7.580 mg); (d) Nd(CP)$_3$.2H$_2$O (7.475 mg); (e) Sm(CP)$_3$.2H$_2$O (7.648 mg); (f) Eu(CP)$_3$.2H$_2$O (7.417 mg); (g) Gd(CP)$_3$.2H$_2$O (7.622 g); (h) Tb(CP)$_3$.2H$_2$O (7.475 mg); (i) Dy(CP)$_3$.2H$_2$O (7.500 mg); (j) Ho(CP)$_3$.2H$_2$O (7.561 mg); (k) Er(CP)$_3$.2H$_2$O (7.564 mg); Tm(CP)$_3$.2H$_2$O (7.504 mg); (m) Yb(CP)$_3$.2H$_2$O (7.644 mg); (n) Lu(CP)$_3$.2H$_2$O (7.372 mg) and (o) Y(CP)$_3$.2H$_2$O (7.381 mg).

carbonate, Ln$_2$O$_2$CO$_3$ (Ln = La, Pr, Nd, Sm) or Ln$_2$O$_2$CO$_3$ accompanied by a small quantity of carbonaceous residue (Ln= Gd, Dy-Lu, Y). In the terbium compound, Fig. 1(h), the formation of dioxycarbonate is not observed.

For the anhydrous cerium and europium compounds, Figs. 1(b), (f), the thermal decompositions occur through two fast process. In the cerium compound, the mass loss up to 280 °C, is due to the thermal decomposition of the ligand with formation of cerium oxide, CeO$_2$, and $\approx$ 18% of carbonaceous residue. The last step, between 280-390 °C is due to the final pyrolysis of the carbonaceous residue. In the europium compound, the mass loss up to 250 °C is in agreement with the losses of 3(–◯–) and 9(CH$_2$), TG = 43.89%, calc.= 44.02%). The following step, between 250-450 °C is due to the final pyrolysis of the ligand with formation of europium dioxycarbonate, Eu$_2$O$_2$CO$_3$.
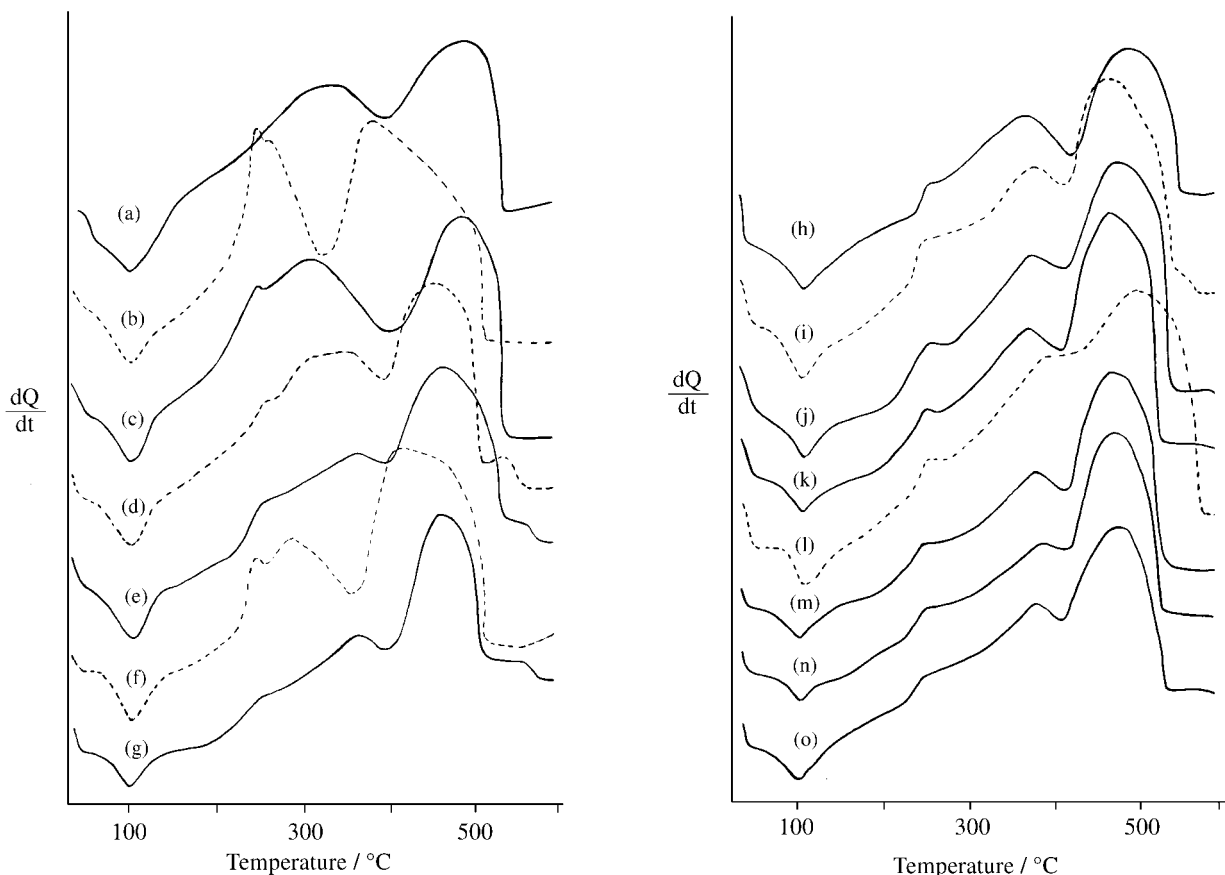
Figure 1. (part).

Figure 2. DSC curves of the compounds: (a) La(CP)$_3$.2H$_2$O; b) Ce(CP)$_3$.2H$_2$O; (c) Pr(CP)$_3$.1.5H$_2$O; (d) Nd(CP)$_3$.2H$_2$O; (e) Sm(CP)$_3$.2H$_2$O; (f) Eu(CP)$_3$.2H$_2$O; (g) Gd(CP)$_3$.2H$_2$O; (h) Tb(CP)$_3$.2H$_2$O; (i) Dy(CP)$_3$.2H$_2$O; (j) Ho(CP)$_3$.2H$_2$O; (k) Er(CP)$_3$.2H$_2$O; Tm(CP)$_3$.2H$_2$O; (m) Yb(CP)$_3$.2H$_2$O; (n) Lu(CP)$_3$.2H$_2$O and (o) Y(CP)$_3$.2H$_2$O.

Tests with hydrochloric acid solution on samples heated up to the temperature of formation of the dioxycarbonate, as indicated by the TG and DTG curves, confirmed the elimination of CO_2, or the presence of carbonaceous residue after the elimination of CO_2.

For the compounds that form the dioxycarbonate, only in the lanthanum compound the TG and DTG curves show that the intermediate is stable up to 590 °C, with the mass loss data in agreement with elimination of 0.5 CO_2. In the other compounds the thermal decomposition of the intermediates occurs through a slow process and the TG curves show a decreasing mass losses in this step, corresponding to the eliminations of CO_2, with increasing atomic number of the lanthanide ions, suggesting that a mixture of the intermediate and oxide occur in this step. This is in agreement with data previously reported[7]. A decreasing stability of these intermediates with increasing atomic number of the lanthanide ions has also been observed[13].

The DSC curves of these compounds are shown in Fig. 2. The broad endothermic peaks at ≈ 100 °C, observed in all compounds are due to the loss of hydration water, in agreement with the first mass loss observed in the TG and DTG curves. The dehydration of these compounds that

Table 2. Temperature range θ, and loss in % corresponding to the first step of the anhydrous compounds Ln(CP)$_3$.nH$_2$O, where Ln represents lanthanides and yttrium and CP is cinnamylidenebenzalpyruvate.

Compound	θ (°C)	Loss (%)	
		Cálc.	TG
La(CP)$_3$.2H$_2$O	180-385	41.42	41.3
Pr(CP)$_3$.1.5H$_2$O	180-382	41.79	41.5
Nd(CP)$_3$.2H$_2$O	180-346	41.14	41.3
Sm(CP)$_3$.2H$_2$O	180-378	40.82	40.9
Gd(CP)$_3$.2H$_2$O	180-384	40.46	40.9
Tb(CP)$_3$.2H$_2$O	180-387	40.38	40.5
Dy(CP)$_3$.2H$_2$O	180-387	40.20	40.4
Ho(CP)$_3$.2H$_2$O	180-387	40.08	40.1
Er(CP)$_3$.2H$_2$O	180-390	39.96	40.0
Tm(CP)$_3$.2H$_2$O	180-395	39.88	40.1
Yb(CP)$_3$.2H$_2$O	180-395	39.81	39.7
Lu(CP)$_3$.2H$_2$O	180-395	30.58	39.7
Y(CP)$_3$.2H$_2$O	180-390	44.26	44.3

occurs through a slow process, as can be seen from the TG, DTG and DSC curves, seems to be characteristic of amorphous compounds, as already observed in the dehydration of other amorphous compounds studied in our laboratory[6-9,13].

The broad exotherms verified after the dehydration, between ≈ 170 °C and ≈ 590 °C, are attributed to the pyrolysis of the ligand. The DSC curves, as well as, the DTG curves show that thermal decomposition of the anhydrous compounds occurs with a large number of consecutive or simultaneous steps and through a more complex pathway than that observed from the TG curves. The same behaviour has also been observed during the thermal decomposition of DMBP and 4-MeO-BP compounds[6-9].

Conclusions

From the TG and DTG curves, a general formula could be established for these compounds in the solid state, and provided information about the thermal stabilities of the compounds and of the decomposition products. These curves also show that the thermal decomposition of the solid compounds seems to occur through the same mechanism, except for the cerium and europium compounds.

Acknowledgements

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