Synthesis, characterization and thermal behaviour of solid-state compounds of light trivalent lanthanide succinates

L.S. Lima [a],[*], F.J. Caires [a], C.T. Carvalho [a], A.B. Siqueira [b], M. Ionashiro [a]

[a] Instituto de Química, UNESP, CP 355, 14801-970 – Araraquara, SP, Brazil
[b] Instituto de Ciências Exatas e da Terra, Campus Pontal do Araguaia, UFMT, Rodovia MT-100, 78698-000, MT, Brazil

ARTICLE INFO

ABSTRACT

Characterization, thermal stability and thermal decomposition of light trivalent lanthanide succinates, $Ln_2(C_4H_4O_4)_3 \cdot nH_2O$ (Ln = La to Gd, except Pm) were investigated employing simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), infrared spectroscopy, TG-FTIR system, elemental analysis and complexometry. The dehydration of the lanthanum and cerium compounds occurs in a single step, while for the praseodymium to gadolinium compounds the dehydration occurs in two consecutive steps. The thermal decomposition of the anhydrous compounds occurs in consecutive and/or overlapping steps, except for the cerium compound, with formation of the respective oxides, CeO_2, Pr_6O_{11} and Ln_2O_3 (Ln = La, Nd to Gd), as final residue. The results also provided information concerning the denticity of the ligand and thermal behaviour of these compounds.

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1. Introduction

Coordination polymers of rare-earth metals have received significant attention in the current research because of their wide range of application [1].

Preparation and investigation of several metal-ion succinates have been investigated in the solid-state using thermoanalytical techniques, X-ray diffractometry and infrared spectroscopy. The papers published are concerned with the thermogravimetric study of rare earth elements, yttrium and scandium malonate and succinates [2], thermal analysis of lanthanum and cerium succinates [3], thermal decomposition of gadolinium fumarate and succinate [4], thermal decomposition of ytterbium fumarate and succinate [5] and thermal studies of praseodymium(III) and dysprosium(III) succinates [6]. In these papers the thermal studies were performed in a static atmosphere.

In the present paper, solid-state compounds of light trivalent lanthanides (i.e. La to Gd, except Pm) with succinate were prepared. The compounds were investigated by means of complexometry, elemental analysis, X-ray diffractometry, infrared spectroscopy, simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) and TG-FTIR system. The thermal studies were performed in dynamical air atmosphere.

2. Experimental

The sodium succinate, $Na_2C_4H_4O_4 \cdot 6H_2O$, with 99% purity was obtained from Sigma–Aldrich and aqueous solution $0.1 \, mol \, L^{-1}$ was prepared by direct weighing of the salt.

Lanthanide chlorides were prepared from the corresponding oxides (except for cerium) by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues redissolved in distilled water, and the solutions again evaporated to near dryness to eliminate the excess of hydrochloric acid. The residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain $0.1 \, mol \, L^{-1}$ solutions, whose pH was adjusted to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. Aqueous solution of cerium(III) nitrate $0.1 \, mol \, L^{-1}$ was prepared by direct weighing of the salt.

The solid-state compounds were prepared by adding slowly, with continuous stirring, the solution of the ligand to the hot solution of the respective lanthanides, until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of chloride (or nitrate) ions, filtered through and dried on Whatman no. 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In the solid-state compounds, hydration water, ligand and metal ion contents were determined from the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [7]. Carbon and hydrogen microanalysis were performed using an EA 1110, CHNS-O Elemental Analyser (CE Instruments).

* Corresponding author. Tel.: +55 16 3301 6617; fax: +55 16 3322 7932.
E-mail address: lispazzapam@yahoo.com.br (L.S. Lima).

Table 1
Analytical and thermoanalytical (TG) data for $Ln_2(L)_3 \cdot nH_2O$ compounds.

Compound	Lanthanide oxide (%)			L (lost) (%)		H_2O (%)		C (%)		H (%)		Final residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd.	E.A.	Calcd.	E.A.	
$La_2(L)_3 \cdot 5H_2O$	45.50	45.24	45.90	41.92	41.83	12.58	12.93	20.12	20.42	3.10	2.80	La_2O_3
$Ce_2(L)_3 \cdot 5H_2O$	47.91	47.76	47.75	39.55	39.48	12.54	12.76	20.06	20.41	3.09	3.34	CeO_2
$Pr_2(L)_3 \cdot 4H_2O$	48.49	48.38	48.59	41.24	41.52	10.27	10.10	20.53	20.35	2.88	2.81	Pr_6O_{11}
$Nd_2(L)_3 \cdot 4H_2O$	47.54	47.56	47.93	42.29	42.14	10.17	10.30	20.33	20.49	2.85	2.50	Nd_2O_3
$Sm_2(L)_3 \cdot 5H_2O$	47.18	47.48	47.43	40.63	40.43	12.19	12.09	19.50	20.01	3.01	2.78	Sm_2O_3
$Eu_2(L)_3 \cdot 4H_2O$	48.60	48.45	48.84	41.45	41.35	9.95	10.20	19.90	19.40	2.79	3.00	Eu_2O_3
$Gd_2(L)_3 \cdot 5H_2O$	48.15	47.94	48.65	39.89	40.22	11.96	11.84	19.16	19.32	2.95	2.80	Gd_2O_3

L = succinate and Ln = lanthanide.

X-ray powder patterns were obtained by using X-ray diffractometer Rigaku RINT 2000 with copper rotatory anode (λ = 1.5406 Å).

The attenuate total reflectance (ATR) spectra for sodium succinate, as well as for its lanthanide compounds were run on a Nicolet iS10 FT-IR spectrophotometer, using an ATR accessory with Ge window.

Simultaneous TG-DTA and DSC curves were obtained with two thermal analysis system, model SDT 2960 and DSC Q10, both from TA Instruments. The purge gas was an air flow of 100 mL min^{-1} for TG-DTA and 50 mL min^{-1} for DSC experiments. A heating rate of 20 °C min^{-1} was adopted, with samples weighing about 7 mg for TG-DTA and 2 mg for DSC. Alumina and aluminium crucibles, the latter with perforated cover, were used for TG-DTA and DSC, respectively.

The measurements of the gaseous products were carried out using a Thermogravimetric Analyzer Mettler TG-DTA coupled to a FTIR spectrophotometer Nicolet with gas cell and DTGS KBr detector. The furnace and the heated gas cell (250 °C) were coupled through a heated (T = 200 °C) 120 cm stainless steel line transfer with diameter 3.0 mm both purged with dry air (50 mL min^{-1}). The FTIR spectra were recorded with 32 scans per spectrum at a resolution of 4 cm^{-1}.

3. Results and discussion

The analytical and thermoanalytical (TG) data are shown in Table 1. These results permitted to establish the stoichiometry of the compounds, which are in agreement with the general formula $Ln(L)_3 \cdot nH_2O$, where Ln represents lanthanides, L is succinate and n = 4 (Pr, Nd, Eu) or 5 (La, Ce, Sm, Gd).

The X-ray powder patterns show that all the compounds were obtained with low crystallinity degree and for the praseodymium, neodymium and samarium compounds with evidence for formation of an isomorphous series.

The difference in the crystallinity degree of these compounds undoubtedly is due to the stirring and/or the adding velocity of the ligand solution to the respective metal chloride or nitrate solutions that were not rigorously controlled, as already observed for other compounds [8].

The attenuate total reflectance infrared spectroscopic data on succinate (sodium salt) and its compounds with the metal ions considered in this work are shown in Table 2. The investigation was focused mainly 1700–1400 cm^{-1} range, because this region is potentially most informative in attempting to assign coordination sites.

In $C_4H_4O_4$ (sodium salt), strong band at 1535 cm^{-1} and a medium intensity band located at 1401 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [9,10]. For the lanthanum and cerium compounds the band assigned to the anti-symmetrical stretching carboxylate frequencies are shifted to lower values and the symmetrical ones to higher, relative to the corresponding frequencies in $C_4H_4O_4$. The $\Delta\nu$ ($\nu_{as} - \nu_{sym}$) for these compounds is indicative that the La(III) and Ce(III) are linked to the carboxylate group by a bridging bond [11].

For the praseodymium to gadolinium compounds the anti-symmetrical and symmetrical stretching carboxylate frequencies are both shifted to higher values relative to the corresponding frequencies in $C_4H_4O_4$ (sodium salt). The $\Delta\nu$ for these compounds suggest that these lanthanides are linked to the carboxylate group by a bridging bidentate bond [11].

The simultaneous TG-DTA curves of the compounds are shown in Fig. 1. These curves show mass losses in two (Ce), four (La, Eu, Gd), five (Pr, Sm) and six (Nd) consecutive and/or overlapping steps and thermal events corresponding to these losses or due to physical phenomenon.

Two patterns of thermal behaviour are observed up to 250 °C. Firstly, a close similarity is noted concerning the TG-DTA profiles of lanthanum and cerium compounds, Fig. 1a and b, or between the praseodymium to gadolinium ones (Fig. 1c–g). On the other hand, praseodymium and samarium compounds (Fig. 1c and e) or europium and gadolinium ones, Fig. 1f and g show a close similarity up to 680 and 720 °C, respectively.

Thus the features of each compound are discussed on the base of their similar thermal profiles up to 720 °C.

3.1. Lanthanum compound

The TG-DTA curves of the lanthanum compound are shown in Fig. 1a. The first mass loss up to 190 °C, corresponding to an endothermic peak at 165 °C is due to dehydration with loss of $5H_2O$ (Calcd. = 12.58%, TG = 12.93%).

After the dehydration the anhydrous compound is stable up to 365 °C and above this temperature the thermal decomposition

Table 2
Spectroscopic data for sodium succinate ($C_4H_4O_4$) and its compounds with light trivalent lanthanides.

Compound	ν_{as} (COO$^-$) cm^{-1}	ν_{sym} (COO$^-$) cm^{-1}	$\Delta\nu$ ($\nu_{as} - \nu_{sym}$)
$Na_2(C_4H_4O_4) \cdot 6H_2O$	1535 s	1401 m	134
$La_2(C_4H_4O_4)_3 \cdot 5H_2O$	1527 s	1422 m	105
$Ce_2(C_4H_4O_4)_3 \cdot 5H_2O$	1528 s	1423 m	105
$Pr_2(C_4H_4O_4)_3 \cdot 4H_2O$	1573 s	1403 m	170
$Nd_2(C_4H_4O_4)_3 \cdot 4H_2O$	1574 s	1404 m	170
$Sm_2(C_4H_4O_4)_3 \cdot 5H_2O$	1578 s	1405 m	173
$Eu_2(C_4H_4O_4)_3 \cdot 4H_2O$	1580 s	1406 m	174
$Gd_2(C_4H_4O_4)_3 \cdot 5H_2O$	1579 s	1407 m	172

s = strong and m = medium.
ν_{as} (COO$^-$) and ν_{sym} (COO$^-$) = anti-symmetrical and symmetrical vibrations of the COO$^-$ group, respectively.
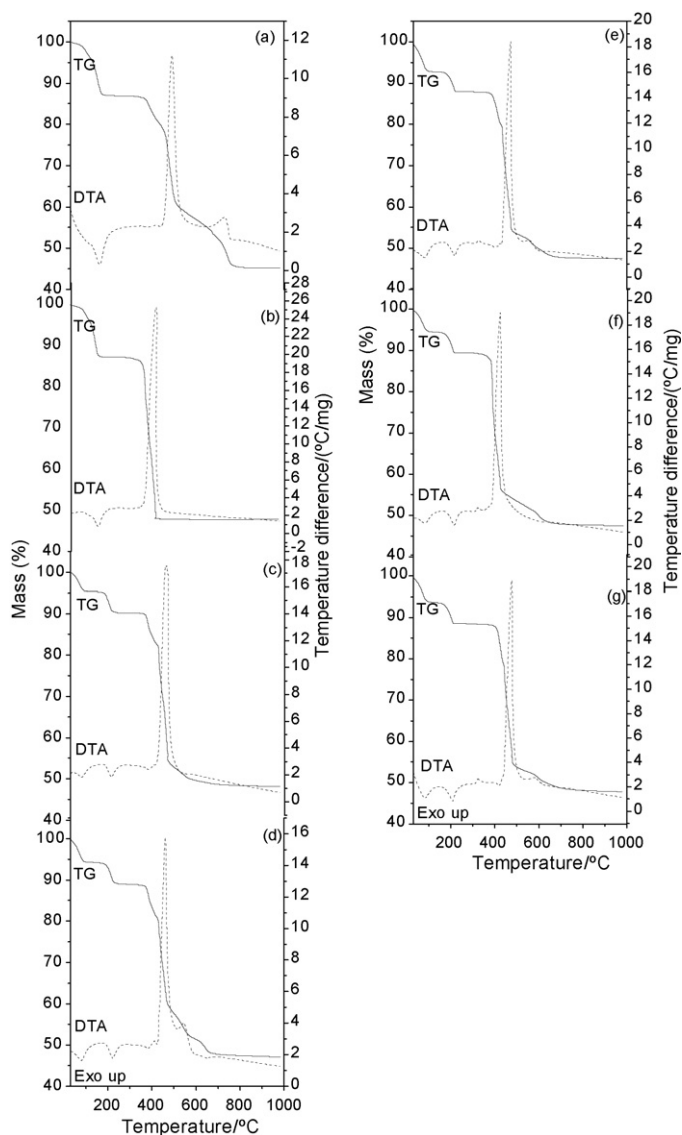
Fig. 1. Simultaneous TG-DTA curves of the compounds: (a) $La_2L_3·5H_2O$ (7.0279 mg); (b) $Ce_2L_3·5H_2O$ (7.3772 mg); (c) $Pr_2L_3·4H_2O$ (6.9885 mg); (d) $Nd_2L_3·4H_2O$ (7.2812 mg); (e) $Sm_2L_3·5H_2O$ (7.0684 mg); (f) $Eu_2L_3·4H_2O$ (7.1891 mg) and (g) $Gd_2L_3·5H_2O$ (7.2186 mg). L = succinate.

occurs in three steps between 365–450, 450–525 and 525–800 °C, with losses of 7.64, 19.31 and 14.88%, respectively, corresponding to the exothermic peaks at 490 and 730 °C attributed to oxidation of the organic matter. No thermal event corresponding to the first mass loss of the anhydrous compound is observed in the DTA curve and this is probably due to the heat involved in this step is not sufficient to produce a thermal event.

The total mass loss up to 800 °C is in agreement with the formation of La_2O_3 as the final residue (Calcd. = 54.50%, TG = 54.76%).

3.2. Cerium compound

The TG-DTA curves are shown in Fig. 1b. The first mass loss up to 170 °C corresponding to an endothermic peak at 155 °C is due to dehydration with loss of $5H_2O$ (Calcd. = 12.54%, TG = 12.76%). The anhydrous compound is stable up to 340 °C and above this temperature the thermal decomposition occurs in a single step up to 415 °C, corresponding to the exothermic peak at 415 °C attributed to the oxidation reaction of Ce(III) to Ce(IV), together with the oxidation of the organic matter. The smaller thermal stability of the cerium compound had already been observed for other cerium compound [12,13].

The total mass loss up to 415 °C is in agreement with the formation of CeO_2 as final residue (Calcd. = 52.09%, TG = 52.24%).

The thermal decomposition of the anhydrous cerium compound that occurs without formation of carbonate as intermediate is in disagreement with the results reported by Sevost'yanov and Dvornikova [3].

3.3. Neodymium compound

The TG-DTA curves are shown in Fig. 1d. The first two mass losses between 30–100 and 180–230 °C, corresponding to the endothermic peaks at 80 and 220 °C, are due to dehydration with loss of $2H_2O$ in each step (Calcd. = 5.15%, TG = 5.10 and 5.20%, respectively). The anhydrous compound is stable up to 365 °C and above this temperature the thermal decomposition occurs in four consecutive and/or overlapping steps between 365–425, 425–475, 475–580 and 580–670 °C, with losses of 8.10, 21.07, 7.70 and 5.27%, respectively, corresponding to the endothermic peaks at 380, 650 °C and exothermic ones at 410, 460 and 545 °C, which are attributed to the thermal decomposition and/or oxidation of the products evolved during the thermal decomposition.

The total mass loss up to 670 °C is in agreement with the formation of Nd_2O_3, as final residue (Calcd. = 52.46%, TG = 52.44%).
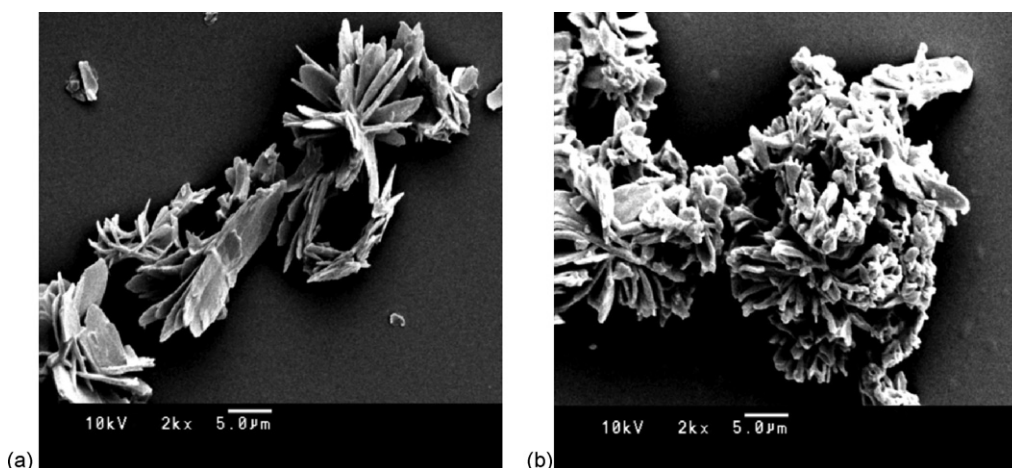

Fig. 2. SEM of the samarium compound heated up to (a) 300 °C and (b) 360 °C.

3.4. Praseodymium and samarium compounds

The TG-DTA curves are shown in Fig. 1c and e, respectively. The first two mass losses between 30–100 °C (Pr, Sm) and 180–230 °C (Pr) or 165–225 °C (Sm), corresponding to the endothermic peaks at 80 °C (Pr, Sm) and 210 °C (Pr) or 215 °C (Sm), are due to dehydration with losses of $2H_2O$ in each step (Pr) (Calcd. = 5.14%, TG = 5.00 and 5.10%) or 3 and $2H_2O$ (Sm) (Calcd. = 7.31 and 4.88%, TG = 7.30 and 4.79%), respectively.

The anhydrous compounds are stable up to 365 °C (Pr) and 375 °C (Sm) and above these temperatures the thermal decomposition occurs in three consecutive and/or overlapping steps between 365–430, 430–475 and 475–680 °C (Pr) or 375–435, 435–470 and 470–670 °C (Sm), with losses of 7.90, 27.69, 5.93% (Pr) and 8.51, 25.0 and 6.92% (Sm), respectively. In correspondence with the mass losses of the TG curves, the DTA ones show endothermic peaks at 385 °C (Pr) and 400 °C (Sm) and exothermic peaks at 465 °C (Pr) or 470 and 565 °C (Sm), which are attributed to the thermal decomposition and oxidation of the products evolved during the thermal decomposition.

The total mass loss up to 680 °C (Pr) and 670 °C (Sm) is in agreement with the formation of Pr_6O_{11} (Calcd. = 51.51%, TG = 51.62%) and Sm_2O_3 (Calcd. = 52.82%, TG = 52.52%), as final residue.

The formation of Pr_6O_{11} as final residue of the decomposition of praseodymium compound is also in disagreement with the result reported by Kaul and Sharma [6].

3.5. Europium and gadolinium compounds

The TG-DTA curves are shown in Fig. 1f and g, respectively. The first two mass losses between 30–100 °C (Eu, Gd)) and 160–220 °C (Eu) or 155–220 °C (Gd), corresponding to the endothermic peaks at 80 and 210 °C (Eu, Gd), are due to dehydration with losses of $2H_2O$ in each step (Eu) (Calcd. = 4.98%, TG = 5.20 and 5.00%) or 3 and $2H_2O$ (Gd) (Calcd. = 7.18 and 4.78%, TG = 7.10 and 4.74%), respectively.

The anhydrous compounds are stable up to 340 °C (Eu) and 390 °C (Gd), and above these temperatures the mass losses occur in two consecutive steps between 340–430 and 430–690 °C (Eu) or 390–485 and 485–720 °C (Gd), with losses of 32.69 and 8.66% (Eu) or 33.29 and 6.93% (Gd), respectively. In correspondence with the mass losses of the TG curves, the DTA ones show an endothermic peak at 420 °C (Gd), attributed to the thermal decomposition and exothermic peaks at 420 °C (Eu) or 480 and 585 °C (Gd) which are attributed to the oxidation of the products evolved during the thermal decomposition.

The total mass loss up to 690 °C (Eu) and 720 °C (Gd) is in agreement with the formation of Eu_2O_3 (Calcd. = 51.40%, TG = 51.55%) and Gd_2O_3 (Calcd. = 51.85%, TG = 52.06%), as final residue.

The thermal decomposition temperature, as well as the thermal stability of the anhydrous gadolinium compound is in disagreement with the results reported by Sevost'yanov and Dvornikova [4].

The formation of Ln_2O_3 (Ln = La, Nd to Gd), CeO_2 and Pr_6O_{11} as final residue of the TG curve were also confirmed by X-ray powder diffractometry.

The small exothermic peak at 320 °C (Sm, Eu) and 325 °C (Gd), without mass loss in the TG curve is attributed to crystallization process which was confirmed by X-ray powder diffractometry, as can be seen in Figs. 2 and 3, as representative of these compounds.

The DSC curves of the compounds are shown in Fig. 4. These curves show endothermic and exothermic peaks that all accord with the thermal events observed in the DTA curves. The endothermic peaks at 166 °C (La), 158 °C (Ce), 94 and 227 °C. (Pr), 97 and 234 °C (Nd), 101 and 244 °C (Sm), 90 and 226 °C (Eu) and 92 and 223 °C (Gd) are attributed to dehydration. The dehydration
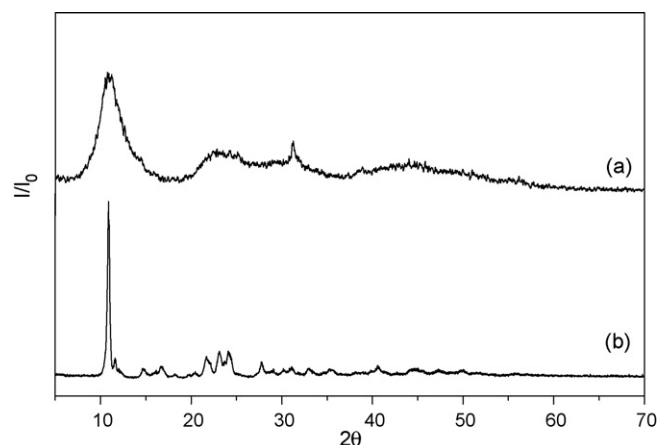

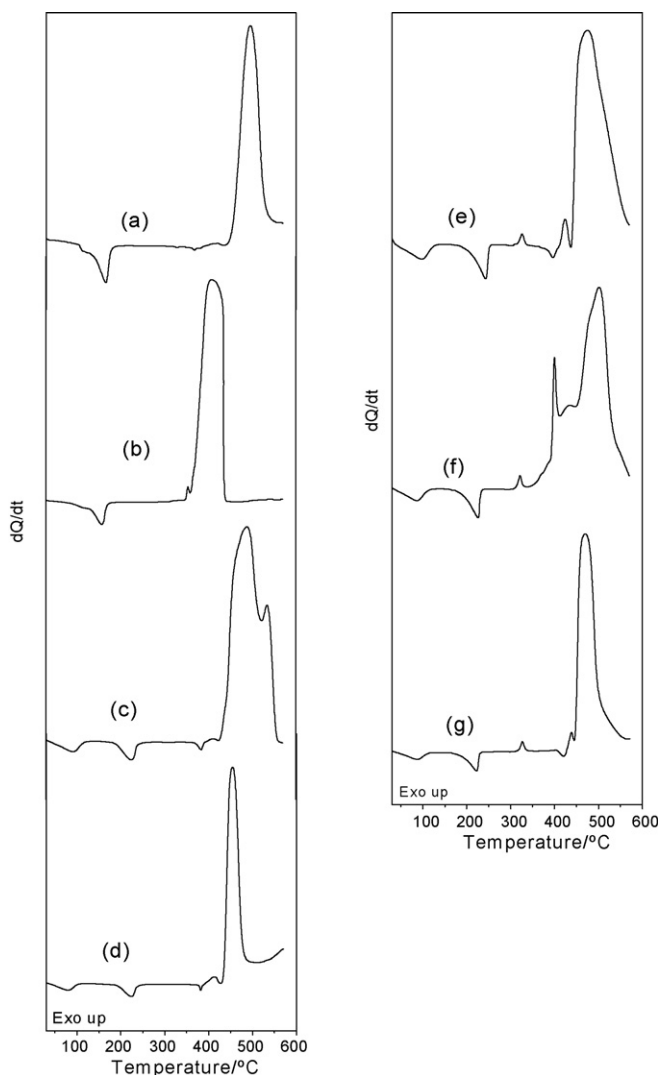**Fig. 3.** X-ray powder pattern of the samarium compound heated up to (a) 300 °C and (b) 360 °C.

Fig. 4. DSC curves of the compounds: (a) $La_2L_3 \cdot 5H_2O$ (2.0420 mg); (b) $Ce_2L_3 \cdot 5H_2O$ (1.9780 mg); (c) $Pr_2L_3 \cdot 4H_2O$ (1.9600 mg); (d) $Nd_2L_3 \cdot 4H_2O$ (2.0220 mg); (e) $Sm_2L_3 \cdot 5H_2O$ (2.0450 mg); (f) $Eu_2L_3 \cdot 4H_2O$ (2.0000 mg) and (g) $Gd_2L_3 \cdot 5H_2O$ (2.0240 mg).
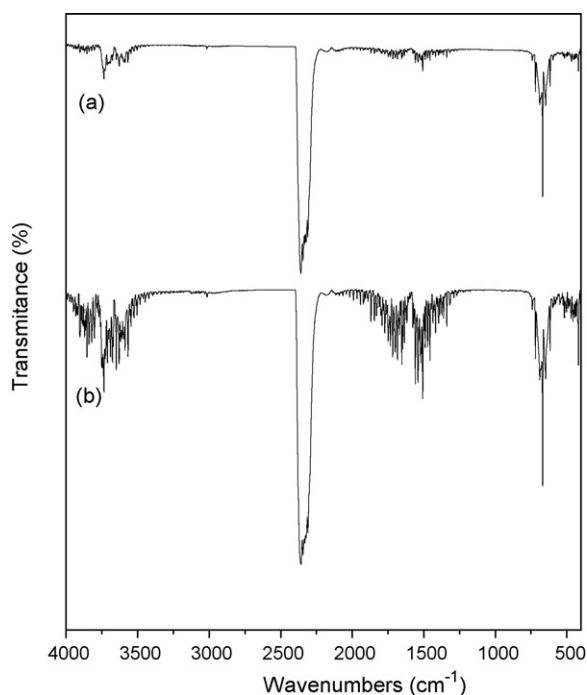
Fig. 5. IR spectra of gaseous products evolved during the decomposition of the compounds: (a) $La_2L_3 \cdot 5H_2O$ and (b) $Eu_2L_3 \cdot 4H_2O$. L = succinate.

enthalpies found for these compounds were: 135.1 (La), 135.3 (Ce), 37.7 and 100.4 (Pr), 60.8 and 121.4 (Nd), 70.0 and 146.3 (Sm), 67.5 and 149.8 (Eu), 66.3 and 153.4 kJ mol^{-1} (Gd).

For all the compounds, the thermal events above 350 °C are due to the thermal decomposition and/or oxidation of organic matter.

The small exothermic peak observed at 325 °C for the Sm, Eu and Gd compounds is due to crystallization, in agreement with DTA curves, and the crystallization enthalpy found was 18.6, 24.4 and 29.4 kJ mol^{-1}, respectively.

The gaseous products evolved during the thermal decomposition of the compounds studied in this work were monitored by FTIR, and it has carbon dioxide as main product due to the decarboxylation and oxidation of organic matter. The IR spectra of the gaseous products evolved during the thermal decomposition of lanthanum and europium, as representative of all the compounds are shown in Fig. 5.

4. Conclusion

From TG, complexometry and elemental analysis data, a general formula could be established for the compounds involving the light trivalent lanthanides and succinate.

The reflectance infrared spectroscopic data suggest that the succinate act as bridging ligand toward the lanthanum and cerium ions, and as bridging bidentate ligand for praseodymium to gadolinium ones.

The TG-DTA and DSC curves show that the lanthanum and cerium compounds, the dehydration occurs in a single step while praseodymium to gadolinium ones, the dehydration occurs in two steps. In the praseodymium to gadolinium compounds, the high dehydration temperature indicates that the last two water molecules are coordinated ones.

The TG-DTA and DSC curves also provided previously unreported information about the thermal behaviour of these compounds in a dynamic air atmosphere.

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