J Therm Anal Calorim (2010) 100:95–100
DOI 10.1007/s10973-009-0537-y

Synthesis, characterization and thermal behaviour of heavy lanthanide and yttrium pyruvates in the solid state

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Received: 2 June 2009 / Accepted: 29 September 2009 / Published online: 1 November 2009

Abstract Solid-state Ln–L compounds, where Ln stands for heavy trivalent lanthanides or yttrium (III) (Tb–Lu, Y) and where L is pyruvate, have been synthesized. Thermogravimetry and derivative thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), X-Ray powder diffractometry, infrared spectroscopy, elemental analysis and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to information about the composition, dehydration, thermal behaviour, ligand denticity of the isolated complexes.

Keywords Heavy lanthanides and yttrium · Pyruvate · Characterization · Thermal behaviour

Introduction

Pyruvic acid is a substance present naturally in our organisms, and it is a Krebs cycle base or citric acid cycle. This cycle is the process from which the body converts the glycogen and the glucose to energy. Pyruvic acid is the result from the transformation of the glucose by aerobic metabolism in a process known as glycolysis. Performing a fundamental role in the Krebs cycle, the pyruvic acid has a vital role in the conversion of food in energy.

Few investigations have been carried out on compound derivatives of pyruvic acid (H_3C–CO–COOH). In aqueous solutions, the formation of some metal–ion complexes with pyruvic acid in a ratio of metal to ligand of 1:1 and 1:2 has been established by the spectroscopic method [1–3]. The stability constants and thermodynamic functions of lanthanide-complex formation with pyruvic acid (ΔG, ΔH, ΔS) have also been determined [4]. In the solid state, preparation of europium pyruvate [5], as well as the preparation and properties of lanthanides and yttrium pyruvates have also been described [6–8].

The aim of this work was to obtain heavy trivalent lanthanide pyruvates in the solid state and to investigate them by means of complexometry, elemental analysis, X-Ray powder diffractometry, infrared spectroscopy, thermogravimetry (TG) and differential scanning calorimetry (DSC).

Experimental

Sodium pyruvate 99% pure was obtained from Sigma. An aqueous solution of sodium pyruvate 0.30 mol L^{-1} was made by direct weighing of the solid salt.

Heavy lanthanide (III) and yttrium (III) chlorides were prepared from the corresponding metal oxides by treating

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with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues were redissolved in distilled water and the solutions were again evaporated to near dryness to eliminate the excess hydrochloric acid. The residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain 0.30 mol L^{-1} solutions whose pH were adjusted to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. The solid-state compounds were prepared by adding equivalent quantities of hot solution of sodium pyruvate to a hot solution of the respective metal chloride. The solutions were maintained in a water bath until the total precipitation of the metal pyruvates was achieved and the precipitates were then washed with hot distilled water to eliminate the chloride. These were then filtered through and dried on Whatman no 42 filter paper and kept in a desiccator over anhydrous calcium chloride.

After igniting the compounds to the respective oxides (Tb_4O_7 and Ln_2O_3, Ln = Dy–Lu, Y) and dissolving them in a hot solution of concentrated hydrochloric acid, their lanthanide contents were determined by complexometric titration with standard EDTA solution, using xylenol orange as indicator [9]. The lanthanide contents were also estimated from their corresponding TG curves. The dehydration of the compounds was first indicated by their DTG curves and subsequently confirmed by the broad endothermic peaks centered at 348–448 K in the respective DSC curves. The water content of the compounds was then determined from the corresponding mass losses observed in the TG curves. Next, the ligand content was also assessed from the TG curves.

X-ray powder patterns were obtained using a Siemens D-5000 X-Ray diffractometer under CuK_{α} radiation ($\lambda = 1.541$ Å) and set at 40 kV and 20 mA. The infrared spectra for sodium pyruvate as well as for its metal–ion compounds were recorded on a Nicolet model Impact 400 FTIR Instrument in the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

The TG and DTG curves were obtained using a Mettler TA 4000 thermal analysis system with an air flow of 100 mL min^{-1}, a heating rate of 5 K min^{-1} and samples weighing about 7 mg. An alumina crucible was used for the TG/DTG curves.

The DSC curves were obtained using a thermal analysis system model DSCQ10 from TA Instruments. The purge gas was an air flow of 50 mL min^{-1}. A heating rate of 10 K min^{-1} was adopted for samples weighing about 5 mg. Aluminium crucibles along with perforated cover were used for recording the DSC curves.

Results and discussion

Table 1 presents the analytical, thermoanalytical (TG) and elemental analysis (E.A) data for the prepared compounds from which the general formula $Ln(L)_3 \cdot nH_2O$ can be established, where Ln represents trivalent lanthanides L is pyruvate and $n = 4.5$ (Tb); 3.5 (Dy, Ho); 3 (Tm − Lu, Y) and 2.5 (Er).

The X-ray powder patterns showed that all compounds are amorphous. The amorphous state is undoubtedly due to the decreasing solubility with increasing temperature, where the precipitation of these compounds occurs quickly near the ebullition temperature.

The infrared spectroscopic data for sodium pyruvate and its compounds with the metal ions considered in this work are shown in Table 2. The investigation was focused mainly within the 1700–1400 cm^{-1} range because this region is potentially more informative in attempting to assign coordination sites. For sodium pyruvate, a strong

Table 1 Analytical and thermoanalytical (TG) data for $Ln(L)_3 \cdot nH_2O$, where Ln = heavy lanthanides or yttrium and L = pyruvate

Compound	Metal oxide/%			L, lost/%		Water/%		Carbon/%		Hidrogen/%	
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd	E.A	Calcd	E.A
$Tb(L)_3 \cdot 4.5H_2O$	37.30	37.08	37.75	46.52	46.92	16.18	16.00	21.57	21.76	3.63	3.56
$Dy(L)_3 \cdot 3.5H_2O$	38.32	38.15	38.52	48.72	49.04	12.96	12.81	22.21	22.36	3.32	3.54
$Ho(L)_3 \cdot 3.5H_2O$	38.62	38.89	39.81	48.49	48.37	12.89	12.74	22.10	21.94	3.30	3.19
$Er(L)_3 \cdot 2.5H_2O$	40.39	40.70	40.10	50.10	49.47	9.51	9.83	22.83	22.54	2.99	2.80
$Tm(L)_3 \cdot 3H_2O$	39.85	40.30	40.65	48.98	48.32	11.17	11.38	22.32	22.02	3.13	3.01
$Yb(L)_3 \cdot 3H_2O$	40.35	40.75	40.87	48.58	48.48	11.07	10.77	22.14	22.09	3.10	2.97
$Lu(L)_3 \cdot 3H_2O$	40.53	40.24	40.35	48.43	48.47	11.04	11.29	22.07	22.29	3.09	3.21
$Y(L)_3 \cdot 3H_2O$	27.93	28.34	28.47	58.68	58.01	13.38	13.65	26.75	26.44	3.75	3.69

Table 2 Spectroscopic data for sodium pyruvate and compounds with heavy trivalent lanthanides

Compound	ν_{OH} (H_2O)	$\nu_{asym(COO^-)}$	$\Delta\nu_{asym(COO^-)}$	$\nu_{sym(COO^-)}/cm^{-1}$	$\nu_{C=O}/cm^{-1}$
NaL	–	1640_s	–	1406_m	1709_m
$Tb(L)_3 \cdot 4.5H_2O$	3370_{br}	1603_s	37	1411_m	–
$Dy(L)_3 \cdot 3.5H_2O$	3373_{br}	1601_s	39	1411_m	–
$Ho(L)_3 \cdot 3.5H_2O$	3387_{br}	1605_s	35	1412_m	–
$Er(L)_3 \cdot 2.5H_2O$	3381_{br}	1595_s	45	1406_m	–
$Tm(L)_3 \cdot 3H_2O$	3387_{br}	1597_s	43	1398_m	–
$Yb(L)_3 \cdot 3H_2O$	3412_{br}	1601_s	39	1396_m	–
$Lu(L)_3 \cdot 3H_2O$	3400_{br}	1599_s	41	1400_m	–
$Y(L)_3 \cdot 3H_2O$	3350_{br}	1605_s	35	1410_m	–

s strong, *m* medium, *br* broad

$\nu_{asym(COO^-)}$ and $\nu_{sym(COO^-)}$: symmetrical and anti-symmetrical vibrations of the COO^- group, respectively

$\Delta\nu_{asym(COO^-)} = \nu_{asym(COO^-)}$ NaL $- \nu_{asym(COO^-)}$ (lanthanide complex)

$\nu_{(C=O)}$: ketonic carbonyl stretching frequency

$\nu_{(O-H)}$: hydroxyl group stretching frequency

band at 1640 cm^{-1} and a medium intensity band located at 1406 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies, respectively, of the carboxylate group [10, 11]. The band centered at 1709 cm^{-1} is attributed to the stretching frequency of the ketonic carbonyl group. For the prepared compounds, the infrared spectra show a broad band in the 3350–3412 cm^{-1} range attributed to hydration water. The anti-symmetrical and symmetrical stretching frequencies of the carboxylate group are observed between 1595–1605 and 1396–1412 cm^{-1}, respectively. No band due to the stretching frequency of the ketonic carbonyl group is observed in the spectrum of these compounds, and its absence is undoubtedly due to the overlapping bands of the anti-symmetrical stretching frequency of the carboxylate and the stretching frequency of the ketonic carbonyl group, as can be seen in Fig. 1. These data show that the bands due to the anti-symmetrical stretching frequency of the carboxylate and the stretching frequency of the ketonic carbonyl group are moved to the lower frequencies in comparison with the ligand frequencies, suggesting that the metal ions are coordinated by α-ketonic carbonyl and carboxylate groups [12, 13]. This behaviour is in agreement with that observed for compounds of lanthanides with phenyl-substituted derivatives of benzylidenepyruvate [14–16].

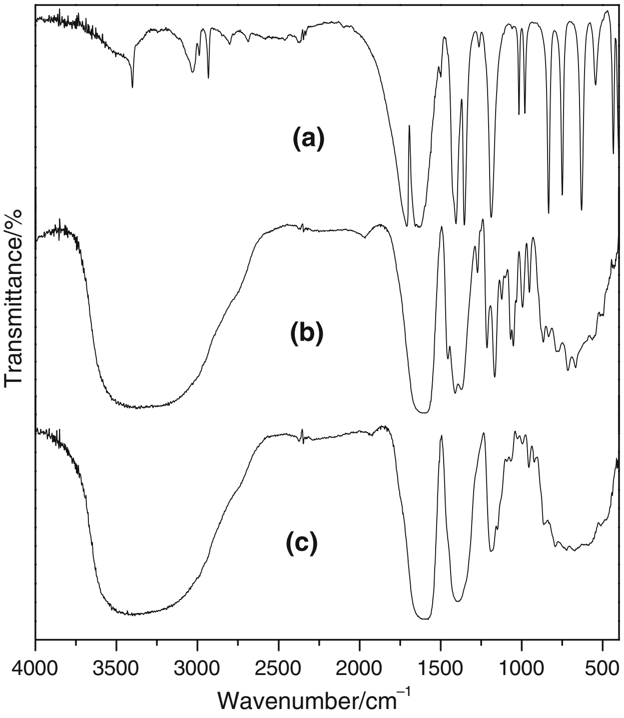

Fig. 1 The IR spectra of: (*a*) NaL; (*b*) $Dy(L)_3.3.5H_2O$ (m = 6.793 mg); (*c*) $Yb(L)_3 \cdot 3H_2O$. L = pyruvate

The TG and DTG curves of the compounds are shown in Fig. 2. These curves show mass losses in four (Tb, Yb, Lu) and five (Dy, Ho, Er, Tm, Y) consecutive and/or overlapping steps, without a plateau between the steps and without evidence concerning the formation of stable anhydrous compounds. As previously stressed, the temperatures corresponding to the mass losses due to dehydration were depicted from the DTG curves. The mass losses beginning at 303 K, observed in all the TG and DTG curves, were undoubtedly provoked by the purge gas (air) flowing at a rate of 100 mL min^{-1}, as already observed for other amorphous compounds [17].

For all the compounds, the first mass loss up to 393 K (Tm, Lu), 423 K (Er, Yb, Y), 408 K (Dy, Ho) and 413 K(Tb) is ascribed to dehydration, which occurs in a

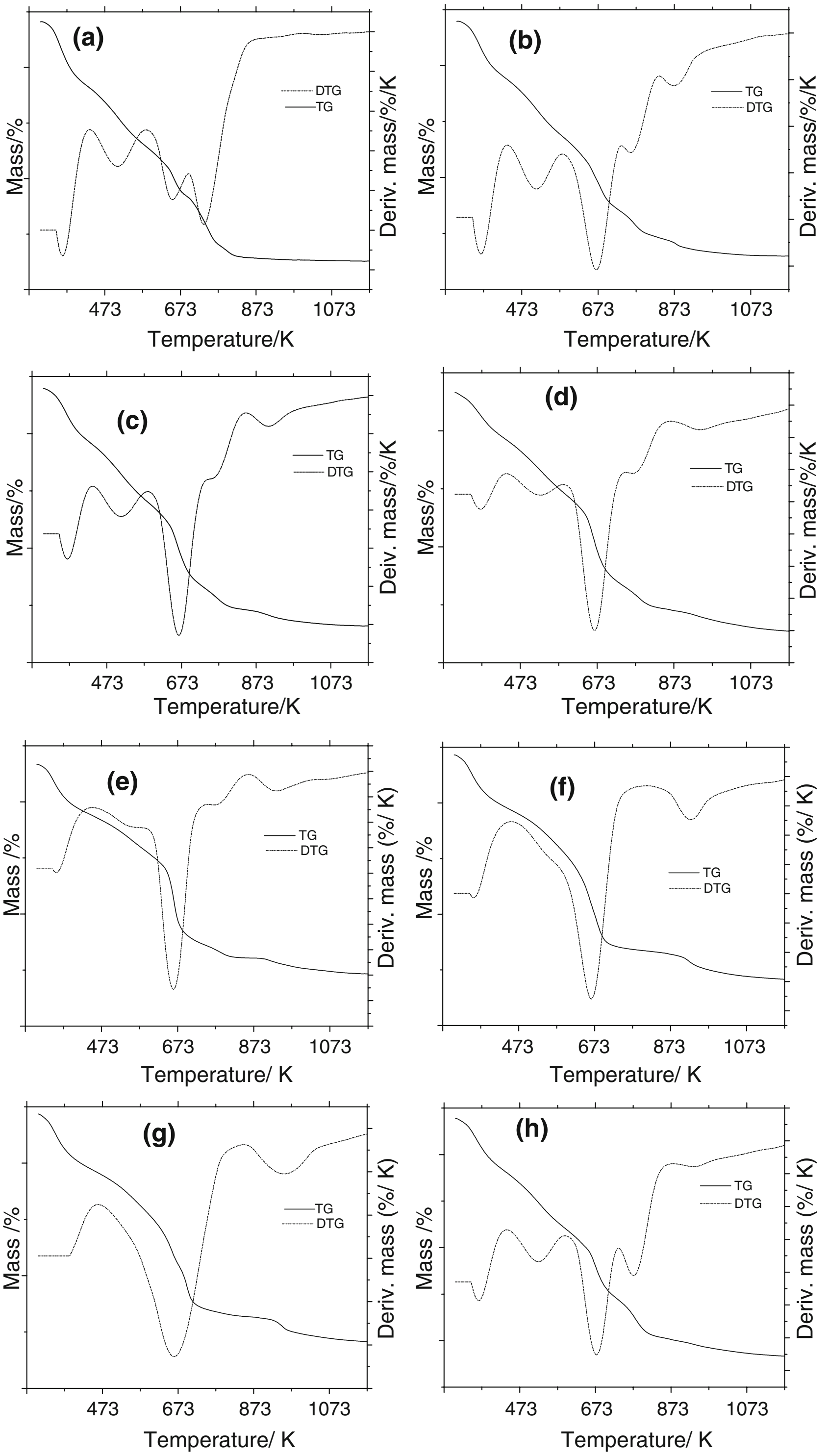

Fig. 2 The TG-DTG curves of: **a** $Tb(L)_3 \cdot 4.5H_2O$ (m = 6.821 mg); **b** $Dy(L)_3 \cdot 3.5H_2O$ (m = 6.793 mg); **c** $Ho(L)_3 \cdot 3.5H_2O$ (m = 6.785 mg); **d** $Er(L)_3 \cdot 2.5H_2O$ (m = 6.662 mg); **e** $Tm(L)_3 \cdot 3H_2O$ (m = 6.670 mg); **f** $Yb(L)_3 \cdot 3H_2O$ (m = 6.863 mg); **g** $Lu(L)_3 \cdot 3H_2O$ (m = 6.876 mg); **h** $Y(L)_3 \cdot 3H_2O$ (m = 6.783 mg). L = pyruvate

single step and via a slow process. This behaviour was also observed during the dehydration of lanthanide and yttrium compounds with phenyl-substituted derivatives of benzylidenepyruvate, and it seems to be characteristic of compounds obtained in the amorphous state [14–18].

After the dehydration, the thermal decomposition of these compounds occurs in three (Tb, Yb, Lu) or four (Dy, Ho, Er, Tm, Y) steps, with the mass losses in each step being characteristic of each compound. After the last step of thermal decomposition, the minimum oxide-level

Table 3 Temperature ranges θ/K, mass losses (%) for each step of the TG curves of the $Ln(L)_3\cdot nH_2O$ compounds, where Ln = lanthanides or and L = pyruvate

Compound	Steps					Δm_T	
	First	Second	Third	Fourth	Fifth	Calcd.	TG
$Tb(L)_3\cdot 4.5H_2O$							
θ/K	303–413	413–580	580–693	693–973		62.70	62.92
Loss/%	16.00	15.30	15.30	16.32			
$Dy(L)_3\cdot 3.5H_2O$							
θ/K	303–408	408–580	580–733	733–833	833–1073	61.68	61.85
Loss/%	12.81	17.83	19.57	7.18	4.46		
$Ho(L)_3\cdot 3.5H_2O$							
θ/K	303–408	408–583	583–723	723–833	833–820	61.38	61.11
Loss%	12.74	16.61	21.01	6.35	4.40		
$Er(L)_3\cdot 2.5H_2O$							
θ/K	303–403	403–573	573–723	723–818	818–1153	59.61	59.30
Loss%	9.83	14.15	22.74	6.76	5.82		
$Tm(L)_3\cdot 3H_2O$							
θ/K	303–393	410–563	563–683	683–823	823–1098	60.15	59.70
Loss%	11.38	13.18	25.26	5.22	4.66		
$Yb(L)_3\cdot 3H_2O$							
θ/K	303–403	403–713	713–963	963–1153		59.65	59.25
Loss%	10.77	38.64	7.33	2.51			
$Lu(L)_3\cdot 3H_2O$							
θ/K	303–393	393–733	733–983	983–1173		59.47	59.76
Loss%	11.29	39.31	7.00	2.16			
$Y(L)_3\cdot 3H_2O$							
θ/K	303–403	403–583	583–723	723–823	823–1173	72.06	71.66
Loss%	13.65	18.96	21.22	11.88	5.95		

Δm_T—Total mass losses calculated assuming that the find solid products of thermal decomposition of the obtained compounds are oxides: Tb_4O_7 and Ln_2O_3 (Ln = Dy–Lu and Y)

temperatures for the respective oxides were: 973 K(Tb), 1073 K(Dy), 1093 K(Ho), 1153 K (Er, Yb), 1098 K(Tm) and 1173 K (Lu, Y). The less final thermal decomposition temperature observed for the terbium compound must be due to the oxidation reaction (exothermic) of Tb(III) to Tb_4O_7.

For all the compounds, except terbium, the last mass loss above 873 K (Dy–Tm, Y) and 923 K (Yb, Lu) that occurs through a slow process is attributed to the thermal decomposition of the carbonaceous residue and carbonate to the respective oxide, Ln_2O_3 (Ln = Dy–Lu, Y). The formation of carbonate and carbonaceous residue in this step was confirmed by tests with hydrochloric acid solution on samples heated up to the temperature as indicated by the TG curves, and this is in agreement with the thermal decomposition of the trivalent lanthanide compounds with phenyl-substituted derivatives of benzylidendepyruvate [14, 18, 19]. The formation of carbonate has already been confirmed by the IR spectra [6, 7].

For all the compounds, the final thermal decomposition residues were the respective oxides: Tb_4O_7, Ln_2O_3 (Ln = Dy–Lu, Y). The temperature ranges (θ/K) and mass losses (%) observed for each step of the TG curve are shown in Table 3.

The DSC curves of the compounds are shown in Fig. 3. These curves show endothermic and exothermic peaks that all agree with the mass losses observed in the TG curves. The broad endothermic peak in the range of 348–448 K for all compounds is attributed to the dehydration. The dehydration enthalpies found for terbium to lutetium and yttrium compounds were: 104.0; 87.3; 69.0; 57.0; 62.2; 43.4; 40.6 and 46.4 kJ mol^{-1}, respectively.

The exotherms observed for all compounds with evidence of two (Tm, Yb, Lu); three (Ho–Er) or four (Tb) peaks between 448 and 823 K are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive and/or overlapping steps.

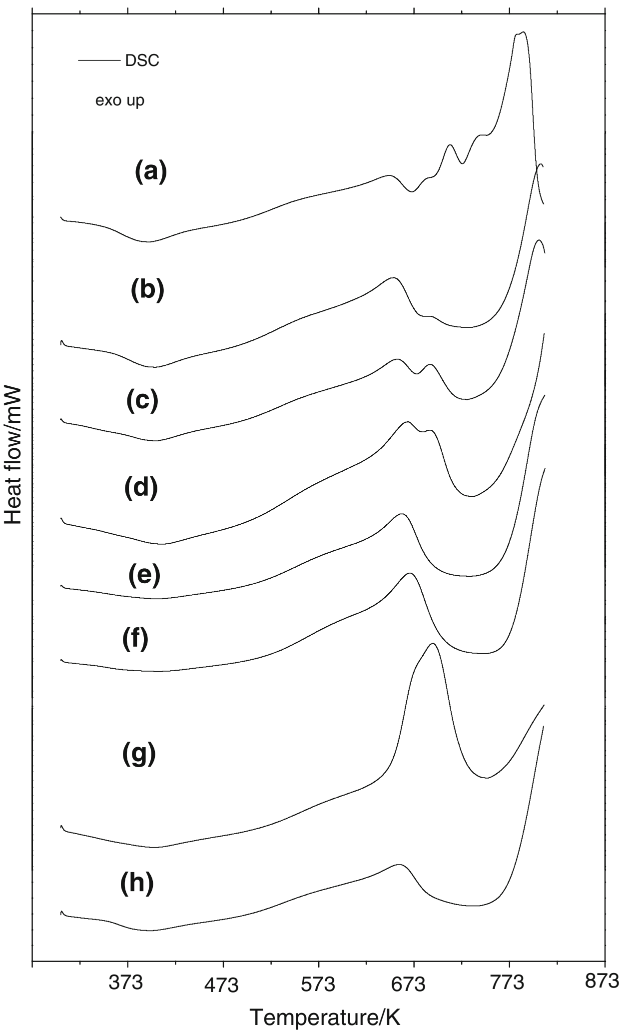

Fig. 3 The DSC curves of: (*a*) $Tb(L)_3{\cdot}4.5H_2O$ (m = 4.932 mg); (*b*) $Dy(L)_3{\cdot}3.5H_2O$ (m = 4.822 mg); (*c*) $Ho(L)_3{\cdot}3.5H_2O$ (m = 5.005 mg); (*d*) $Er(L)_3{\cdot}2.5H_2O$ (m = 5.115 mg); (*e*) $Tm(L)_3{\cdot}3H_2O$ (m = 5.008 mg); (*f*) $Yb(L)_3{\cdot}3H_2O$ (m = 5.064 mg); (*g*) $Lu(L)_3{\cdot}3H_2O$ (m = 5.131 mg); (*h*) $Y(L)_3{\cdot}3H_2O$ (m = 5.017 mg). L = pyruvate

Conclusions

The general formula of the compounds were obtained with respect to the first steps of mass loss in TG/DTG curves, referring to water of hydration and final residue, oxide, their compounds and complexometry with EDTA.

The X-ray powder patterns verified that the heavy trivalent lanthanide pyruvates were obtained in the amorphous state.

The TG/DTG and DSC curves provided information concerning the thermal stability and thermal decomposition of these compounds.

Acknowledgements The authors thank FAPESP (Procs. 90/2932-4 and 2005/00926-4), CNPQ and CAPES Foundations (Brazil) for financial support.

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