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Synthesis, characterization and thermal behaviour of solid 4-methoxybenzoates of heavier trivalent lanthanides

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Abstract

Solid-state Ln–4-MeO-Bz compounds, where Ln stands for trivalent Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y and 4-MeO-Bz is 4-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to information about the composition, dehydration, phase transition, coordination mode, structure, thermal behaviour and thermal decomposition of the isolated compounds. The phase transition observed in the some compounds has been reported for the first time.

Keywords: Heavier lanthanides; 4-Methoxybenzoate; Characterization; Thermal behaviour

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1. Introduction

Benzoic acid and some of their derivatives have been used as conservant, catalyst precursors polymers, in pharmaceutical industries, beyond other applications. A survey of literature shows that the complexes of rare earth and d-block elements with benzoic acids and some of its derivatives have been investigated in aqueous solutions and in the solid-state.

In aqueous solutions, the publications reported the thermodynamics of complexation of lanthanides by some benzoic acid derivatives [1]; the spectroscopic study of trivalent lanthanides with several carboxylic acids including benzoic acid [2]; the influence of pH, surfactant and synergic agent on the luminescent properties of terbium chelates with benzoic acid derivatives [3]; the thermodynamic of complexation of lanthanides by methoxybenzoates [4] and the synthesis, crystal structure and photophysical and magnetic properties of dimeric and polymeric lanthanide complexes with benzoic acid and its derivatives [5].

In the solid-state the publications reported the thermal and spectral behaviour on solid compounds of benzoates and derivates with rare earth elements [6–11]; the vibrational and electronic spectroscopic study of lanthanides and effect of sodium on the aromatic system of benzoic acid [12,13]; the reaction of bivalent cooper, cobalt and nickel with 3-hidroxy-4-methoxy and 3-methoxy-4-hidroxybenzoic acids and a structure for these compounds has been proposed on the basis of spectroscopic and thermogravimetric data [14]; the thermal decomposition of thorium salts of benzoic and 4-methoxybenzoic acids in air atmosphere [15] and thermal behaviour of solid-state methoxybenzoates of some bivalent transition metal ions [16–18].

In this work 4-methoxybenzoates of Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) were synthesized. The compounds were investigated by means of infrared spectroscopy, X-ray powder diffractometry, simultaneous thermogravimetry and differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC) and other methods of analysis.

2. Experimental

The 4-methoxybenzoic acid (4-MeO–HBz) 98% was obtained from Acros Organics and purified by recrystallization.

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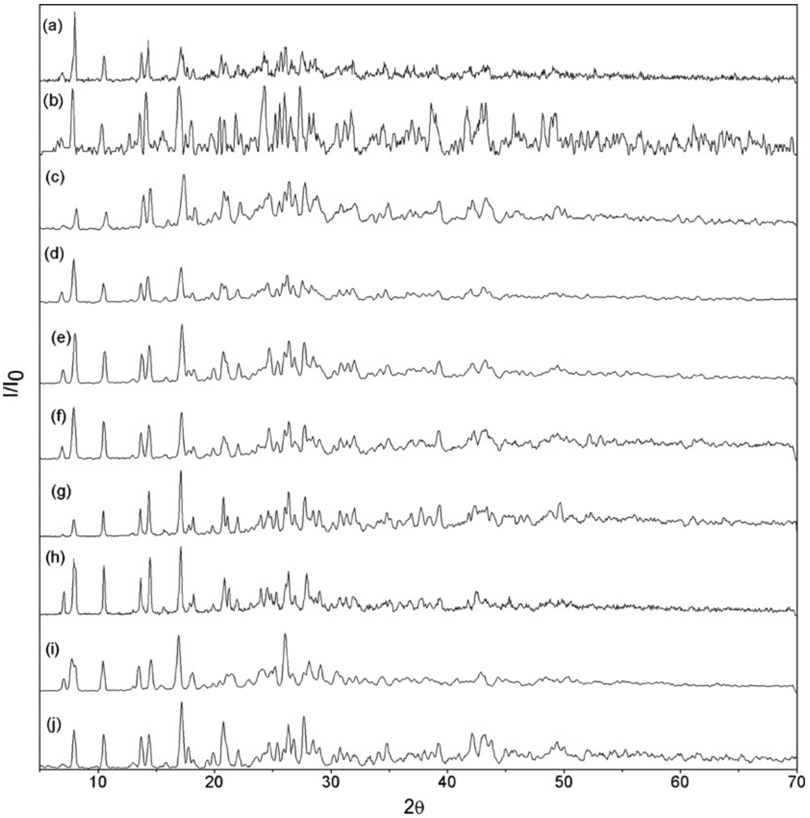

Fig. 1. X-ray powder diffraction patterns of the compounds: (a) Eu(L)$_3$; (b) Gd(L)$_3$; (c) Tb(L)$_3$; (d) Dy(L)$_3$; (e) Ho(L)$_3$; (f) Er(L)$_3$; (g) Tm(L)$_3$; (h) Yb(L)$_3$; (i) Lu(L)$_3$ and (j) Y(L)$_3$.

Aqueous solution of Na–4-MeO-Bz 0.1 mol L^{-1} was prepared from aqueous 4-MeO–HBz suspension by treatment with sodium hydroxide solution 0.1 mol L^{-1}. Lanthanide chlorides were prepared from the corresponding metal oxides (except for yttrium) by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.1 mol L^{-1} solutions, whose pH were adjusted to 5.5 adding diluted sodium hydroxide or hydrochloric acid solutions. Yttrium (III) was used as its chloride and ca. 0.1 mol L^{-1} aqueous solutions of this ion were 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 respective metal chloride solutions, until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of the chloride ions, filtered through and dried on Whatmann 42 filter paper, and kept in a desiccator over anhydrous calcium chloride, under reduced pressure to constant mass.

In the solid-state compounds, hydration water, ligand and metal ion contents were determined from TG curves. The

Table 1
Analytical and thermoanalytical (TG) data of the compounds

Compounds	Metal (%)			Loss (%)		Residue[a]
	Calcd.	EDTA	TG	Calcd.	TG	
Eu(L)$_3$	25.10	25.24	25.16	70.94	70.88	Eu$_2$O$_3$
Gd(L)$_3$	25.75	25.65	25.81	70.32	70.16	Gd$_2$O$_3$
Tb(L)$_3$	25.95	26.12	25.87	69.48	69.49	Tb$_4$O$_7$
Dy(L)$_3$	26.38	26.48	26.24	69.72	69.85	Dy$_2$O$_3$
Ho(L)$_3$	26.67	26.86	26.61	69.45	69.59	Ho$_2$O$_3$
Er(L)$_3$	26.95	26.67	26.78	69.18	69.26	Er$_2$O$_3$
Tm(L)$_3$	27.14	27.49	27.52	69.00	68.57	Tm$_2$O$_3$
Yb(L)$_3$	27.62	27.75	27.57	68.55	68.61	Yb$_2$O$_3$
Lu(L)$_3$	27.84	27.90	28.34	68.33	67.80	Lu$_2$O$_3$
Y(L)$_3$	16.39	16.50	16.50	79.18	78.86	Y$_2$O$_3$

L means 4-methoxybenzoate.

[a] All the residues was confirmed by X-ray powder diffractometry.

Table 2
Spectroscopic data for sodium 4-methoxybenzoate and compounds with some trivalent íons

Compound	ν_{as} (COO$^-$) (cm^{-1})	ν_{sym} (COO$^-$) (cm^{-1})	$\Delta\nu$
NaL	1543_s	1416_s	127
Eu(L)$_3$	1508_s	1393_s	115
Gd(L)$_3$	1510_s	1394_s	116
Tb(L)$_3$	1510_s	1393_s	117
Dy(L)$_3$	1510_s	1400_s	110
Ho(L)$_3$	1510_s	1400_s	110
Er(L)$_3$	1512_s	1404_s	108
Tm(L)$_3$	1512_s	1404_s	108
Yb(L)$_3$	1514_s	1410_s	104
Lu(L)$_3$	1518_s	1412_s	106
Y(L)$_3$	1514_s	1410_s	104

Key: s, strong; L, 4-methoxybenzoate; $\Delta\nu = \nu_{as} - \nu_{sym}$. ν_{sym} (COO$^-$) and ν_{as} (COO$^-$) symmetrical and anti-symmetrical vibrations of the COO$^-$ structure, respectively.

metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [19,20]. X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer, employing Cu Kα radiation (λ = 1.541 Å) and settings of 40 kV and 20 mA.

Infrared spectra for Na–MeO–Bz as well as for its metal–ion compounds were run on a Nicolet model Impact 400 FT-IR instrument, within the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

Simultaneous TG–DTA curves were obtained with thermal analysis system model SDT 2960 from TA Instruments. The purge gas was an air flow of 100 mL min^{-1}. A heating rate of 20 °C min^{-1} was adopted with samples weighing about 7 mg. Platinum crucibles were used for recording the TG–DTA curves.

DSC curves were obtained with thermal analysis systems model Q 10 from TA Instruments. The purge gas was an air flow of 100 mL min^{-1}. A heating rate of 20 °C min^{-1} was adopted with samples weighing about 5 mg. Aluminium crucibles, with perforated cover, were used for recording the DSC curves.

Table 3
Temperature ranges (θ), mass losses (%) and peak temperatures observed for each step of the TG–DTA curves of the compounds

Compound	Steps			
		First	Second	Third
EuL_3	θ °C	280–393	393–467	467–705
	Loss (%)	35.84	33.70	1.34
	Peak (°C)	393 (exo)	466 (exo)	–
GdL_3	θ °C	280–426	426–488	488–725
	Loss (%)	38.15	29.52	2.49
	Peak (°C)	426 (exo)	455 (exo)	–
TbL_3	θ °C	280–422	422–467	–
	Loss (%)	40.68	28.81	–
	Peak (°C)	422 (exo)	469 (exo)	–
DyL_3	θ °C	280–418	418–475	475–715
	Loss (%)	45.36	22.38	2.11
	Peak (°C)	418 (exo)	464 (exo)	–
HoL_3	θ °C	280–418	418–464	464–715
	Loss (%)	45.36	22.14	2.08
	Peak (°C)	418 (exo)	464 (exo)	–
ErL_3	θ °C	280–426	426–480	480–710
	Loss (%)	36.87	32.39	–
	Peak (°C)	426 (exo)	480 (exo)	–
TmL_3	θ °C	280–431	431–470	470–710
	Loss (%)	42.06	26.51	–
	Peak (°C)	431 (exo)	469 (exo)	–
YbL_3	θ °C	280–425	425–475	475–750
	Loss (%)	49.49	16.29	2.83
	Peak (°C)	425 (exo)	476 (exo)	–
LuL_3	θ °C	280–410	410–488	488–720
	Loss (%)	30.04	35.56	–
	Peak (°C)	410 (exo)	422, 488 (exo)	2.20
YL_3	θ °C	280–431	431–480	480–700
	Loss (%)	45.99	31.61	1.26
	Peak (°C)	431 (exo)	481 (exo)	–

L means 4 methoxybenzoate.

3. Results and discussion

The analytical and thermoanalytical (TG) data are shown in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the general formula $Ln(L)_3$, where Ln represents trivalent Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu or Y and L is 4-methoxybenzoate.

The X-ray diffraction powder patterns (Fig. 1) show that all the compounds have a crystalline structure, with evidence for formation of an isomorphous series.

Infrared spectroscopic data on 4-methoxybenzoate and its compounds with trivalent 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 most informative to assign coordination sites. In the sodium 4-methoxybenzoate strong bands located at 1543 and 1416 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [21,22]. In the compounds considered in this work analysis of the frequencies of the ν_{as} and ν_{sym} (COO^-) bands shows that the lanthanides are linked to the carboxylic group by a bridge bond and/or a bidentate bond with an incomplete equalization of bond lengths in the carboxylate anion; this is in agreement with the literature [5,12].

All attempts at growing good single crystals of the presently investigated compounds were unsuccessful. The insolubility in

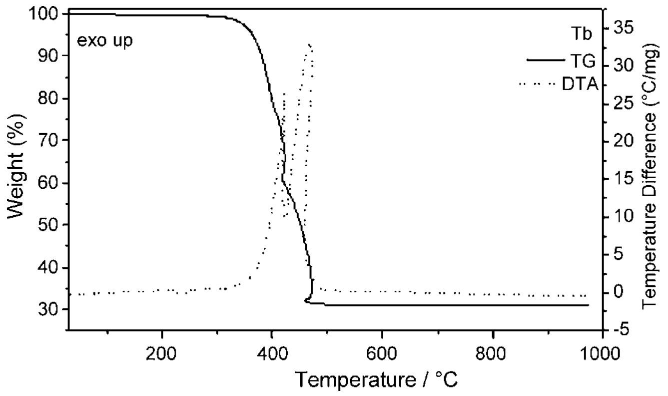

Fig. 2. TG–DTA curves of $Tb(L)_3$ (L = 4-methoxybenzoate); m = 7.310 mg.

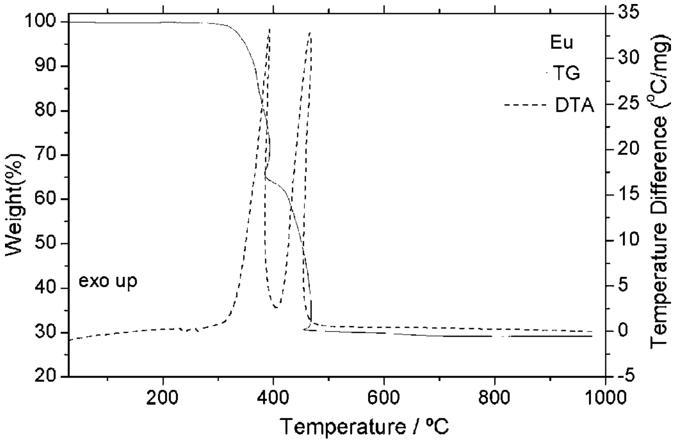

Fig. 3. TG–DTA curves of $Eu(L)_3$ (L = 4-methoxybenzoate); m = 6.981 mg.

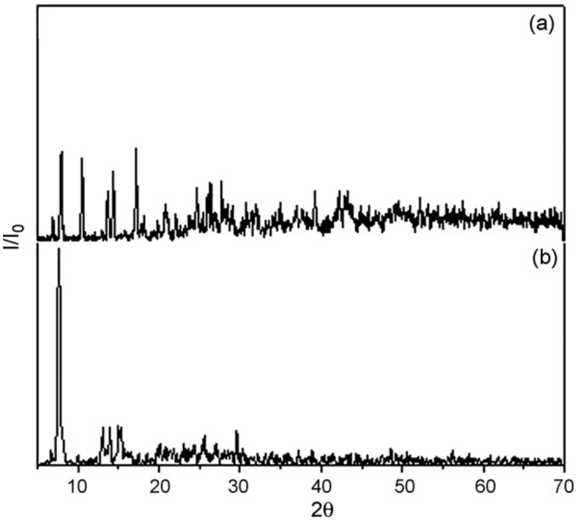

Fig. 4. X-ray powder diffraction patterns of the: (a) Er(L)$_3$; (b) Er(L)$_3$ heated up to 280 °C (L = 4-methoxybenzoate).

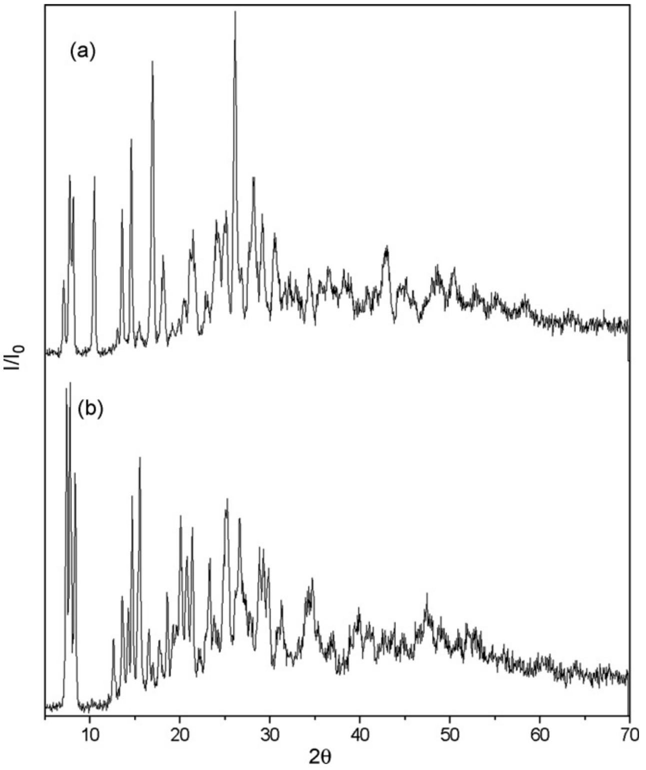

Fig. 6. X-ray powder diffraction patterns of the: (a) Lu(L)$_3$; (b) Lu(L)$_3$ heated up to 280 °C (L = 4-methoxybenzoate).

a wide variety of solvents suggest that these compounds might be polymeric in nature. It is known that high molecular mass metal coordination polymers bearing oxygen as donor atoms are generally hard, fiber- or film-like materials, stable at relatively elevated temperatures [23,24]. The presently prepared compounds do not display these features. So, if polymeric, they should be, almost certainly, of low nuclearity.

Simultaneous TG and DTA curves of the compounds exhibit mass losses in steps and thermal events corresponding to these losses or due to physical phenomenon.

For all the compounds, except terbium, the TG curve shows that the mass loss in the last step occurs through a slow process, without thermal event in the DTA curve. Calculations based on the mass observed in this step of the TG curve, suggest the formation of a mixture of lanthanide oxide, Ln_2O_3 and lanthanide dioxycarbonate, $Ln_2O_2CO_3$ (Ln = Eu, Gd, Dy–Lu, Y), in no simple stoichiometric relation. Tests with hydrochloric acid solution on samples heated up to the temperatures of formation of this intermediate, as indicated by the corresponding TG curves, confirmed, in all cases, evolution of CO_2. The formation of dioxycarbonate as intermediate, had already been observed during the thermal decomposition of other lanthanide compounds [25,26]. For the terbium compound, the thermal decomposition occurs without formation of intermediate, probably due to the oxidation reaction of Tb(III) to Tb_4O_7 (exothermic) together the oxidation and combustion of the organic matter.

The TG and DTA curves also show that the anhydrous compounds are stable up to 280 °C. Two patterns of thermal behaviour are observed for the compounds: those characterized

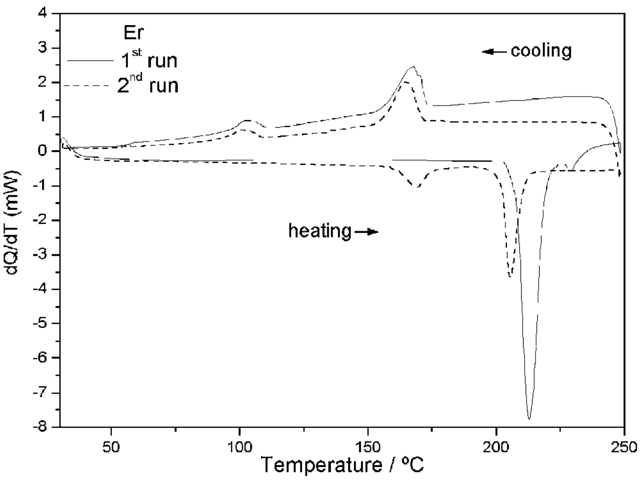

Fig. 5. DSC curves of heating and cooling of the compound Er(L)$_3$ (L = 4-methoxybenzoate).

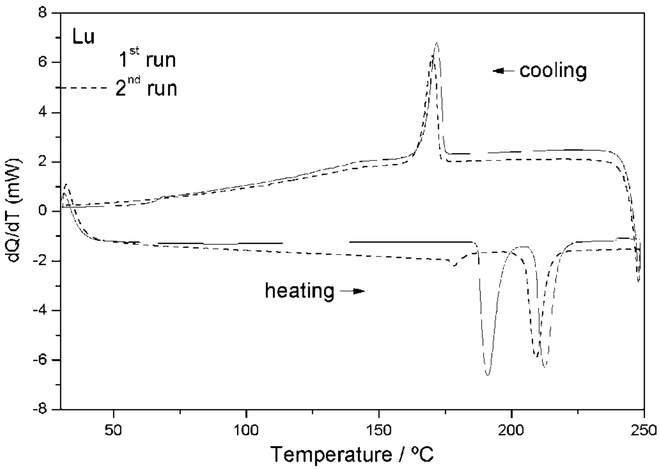

Fig. 7. DSC curves of heating and cooling of the compound Lu(L)$_3$ (L = 4-methoxybenzoate).

by a single phase transition (Tb, Dy, Ho, Er, Tm and Y) and those showing double one (Eu, Gd, Yb and Lu).

The mass losses, temperature ranges and the peak temperatures observed in each step of the TG–DTA curves are shown in Table 3.

Therefore, the features of these compounds are discussed based on the similarity of the TG–DTA profiles.

3.1. Terbium, dysprosium, holmium, erbium, thulium and yttrium compounds

The TG–DTA curves of the terbium compound are shown in Fig. 2. The endothermic peak at 231 °C (Tb), 226 °C (Dy), 222 °C (Ho), 213 °C (Er), 207 °C (Tm) and 212 °C (Y) is attributed to the reversible phase transition.

The thermal decomposition of the terbium compound occurs between 280 and 467 °C in two overlapping steps, corresponding to exothermic peaks attributed to oxidation and combustion of the organic matter in both mass losses. The total mass loss up to 467 °C is in agreement with the formation of terbium oxide, Tb_4O_7, as final residue (Calcd. = 69.48%; TG = 69.49%), which was confirmed by X-ray powder diffractometry.

For the other compounds the thermal decomposition occurs in three steps between 280 and 715 °C (Dy, Ho), 280–710 °C (Er, Tm) and 280–700 °C (Y), with the two first corresponding to exothermic peaks. The last step is ascribed to the

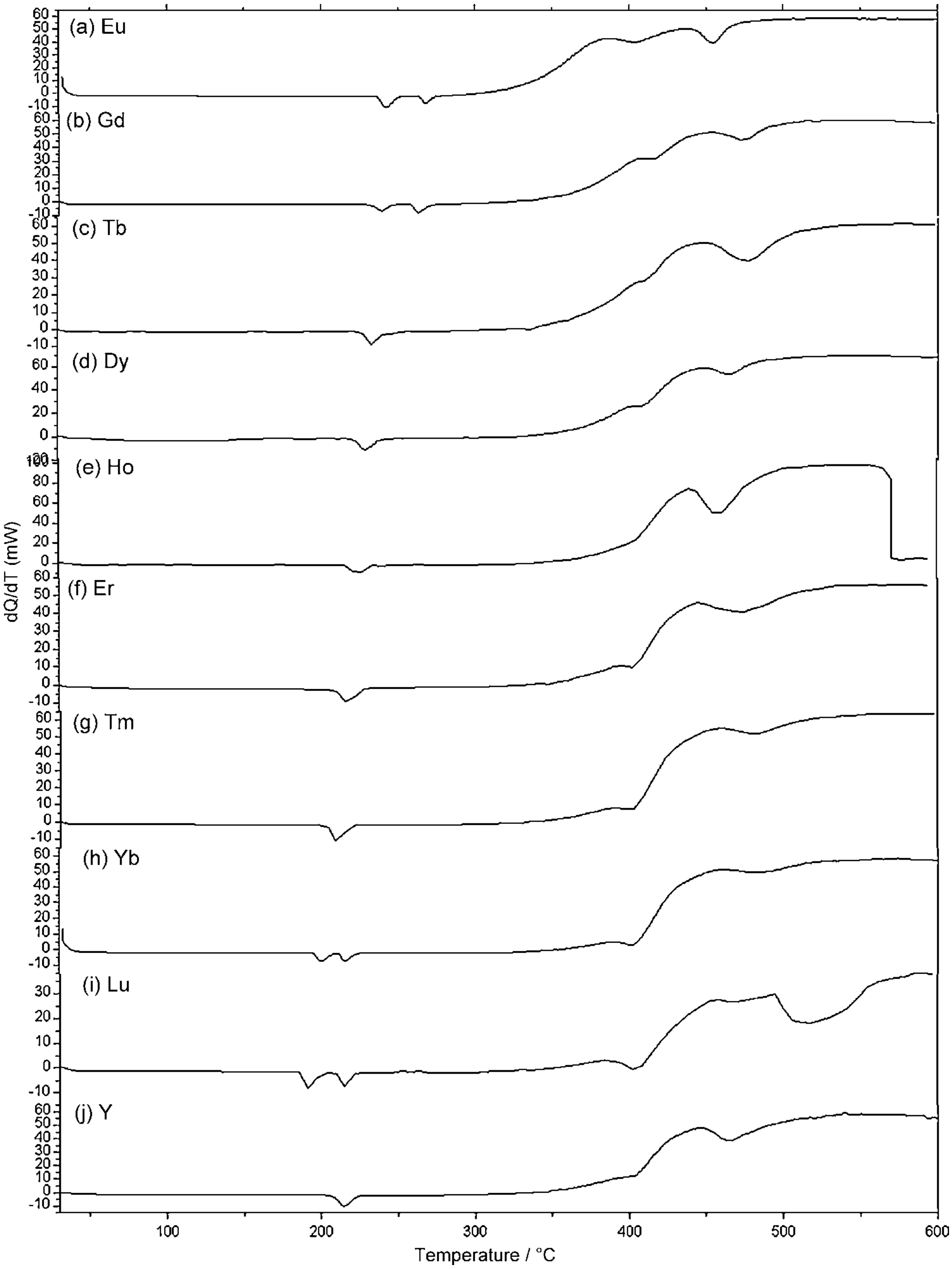

Fig. 8. DSC curves of the compounds: (a) Eu(L)$_3$ (5.400 mg); (b) Gd(L)$_3$ (5.000 mg); (c) Tb(L)$_3$ (4.700 mg); (d) Dy(L)$_3$ (6.200 mg); (e) Ho(L)$_3$ (5.200 mg); (f) Er(L)$_3$ (5.600 mg); (g) Tm(L)$_3$ (5.900 mg); (h) Yb(L)$_3$ (5.300 mg); (i) Lu(L)$_3$ (5.600 mg) and (j) Y(L)$_3$ (4.500 mg) (L = 4-methoxybenzoate).

thermal decomposition of the lanthanide dioxycarbonate to the respective oxides, as final residue (Calcd. (%) TG (%); Dy_2O_3 = 69.72–69.85; HO_2O_3 = 69.45–69.59; Er_2O_3 = 69.19–69.26; Tm_2O_3 = 69.00–68.57 and Y_2O_3 = 79.18–78.86), which were confirmed by X-ray powder diffractometry.

For the last step, no endothermic peak is observed in the DTA curve, probably due to the absorbed heat in this step is not enough to produce the thermal event.

3.2. Europium, gadolinium, ytterbium and lutetium compounds

The TG–DTA curves of the europium compound are shown in Fig. 3. The endothermic peak at 239 °C (Eu), 234 °C (Gd), 197 °C (Yb) and 190 °C (Lu) is due to the irreversible phase transition and the endothermic peak at 264 °C (Eu), 260 °C (Gd), 212 °C (Yb) and 211 °C (Lu) is attributed to the reversible phase transition.

The thermal decomposition of these compounds occurs in three steps between 280–705 °C (Eu), 280–725 °C (Gd), 280–750 °C (Yb) and 280–720 °C (Lu), with the two first corresponding to exothermic peaks. The last step is ascribed to the thermal decomposition of the lanthanide dioxycarbonate to the respective oxides, as final residue (Calcd. (%) – TG (%); Eu_2O_3 = 70.94–70.88; Gd_2O_3 = 70.32–70.16; Yb_2O_3 = 68.55–68.61 and Lu_2O_3 = 68.33–67.80), which were confirmed by X-ray powder diffractometry. For these compounds, no thermal event corresponding to the last step is also observed in the DTA curves.

3.3. Phase transitions

The endothermic peaks attributed to the irreversible (Eu, Gd, Yb, Lu) and reversible (Eu-Lu, Y) phase transitions were confirmed by X-ray powder diffraction patterns and DSC curves. Figs. 4–7 are shown the X-ray powder diffraction patterns and DSC curves of the erbium and lutetium compounds, as representative of all the compounds.

The reversible phase transition observed in all the compounds, is in agreement with the literature data [6], except the temperature where this event occurs. The disagreement in the temperature undoubtedly is because the TG and DTA curves were obtained in enough different conditions.

The irreversible phase transition observed in the europium, gadolinium, ytterbium and lutetium compounds, have been reported for the first time.

3.4. DSC curves

The DSC curves of the compounds are shown in Fig. 8. These curves show endothermic and exothermic events that all accord with the mass losses observed in the TG curves and endothermic peaks due to crystalline phase transition. The small endothermic peaks at 268 °C (Eu), 263 °C (Gd), 233 °C (Tb), 229 °C (Dy), 227 °C (Ho), 216 °C (Er), 209 °C (Tm), 216 °C (Yb), 215 °C (Lu) and 214 °C (Y) are attributed to the reversible phase transition, while the small endothermic peaks at 242 °C (Eu), 239 °C (Gd), 200 °C (Yb) and 191 °C (Lu) are due to the irreversible phase transition. The broad exotherms observed for all compounds between 350 and ≥600 °C, without the appearance of definitive peaks, are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive steps.

4. Conclusion

From analytical and thermoanalytical (TG) results a general formula could be established for these compounds in the solid-state.

The X-ray powder patterns pointed out that the synthesized compounds have a crystalline structure with evidence concerning to the formation of isomorphous compounds.

The infrared spectroscopic data suggest that 4-methoxybenzoate act as a bridge and/or bidentate ligand toward the metal ions considered in this work.

The TG–DTA and DSC curves provided previously unreported information about the thermal behaviour and thermal decomposition of these compounds.

Acknowledgements

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