



Study of thermoanalytical behavior of heavier lanthanides terephthalates in air atmosphere

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Abstract

Coordination compounds of heavier lanthanides with terephthalate ligand have been synthesized and characterized employing simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), TG coupled to FTIR, elemental analysis and complexometry. The results from complexometry with EDTA and from TG curves allowed to establish the stoichiometry of these compounds, which are in agreement with the $\text{Ln}_2(\text{TFTa})_3 \cdot n\text{H}_2\text{O}$ general formula where Ln represents trivalent lanthanides or yttrium, TFTa is terephthalate and $n = 4$ (Er, and Y); 4.5 (Tb, Dy, Ho and Tm); 5 (Yb) and 6.5 (Lu). The thermal decomposition of the anhydrous compounds occurs in two or three consecutive and/or overlapping steps, with the formation of the respective oxides: Tb_4O_7 and Ln_2O_3 (Ln = Dy to Lu and Y). The TG-FTIR of the evolved gases obtained from the thermal decomposition of the synthesized compounds, identified the formation of CO_2 and water as main gaseous products. The FTIR results also led to information about the type of coordination of the isolated compounds which suggest that the lanthanides are linked to the carboxylate groups by a bridging bond.

Keywords Terephthalate · Heavier lanthanides · Thermal behavior · Lanthanides coordination compounds

Introduction

Rare earth coordination compound has attracted attention due to their interesting luminescent properties. Lanthanide compounds exhibit intense luminescence and are useful in biochemical fluorescent probes in addition to other emission-based applications [1, 2]. Recent studies show that benzoic acid and its derivatives offer an excellent choice to sensitize and observe the lanthanide emission [3]. Other applications of these compounds show interest in the areas

of gas storage and separation, in the magnetic devices fields and catalysis [4, 5].

A literature survey shows that the studies of some lanthanides terephthalate compounds have been carried out using single-crystal X-ray diffraction, TG [6, 7] and luminescence [8]. These works reported the crystalline structure, thermal stability and the fluorescence resonance energy transfer for the lanthanides compounds, in comparison with the free lanthanide ions.

In this paper, solid-state compounds of some heavier trivalent lanthanide terephthalate (Tb to Lu) and yttrium were prepared. These compounds were investigated by complexometry, infrared spectroscopy, simultaneous thermogravimetry and differential thermal analysis (TG-DSC) coupled with FTIR for gas analysis, and differential scanning calorimetry (DSC). The results allowed us to acquire information concerning these compounds in the solid state including their thermal stability, thermal decomposition, ligand's denticity and the thermal decomposition evolved gases using air atmosphere.

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Experimental

Terephthalic acid ($C_6H_4(COOH)_2$) with 98% purity was obtained from Sigma, and aqueous solution 0.1 mol L^{-1} was prepared by direct weighing of the salt. The pH of the resulting solution was adjusted to 8.0, by adding diluted sodium hydroxide and using a glass electrode PH meter.

Lanthanide chlorides were prepared from the corresponding metal oxides by treatment with concentrated hydrochloric acid [9]. The resulting solutions were evaporated close to dryness, and the residues re-diluted in distilled water. This procedure was repeated until the elimination of the excess of hydrochloric acid. The resulting residues were transferred to a volumetric flask and diluted in order to obtain a ca 0.10 mol L^{-1} solution, whose pH was adjusted to 5.0. The solid-state compounds were prepared by slowly adding, with continuous stirring, the solution of the ligand to the respective metal chloride, until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of the chloride (or nitrate) ions, filtered through and dried on Whatman no. 40 filter paper and kept in desiccators over anhydrous calcium chloride.

In the solid-state compounds, hydration water, terephthalate and lanthanide ions were determined from TG curves. The lanthanide ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [9].

The attenuate total reflectance infrared spectra of sodium terephthalate, as well as of its metal-ion compounds, were recorded on a Nicolet iS10 FTIR spectrophotometer, using an ATR accessory with a Ge window. The FTIR spectra were recorded with 32 scans per spectrum at resolution of 4 cm^{-1} .

Simultaneous TG–DSC and DSC curves were obtained with two thermal analysis systems, Thermogravimetric Analyzer Mettler TGA–DSC 1 from Mettler and DSC Q10, from TA Instruments. For the TG–DSC curves, air

was used as purge gas with flow rate of 100 mL min^{-1} . It was adopted a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ with samples weighting about 4 mg and α -alumina crucibles. For DSC experiments, air was adopted as purge gas with flow rate of 50 mL min^{-1} using as experimental conditions a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, samples weighting about 2 mg and aluminum crucibles with perforated cover.

Table 2 Temperature ranges, mass losses (%) and peak temperatures observed for each step of TG–DSC curves of the compounds

Compounds		Steps	
		First	Second
$Tb_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	119–165	412–513
	Loss/%	9.41	48.21
	Peak DSC/ $^\circ\text{C}$	144	465, 500
$Dy_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	108–153	464–556
	Loss/%	9.03	48.86
	Peak DSC/ $^\circ\text{C}$	137	532
$Ho_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	101–144	453–565
	Loss/%	8.98	48.82
	Peak DSC/ $^\circ\text{C}$	135	529, 539
$Er_2(TFTA)_3 \cdot 4 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	98–151	507–586
	Loss/%	8.02	48.81
	Peak DSC/ $^\circ\text{C}$	139	548, 562
$Tm_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	85–134	502–580
	Loss/%	7.99	48.30
	Peak DSC/ $^\circ\text{C}$	117	555
$Yb_2(TFTA)_3 \cdot 5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	76–138	505–588
	Loss/%	9.70	47.72
	Peak DSC/ $^\circ\text{C}$	114	555
$Lu_2(TFTA)_3 \cdot 6.5 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	43–164	517–595
	Loss/%	12.21	45.74
	Peak DSC/ $^\circ\text{C}$	65, 95	565, 579
$Y_2(TFTA)_3 \cdot 4.0 \text{ H}_2\text{O}$	$\theta/^\circ\text{C}$	98–148	492–586
	Loss/%	9.71	59.19
	Peak DSC/ $^\circ\text{C}$	136	552

Table 1 Analytical data for $Ln_2(TFTA)_3 \cdot n \text{ H}_2\text{O}$

Compounds	$H_2O/\%$		Ligand/%		Oxide/%			Final residue
	Calc.	TG	Calc.	TG	Calc.	TG	EDTA	
$Tb_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	9.10	9.41	48.96	48.21	41.04	41.54	41.12	Tb_2O_3
$Dy_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	9.03	9.18	49.46	48.86	41.51	41.90	41.48	Dy_2O_3
$Ho_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	8.98	9.05	49.19	48.82	41.83	42.19	42.06	Ho_2O_3
$Er_2(TFTA)_3 \cdot 4 \text{ H}_2\text{O}$	8.02	8.10	49.43	48.81	42.55	43.09	42.43	Er_2O_3
$Tm_2(TFTA)_3 \cdot 4.5 \text{ H}_2\text{O}$	7.99	8.36	49.25	48.30	42.76	43.32	43.53	Tm_2O_3
$Yb_2(TFTA)_3 \cdot 5 \text{ H}_2\text{O}$	9.70	9.61	47.85	47.72	42.44	42.59	42.03	Yb_2O_3
$Lu_2(TFTA)_3 \cdot 6.5 \text{ H}_2\text{O}$	12.21	12.13	46.31	45.74	41.47	41.88	40.97	Lu_2O_3
$Y_2(TFTA)_3 \cdot 4 \text{ H}_2\text{O}$	9.71	10.13	59.87	59.19	30.42	30.60	30.34	Y_2O_3

Ln lanthanides, *TFTA* terephthalate

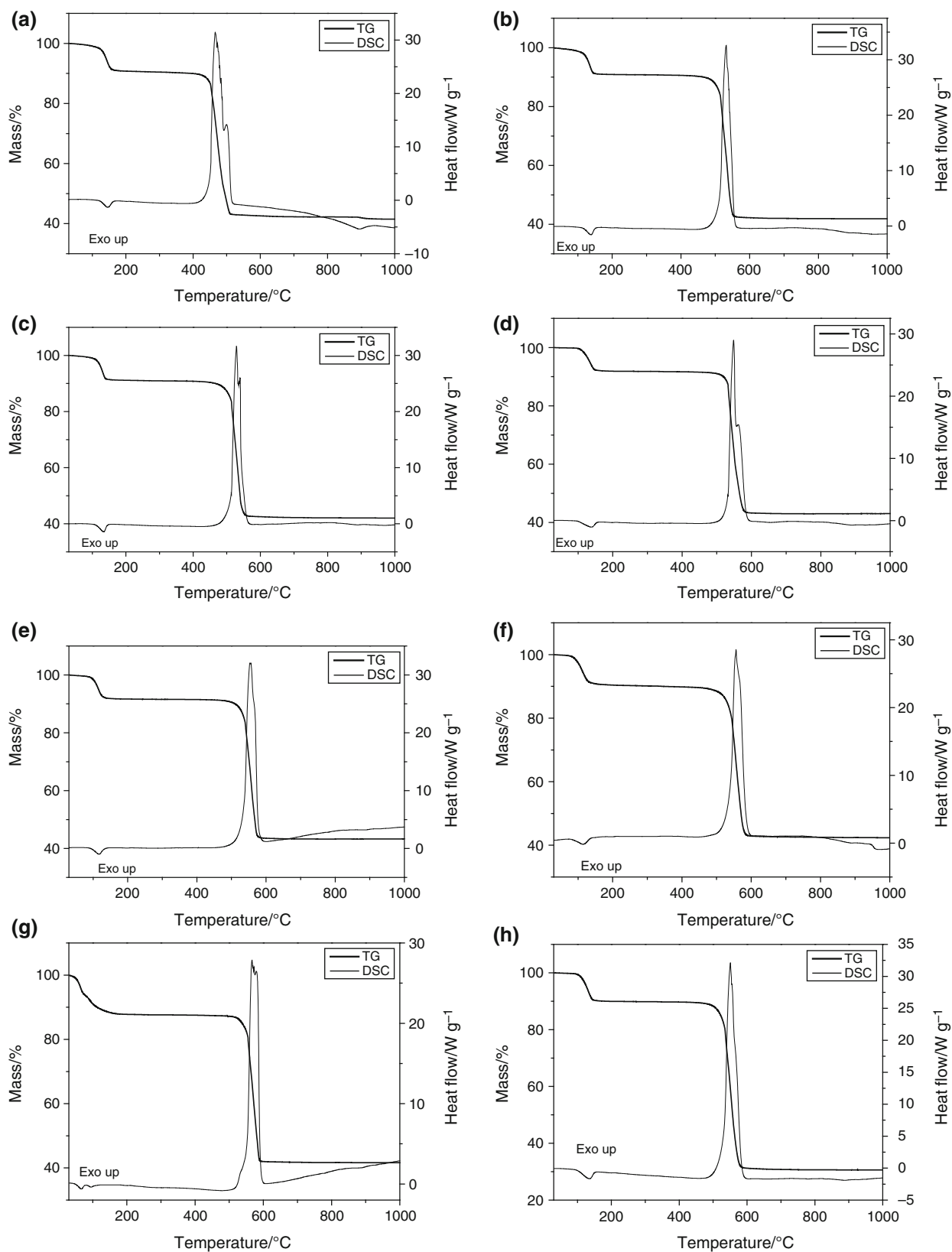


Fig. 1 Simultaneous TG–DSC curves of the compounds **a** $\text{Tb}_2(\text{TFTA})_3 \cdot 4.5\text{H}_2\text{O}$, **b** $\text{Dy}_2(\text{TFTA})_3 \cdot 4.5\text{H}_2\text{O}$, **c** $\text{Ho}_2(\text{TFTA})_3 \cdot 4.5\text{H}_2\text{O}$, **d** $\text{Er}_2(\text{TFTA})_3 \cdot 4.0\text{H}_2\text{O}$, **e** $\text{Tm}_2(\text{TFTA})_3 \cdot 4.5\text{H}_2\text{O}$, **f** $\text{Yb}_2(\text{TFTA})_3 \cdot 5\text{H}_2\text{O}$, **g** $\text{Lu}_2(\text{TFTA})_3 \cdot 6.5\text{H}_2\text{O}$, **h** $\text{Y}_2(\text{TFTA})_3 \cdot 4\text{H}_2\text{O}$

The TG-FTIR experiments were performed using a Thermogravimetric Analyzer Mettler TG-DSC 1, coupled with a Nicolet iS10 FTIR spectrometer equipped with an IR gas cell. The transfer line used consisted of a stainless steel tube of 120 cm in length (2 mm in inner diameter) heated at a constant temperature of 250 °C. FTIR measurements were taken with a DTGS detector in a specifically developed gas cell, heated at a constant temperature of 225 °C. The interferometer and the gas cell compartments were purged with high purified N₂. The FTIR spectra were recorded with 16 scans per spectrum at resolution of 4 cm⁻¹.

The procedures of TG-DSC, DSC, and evolved gas analysis are in agreement with Ref. [9].

Results and discussion

The analytical and thermoanalytical (TG) data are shown in Tables 1 and 2. These results establish the stoichiometry of these compounds, which are in agreement with the Ln₂(TfTa)₃·nH₂O general formula where Ln represents trivalent lanthanides or yttrium, TfTa is terephthalate, and *n* = 4 (Er, and Y); 4.5 (Tb, Dy, Ho and Tm); 5 (Yb) and 6,5 (Lu).

Simultaneous TG-DSC curves of the compounds are shown in Fig. 1. The percentages of mass losses and the temperature of the thermal decomposition of each step of mass loss are shown in Tables 1 and 2, respectively. The thermogravimetric curves of all compounds exhibit similar showing mass losses in three consecutive and/or overlapping steps and thermal events corresponding to these losses. For all compounds, the first mass loss (in the 60–110 °C range) associated with endothermic peaks at 95–100 °C is ascribed to the dehydration, which occurs in a single step, except for lutetium compound, which occurs in two steps. All compounds show stable anhydrous compounds as cited by Daiguenbonne [6]. The anhydrous compounds are stable up to 415° and between the temperatures of 415–511 °C show a mass loss corresponding to the exothermic events that are attributed to the oxidation of the organic matter. The similarity in thermal profiles suggests that the interaction between metal and the terephthalate is occurring in the same way.

For all compounds, the final thermal decomposition residues were the respective oxides, Tb₄O₇ and Ln₂O₃ (Ln= Dy–Lu, Y).

Differential scanning calorimetry curves are shown in Fig. 2. The results provided information about the dehydration step of the synthesized compounds. These curves show endothermic peaks at 175 (Tb), 169 (Dy), 164 (Ho), 165 (Er), 145 (Tm), 142 (Yb), 93 and 127 (Lu) and 165 °C (Y) attributed to dehydration, and the dehydration

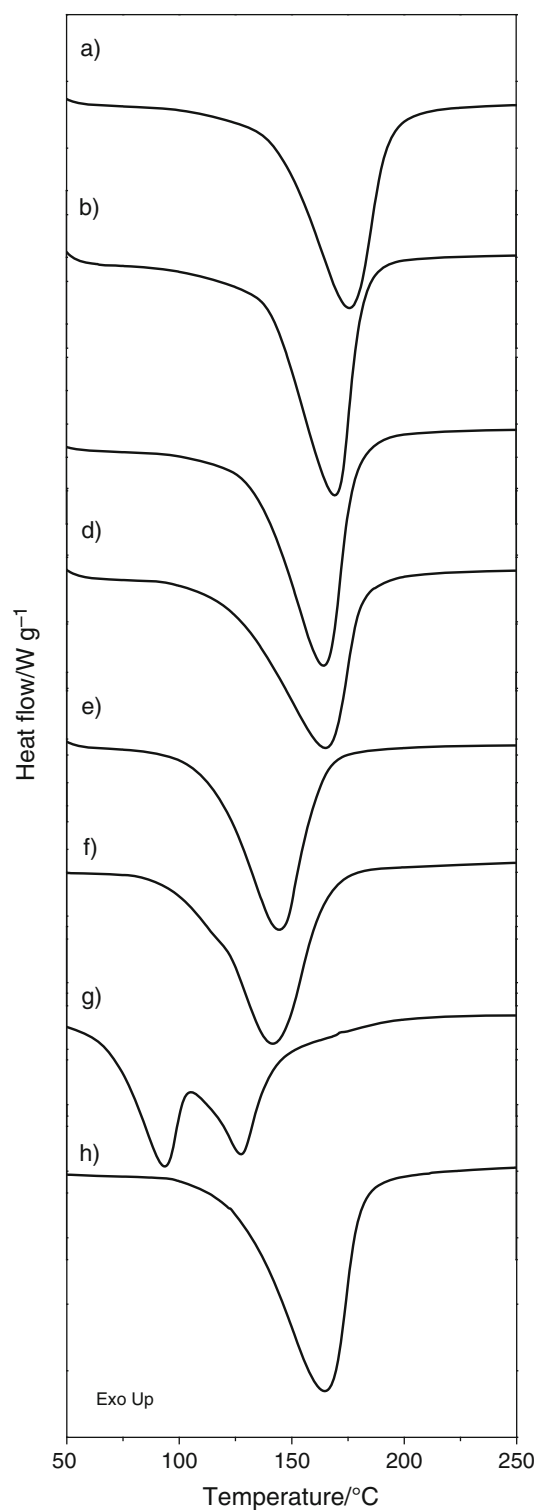
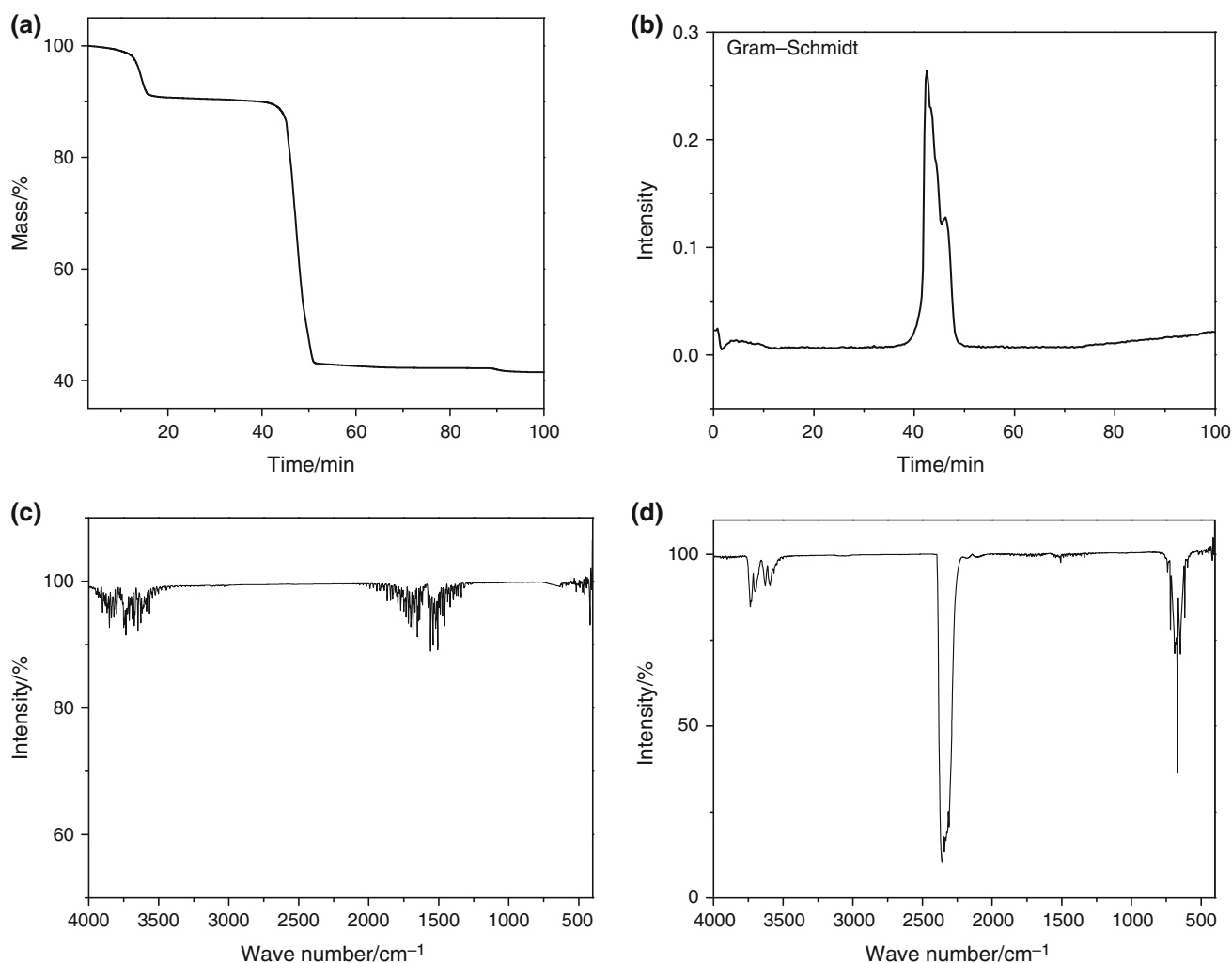


Fig. 2 DSC curves of the compounds. **a** Tb₂(TfTa)₃·4.5H₂O, **b** Dy₂(TfTa)₃·4.5H₂O, **c** Ho₂(TfTa)₃·4.5H₂O, **d** Er₂(TfTa)₃·4.0H₂O, **e** Tm₂(TfTa)₃·4.5H₂O, **f** Yb₂(TfTa)₃·5H₂O, **g** Lu₂(TfTa)₃·6.5H₂O, **h** Y₂(TfTa)₃·4 H₂O

enthalpies found for these compounds were 232 (Tb), 224 (Dy), 235 (Ho), 226 (Er, Tm), 206 (Yb), 284 (Lu) and 270 (Y) KJ mol⁻¹.

Table 3 Infrared spectroscopic data for sodium terephthalate and its compounds with heavy trivalent lanthanides

Compounds	$\nu_{\text{O-H H}_2\text{O}}/\text{cm}^{-1}$	$\nu_{\text{assim COO}^-}/\text{cm}^{-1}$	$\nu_{\text{sim COO}^-}/\text{cm}^{-1}$	$\Delta\nu/\nu_{\text{assim}} - \nu_{\text{sim}}/\text{cm}^{-1}$
Ln–Na	–	1550	1383	167
Tb ₂ (TFTA) ₃ ·4.5H ₂ O	3462	1539	1400	139
Dy ₂ (TFTA) ₃ ·4.5H ₂ O	3462	1540	1400	140
Ho ₂ (TFTA) ₃ ·4.5H ₂ O	3460	1540	1400	140
Er ₂ (TFTA) ₃ ·4H ₂ O	3461	1541	1400	141
Tm ₂ (TFTA) ₃ ·4.5H ₂ O	3453	1546	1400	146
Yb ₂ (TFTA) ₃ ·5H ₂ O	3453	1542	1400	142
Lu ₂ (TFTA) ₃ ·6.5H ₂ O	3386	1541	1404	137
Y ₂ (TFTA) ₃ ·4.0H ₂ O	3463	1543	1402	141

**Fig. 3** TG–FTIR data obtained from Tb₂(TFTA)₃·4.5H₂O: **a** thermogravimetric curve of Tb₂(TFTA)₃·4.5H₂O. **b** Gram-schmidt graphic of intensity of the absorbed radiation of the thermaldecomposition gases versus time. **c** FTIR spectra of the decomposition gases obtained after 5 min of thermal analysis. **d** FTIR spectra of the decomposition gases obtained after 42 min of thermal analysis

The low variation in the values suggests that the compounds have similar interaction with water and low dehydration temperature, and values of enthalpy suggest that the compound presents a weak interaction with the water.

Infrared spectroscopic data on sodium terephthalate and its compounds with the metal ions considered in this work are shown in Table 3. The investigation was focused mainly within the 1700–1400 cm⁻¹ range because this

region is potentially the most informative in attempting to assign coordination sites. The spectra obtained from sodium terephthalate and its compounds were very similar. The main bands are from the symmetric and asymmetric carboxylate groups (1500–1550 and 1383–1407 cm^{-1} , respectively), aromatic ring stretching (1504–1508), in-plane C–H aromatic bending (1000–1315 cm^{-1}) and aromatic C–H out-plane bending (690–900 cm^{-1}). For all the compounds, the bands assigned to the anti-symmetrical stretching carboxylate frequencies, as well as that assigned to the ketonic carbonyl, are shifted to lower values relative to the corresponding frequencies in TFTA itself (sodium salt). This behavior indicates that both groups act as coordination centers in the metal compounds [10]. The data are displayed in Table 2. Analysis of the frequencies of the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ bands suggests that the lanthanides are linked to the carboxylate groups by a bridging bond, which is an agreement with the literature [9, 10].

The gaseous products evolved in the thermal decomposition of heavy trivalent lanthanides fumarates were monitored by FTIR. The results indicate that water were liberated during the dehydration step (119–165 °C), and carbon dioxide (anti-symmetrical stretching in 2360 and 2345 cm^{-1} and scissoring (degenerated) in 666 cm^{-1}) and water were detected as main products during the decarboxylation and oxidation of the organic matter step (412–513 °C). The FTIR spectrum of the gaseous products evolved during the thermal decomposition of terbium terephthalate, as representative of all compounds, is shown in Fig. 3.

Conclusions

From TG curves and complexometry results, a general formula could be established for these compounds in solid state. The infrared spectroscopic data suggest that terephthalate acts as a bridging ligand by carboxylate groups of the ligand toward the metal ions considered in this work. The TG–DSC, TG/DTG and DSC curves have shown that the interactions between metal, ligand and water are very similar due to the little variation in the dehydration enthalpy and thermal decomposition temperatures, providing with previously unreported information concerning

the thermal behavior and thermal decomposition of these compounds.

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