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Synthesis, thermal properties and spectroscopic study of solid mandelate of light trivalent lanthanides

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ABSTRACT

Characterization, thermal stability and thermal decomposition of light trivalent lanthanide mandelates $Ln(C_6H_5CH(OH)CO_2)_3 \cdot nH_2O$ (Ln = La to Gd, except Pm) were investigated employing simultaneous thermogravimetry and differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), experimental and theoretical infrared spectroscopy, elemental analysis, X-ray diffractometry, complexometry and TG–DSC coupled to FTIR. The dehydration of the lanthanum, samarium, europium and gadolinium compounds occurs in a single step while for praseodymium and neodymium ones it occurs in two consecutive steps. The thermal decomposition of the anhydrous compounds occurs in three, four or five consecutive steps, with formation of the respective oxides CeO_2 , Pr_6O_{11} and Ln_2O_3 (Ln = La, Nd to Gd) as final residues. The results also provide information concerning the composition, thermal behavior and gaseous products evolved during the thermal decomposition of these compounds. The theoretical and experimental spectroscopic data suggest the possible modes of coordination of the ligand with the lanthanum.

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1. Introduction

Mandelic acid has a long history of use in the medical community as an antibacterial, particularly in the treatment of urinary tract infections [1]. Thermogravimetry, differential thermal analysis and TG–DSC coupled to FTIR spectroscopy have been used to characterize compounds of bivalent transition metal ions and trivalent lanthanides [2,3]. However, similar study on lanthanide (III) ion with mandelic acid is lacking and the papers published are concerned to the stability of some lanthanide complexes with mandelate and atrolactate [4], the complexation of lanthanide ions with mandelate [5], preparation and some properties of lanthanum, neodymium and yttrium mandelates [6] and bonding trends in lanthanide mandelates [7].

In addition, the lanthanides show widely diverse coordination compounds. These compounds often possess remarkable and unique spectroscopic properties and photophysical and electrochemical applications can be explored in sensory, pharmacological and diagnostic [8–11].

Thus, the present paper deals with the preparation of solid-state compounds of light trivalent lanthanides, except promethium, with mandelate and investigation by means of complexometry, elemental analysis, infrared spectroscopy (FTIR), simultaneous

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thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) and TG-DSC coupled to FTIR.

2. Experimental

The mandelic acid (C₆H₅CH(OH)CO₂H) with 99% purity was obtained from Aldrich. Aqueous solution of sodium mandelate 0.10 mol L⁻¹ was prepared by the neutralization of aqueous solution of mandelic acid with sodium hydroxide solution 0.10 mol L⁻¹.

Lanthanide chlorides were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness to eliminate the excess of hydrochloric acid. The residues were dissolved in distilled water and diluted in order to obtain ca. $0.10 \text{ mol } \text{L}^{-1}$ solutions, whose pH were adjusted to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. Cerium (III) was used as its nitrate and ca. $0.10 \text{ mol } \text{L}^{-1}$ aqueous solution of this ion was prepared by direct weighing of the salt.

Solid-state compounds were obtained by adding slowly with stirring 150.0 mL of sodium mandelate solution $0.10 \text{ mol } L^{-1}$ heated up to near ebullition to 50.0 mL of the respective metal ions solutions $0.10 \text{ mol } L^{-1}$, heated too. For samarium, europium and gadolinium, the formation of precipitate was observed during the addition of sodium mandelate solution. For lanthanum to neodymium the formation of precipitate occurred only after to maintain the respective solutions heated at ebullition for about 0.5 h. Tests with sodium oxalate solution on mother liquor showed

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that the lanthanum to neodymium mandelates are more soluble than samarium to gadolinium ones.

The precipitates were washed with distilled water until chloride (or nitrate) ions were eliminated, filtered and dried at $50 \,^{\circ}$ C in a forced circulation air oven during 12 h and maintained in a desiccator over anhydrous calcium chloride.

For the La to Nd compounds, due to a great loss during the washing of the precipitates, small quantity of these mandelates were obtained. Thus, the same were also prepared by neutralization of the respective lanthanide carbonates with mandelic acid.

The carbonates of lanthanum to neodymium were prepared by adding slowly with continuous stirring saturated sodium hydrogen carbonate solution to the corresponding metal chloride or nitrate for cerium until total precipitation of the metal ions. The precipitates were washed with distilled water until the elimination of chloride or nitrate ions (qualitative test with AgNO₃/HNO₃ solution for chloride ions or diphenylamine/H₂SO₄ solution for nitrate ions) and maintained in aqueous suspension.

Solid-state La(III) to Nd(III) compounds were prepared by mixing the corresponding metal carbonates maintained in aqueous suspension with mandelic acid in slight excess. The aqueous suspension was heated up to ebullition until total neutralization of the carbonate. The solutions of the respective metal mandelates were evaporated up to dryness in water bath, washed with ethanol to eliminate the mandelic acid in excess, dried at 50 °C in a forced circulation air oven during 12 h and kept in a desiccator over anhydrous calcium chloride.

In the solid-state, metal ions, hydration water and mandelate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution [12,13].

Carbon and hydrogen contents were determined by calculation based on the mass losses observed in the TG curves, since the hydration water and ligand lost during the thermal decomposition occur with the formation of the respective oxides with stoichiometry known, as final residues.

X-ray powder patterns were obtained by using a Siemens D-5000 X-Ray Diffractometer employing CuK α radiation (λ = 1.541 Å) and setting of 40 kV and 20 mA.

The attenuate total reflectance infrared spectra for sodium mandelate and for its metal-ion compounds were run on a Nicolet iS10 FTIR spectrophotometer, using ATR accessory with Ge window.

Simultaneous TG–DTA and DSC curves were obtained with two thermal analysis systems, model SDT 2960 and Q10, both from TA Instruments. The purge gas was an air flow of $100 \,\mathrm{mL\,min^{-1}}$. A heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ was adopted, with samples weighing about 7 mg. Alumina and aluminum crucibles, the latter with perforated cover, were used for recording the TG–DTA and DSC curves, respectively.

The measurements of the gaseous products were carried out using a TG–DSC1 Mettler Toledo coupled to a FTIR spectrophotometer Nicolet with gas cell and DTGS KBr detector. The furnace and the heated gas cell ($250 \circ C$) were coupled through a heated ($200 \circ C$) 120 cm stainless steel line transfer with diameter of 3 mm, both purged with dry air (50 mLmin^{-1}). The FTIR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm⁻¹.

2.1. Computational strategy

In this study, the employed quantum chemical approach to determine the molecular structures was Becke three parameter hybrid theory [14] using the Lee–Yang–Par (LYP) correlation functional [15], and the basis sets used for calculations were: 4s for H (²S) [16], [5s4p] for C (³P) and O (³P) [16], [10s6p] for Na (²S) and [17s11p7d] for La (²D) [17]. The diffuse functions for the lanthanum

Table 1

Theoretical geometry parameters of lanthanum(III) complex with mandelate.

dO _{water} —La	2.62 Å	
dO _{COO} —La	2.52 Å	
dC _{coo} —O _{coo}	1.27 Å	
$dC_{R-C}-C_{COO}$	1.52 Å	
$dC = C_{(ring)}$	1.39 Å	
<h<sub>water—O_{water}—La</h<sub>	106.09°	
<o<sub>COO—La—O_{COO}</o<sub>	52.17 °	
<c—o<sub>COO—La</c—o<sub>	93.66°	
$< C_{R-C} - C_{COO} - O_{COO}$	118.48°	

d: distance; <: angle; COO: carboxylate group; R—C: benzyl carbon.

atom (²D) were calculated according to the procedure described in Ref. [16] and these values are: α s = 0.00669534, α p = 0.079333735, α d = 0.096432865.

Basis set for Na (²S) atom. The 22s13p [discretization parameters: $\Omega(s) = -0.620$, $\Delta \Omega(s) = 0.136$, N(s) = 6.0; $\Omega(p) = -0.268$, $\Delta \Omega(p) = 0.127$, N(p) = 6.0]/10s6p.

(13,1,1,1,1,1,1,1,1,8,1,1,1,1) basis set were built with the aid of the Generator Coordinate Hartree–Fock method. The polarization function is $\alpha d = 0.42912802$. Full details about the wave function developed in this work for sodium mandelate are available upon request to the oswatreu@iq.unesp.br.

In order to better describe the properties of the compound in the implementation of the calculations, it was necessary to include polarization functions [16–18] for all atoms of the compound.

The polarization functions are: $\alpha p = 0.33353749$ for H (²S), $\alpha d = 0.72760279$, and $\alpha d = 0.36059494$ for C (³P), O (³P), $\alpha d = 0.42912802$ for Na (²S) respectively, and $\alpha f = 0.36935391$ for La (²D) atoms. The role of a basis set is a crucial point in theoretical studies of metal complexes, since the description of the configuration of the metal in the complex differs from the neutral state. The performed molecular calculations in this study were done using the Gaussian 09 routine [19].

The theoretical infrared spectrum was calculated using a harmonic field [20] based on C_1 symmetry (electronic state ¹A). Frequency values (not scaled), relative intensities, assignments and description of vibrational modes are presented. The geometry optimization was computed using the optimized algorithm of Berny and the calculations of vibrational frequencies were also implemented to determine an optimized geometry constitutes minimum or saddle points [21]. The principal infrared active fundamental modes assignments and descriptions were done by the GaussView 5.0.2W graphics routine [22].

The geometry optimization computed by the optimized algorithm of Berny can be seen in Fig. 1. It was also shown that the compound in Fig. 1a is 5.74 kcal mol⁻¹ more stable than the analogous one in Fig. 1b. The structure parameters obtained for the most stable compound are shown in Table 1.

3. Results and discussion

The analytical and thermoanalytical (TG) data are shown in Table 2. These results permitted to establish the stoichiometry of these compounds, which are in agreement with the general formula $Ln(L)_3 \cdot nH_2O$, where Ln represents lanthanides, L is mandelate and n = 0 (Ce), 1 (La) or 2 (Pr to Gd).

The X-ray powder patterns (Fig. 2) show that the lanthanum compound was obtained in the amorphous state, while the other compounds have a crystalline structure, evidencing the formation of two isomorphous series: being the praseodymium and neodymium compounds the first one and samarium to gadolinium compounds the other series. The X-ray powder patterns also show that the crystallinity of these compounds follows the order: $Gd > Sm > Eu > Ce > Nd \cong Pr > La$.



Fig. 1. Theoretical 3D structure of La(L)₃·1H₂O: (a) lanthanum coordination by carboxylate group; (b) lanthanum coordination by hydroxyl and carboxylate group.

Table 2	
Analytical and thermoanalytical (TG) data for $LnL_3 \cdot nH_2O$.	

Compounds	ompounds Ln (oxide) (%)		L (lost) (%	L (lost) (%) H ₂ O		H ₂ O (%) C (%)		C (%) H (%)			Final residue	
	Calcd.	EDTA	TG	Calcd.	TG	Calcd.	TG	Calcd.	TG	Calcd.	TG	
La(L)3·1H2O	26.69	26.99	26.75	70.36	70.17	2.95	3.08	47.22	47.09	3.81	3.80	La ₂ O ₃
$Ce(L)_3$	29.00	29.11	28.86	71.00	71.14	-	-	48.56	48.66	3.57	3.58	CeO ₂
$Pr(L)_3 \cdot 2H_2O$	27.01	27.36	27.21	67.27	67.01	5.72	5.78	45.72	45.54	4.01	3.99	Pr_6O_{11}
$Nd(L)_3 \cdot 2H_2O$	26.55	26.65	26.48	67.76	67.78	5.69	5.74	45.48	45.49	3.98	3.98	Nd_2O_3
Sm(L) ₃ ·2H ₂ O	27.25	27.65	27.66	67.12	66.52	5.63	5.82	45.05	44.65	3.95	3.91	Sm ₂ O ₃
Eu(L)3·2H2O	27.44	28.07	26.98	66.94	67.15	5.62	5.87	44.93	45.07	3.94	3.95	Eu ₂ O ₃
$Gd(L)_3 \cdot 2H_2O$	28.03	28.88	28.11	66.40	66.29	5.57	5.60	44.57	44.50	3.91	3.90	Gd_2O_3

Ln: lanthanide; L: mandelate.

The difference in the crystallinity degree of these compounds must be probably due to solubility of each compound since the velocity of evaporation and precipitation were not controlled.

The attenuate total reflectance infrared spectroscopic data on sodium mandelate, mandelic acid and the mandelate compounds with the metal ions considered in this work are shown in Table 3 and, for lanthanum compound, the main experimental infrared spectroscopic data were assigned based on theoretical infrared one calculated and it is shown in Table 4.

For sodium mandelate, the bands centered at 1606 cm^{-1} and 1410 cm^{-1} were assigned to antisymmetric (ν_{as} COO⁻) and

symmetric (ν_s COO⁻) carboxyl stretching frequencies, respectively. The values of $\Delta \nu$ (ν_{as} COO⁻- ν_s COO⁻, carboxylate vibrations) for the synthesized compounds are smaller than those ones calculated for the sodium salt (Table 3), suggesting that the coordination is carried out through the carboxylate group of the mandelate in a bidentate mode (chelating ligand) [24] and in agreement with the theoretical calculation of lanthanum compound (more stable molecule, Fig. 1a). On the other hand, the results of Table 3 show that the ν (C–OH) is shifted towards lower energy than those observed in the mandelic acid and its sodium salt, suggesting that lanthanum ion can be coordinated by the hydroxyl group which is

Table 3

Experimental spectroscopic data for sodium mandelate and its compounds with light trivalent lanthanide ions.

Compounds	$\nu_{as} (\text{COO}^{-}) (\text{cm}^{-1})^{a}$	$\nu_{\rm s}~({\rm COO^-})~({\rm cm^{-1}})^{\rm b}$	δ (O—H) (cm ⁻¹) ^c	ν (C—OH) (cm ⁻¹) ^d	$\Delta u (\mathrm{cm}^{-1})^{\mathrm{e}}$
HL	1711 _s	-	1377 _w	1062 _m	-
NaL	1606 _s	1410 _m	1358 _m	1065 _w	196
La(L)3·1H2O	1581s	1453 _m	1394 _m	1064 _w	128
Ce(L) ₃	1583s	1449 _m	1384 _m	1037 _w	134
$Pr(L)_3 \cdot 2H_2O$	1591s	1431 _m	1377 _m	1020 _w	160
$Nd(L)_3 \cdot 2H_2O$	1592 _s	1432 _m	1377 _m	1023 _w	160
$Sm(L)_3 \cdot 2H_2O$	1595 _s	1429 _m	1377 _m	1032 _w	166
$Eu(L)_3 \cdot 2H_2O$	1595 _s	1429 _m	1377 _m	1033 _w	166
$Gd(L)_3 \cdot 2H_2O$	1595s	1430 _m	1379 _m	1033 _w	165

L: mandelate; w, br: weak, broad; s: strong; m: medium.

 $^{\rm a}~\nu_{\rm as}$ (COO⁻), antisymmetric carboxyl stretching frequency.

 $^{\rm b}$ $\nu_{\rm s}$ (COO⁻), symmetric carboxyl stretching frequency.

 $^{\rm c}~\delta$ (OH), hydroxyl oxygen-hydrogen bending frequency.

 $^{\rm d}~\nu$ (C—OH), carbon hydroxyl stretching frequency.

^e $\Delta \nu$, difference between ν_{as} (COO⁻) and ν_{s} (COO⁻) frequencies.



Fig. 2. X-ray powder diffraction patterns of the compounds: (a) $La(L)_3 \cdot 1H_2O$, (b) $Ce(L)_3$, (c) $Pr(L)_3 \cdot 2H_2O$, (d) $Nd(L)_3 \cdot 2H_2O$, (e) $Sm(L)_3 \cdot 2H_2O$, (f) $Eu(L)_3 \cdot 2H_2O$ and (g) $Gd(L)_3 \cdot 2H_2O$ (L=mandelate).

Table	4

Main infrared absorptions of $La(L)_3 \cdot 1H_2O$ (bounded by the COO⁻ group).

Frequencies (cm ⁻¹)		Assignments
Experimental	Theoretical	
3534 _m	3767	V _{HOH} (s)
3449 _w	3733 _w /3731 _w	VOH
Overlap, br	3649 _{vw}	V _{HOH} (as)
Overlap, br	3632 _w	V _{OH}
3062 _w /3041 _{vw}	3180 _w /3169 _w	$v_{C(sp)^2-H}$
2939 _{vw}	3026 _{vw}	$v_{C(sp)^3-H}$
1673 _w	1611 _w	δ_{HOH}
1581 _s	1553 _m /1539 _w	$v_{as(COO)} + \delta_{C(sp)^3 - H} +$
		$\delta_{OH} + \delta_{HOH}$
1493 _w	1487 _{vw} /1485 _w	$\delta_{C-Hring(inplane)}$
1453 _m	1454s	$\nu_{s(COO)} + \delta_{C(sp)^3 - H} + \delta_{OH}$
1431 _m	1438 _s	$\nu_{s(COO)} + \delta_{C(sp)^3 - H} + \delta_{OH}$
1394 _m	1378 _m	$\delta_{OH} + \delta_{C(sp)^3 - H}$
1378 _m	1351 _m	$\delta_{c(m)3-\mu} + \delta_{OH} +$
	***	$\delta_{C-Hring(inplane)}$
1290 _w /1194 _m	1296w/1216w	$\delta_{a'} \rightarrow 3 - \alpha + \delta_{OH} + \beta_{a'}$
		δ_{C}
1084/1062/1047	1113ww/1076w/1062m	$V_{C} = OH / \delta_{C} = Uring(inplane)$
1026w	1046w	$\delta_{C-Cring(inplane)}$
735 _m	748 _m	$\delta_{C-Hring(outofplane)}$

L: mandelate; br: broad; vw: very weak; w: weak; m: medium; s: strong.

in agreement with the literature [7]. Thus, the coordination of ligand is carried out through the oxygen atoms of the carboxylate and the hydroxyl groups, as shown in Fig. 1b. The likeness between the experimental spectra of all the compounds suggests that they are coordinated in a similar way.

A comparative analysis between the experimental an theoretical spectra in Fig. 3, has shown that: (i) the first assignment shows



Fig. 3. Comparison between FTIR spectra of: (a) experimental and (b) theoretical-more stable; (c) theoretical-less stable of $La(L)_3 \cdot 1H_2O$.



Fig. 4. Simultaneous TG–DTA curves of the compounds: (a) $La(L)_3 \cdot 1H_2O$ (m = 7.136 mg), (b) $Ce(L)_3 \cdot (m = 7.064$ mg), (c) $Pr(L)_3 \cdot 2H_2O$ (m = 7.222 mg), (d) $Nd(L)_3 \cdot 2H_2O$ (m = 7.639 mg), (e) $Sm(L)_3 \cdot 2H_2O$ (m = 7.011 mg), (f) $Eu(L)_3 \cdot 2H_2O$ (m = 7.078 mg) and (g) $Gd(L)_3 \cdot 2H_2O$ (m = 7.109 mg) (L = mandelate).

a strong contribution at 1581 cm⁻¹, suggesting an antisymmetric carboxyl stretching, while the theoretical results show the corresponding peak at 1539 cm⁻¹ with discrepancies of 2.72%; (ii) the second assignment shows a strong contribution at 1453 cm⁻¹ and 1431 cm⁻¹ suggesting a symmetric carboxyl stretching, while the theoretical results show the corresponding peak at 1454 cm⁻¹ and 1438 cm⁻¹ with discrepancies of 0.07% and 0.49%, respectively. The theoretical results are therefore in agreement with the experimental data.

Simultaneous TG–DTA and DSC curves of the compounds are shown in Figs. 4 and 5. The TG–DTA curves show mass losses in three, four, five, six or seven steps, corresponding to endothermic peaks due to dehydration and exothermic peaks attributed to oxidation of the organic matter. The DSC curves up to 300 °C also show endothermic peaks corresponding to the mass losses displayed by the TG curves. The thermal stability of the hydrated compounds (I) or anhydrous compounds (II) and the final temperature of thermal decomposition (III) as shown by TG–DTA curves depend on the nature of the metal ion and they follow the order:

(I) La > Sm > Eu = Gd > Pr = Nd

- (II) La > Sm = Eu > Gd > Pr = Nd > Ce
- (III) Sm > Eu > La > Nd > Pr > Gd > Ce

The TG–DTA curves also show that the formation of stable anhydrous compounds is observed for praseodymium to gadolinium, while for lanthanum compound the thermal decomposition occurs immediately after the dehydration and it is undoubtedly due to the higher thermal stability of the hydrated compound. The cerium compound was obtained in the anhydrous state. The thermal behavior of the compounds is heavily dependent on the nature



Fig. 5. DSC curves of the compounds: (a) $La(L)_3 \cdot 1H_2O$ (m = 2.384 mg), (b) $Pr(L)_3 \cdot 2H_2O$ (m = 2.139 mg), (c) $Nd(L)_3 \cdot 2H_2O$ (m = 2.295 mg), (d) $Sm(L)_3 \cdot 2H_2O$ (m = 2.290 mg), (e) $Eu(L)_3 \cdot 2H_2O$ (m = 2.042 mg) and (f) $Gd(L)_3 \cdot 2H_2O$ (m = 2.058 mg) (L = mandelate).

of the lanthanide ion and so the features of each of these compounds are discussed individually.

corresponding TG–DTA curve, confirmed evolution of CO₂ and presence of the carbonaceous residue.

3.1. Lanthanum compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4a and 5a. The first mass loss observed between 150 and 215 °C, corresponding to an endothermic peak at 200 °C (DTA) and 202 °C (DSC) is due to dehydration with loss of 1H₂O (Calcd. = 3.08%; TG = 2.95%). The thermal decomposition of the anhydrous compound occurs in five steps, being the first four corresponding to exothermic peaks attributed to oxidation of the organic matter. The oxidation of the organic matter yields an intermediate derivative, accompanied by a carbonaceous residue. The intermediate is probably the corresponding dioxycarbonate, La₂O₂CO₃, as already observed for the complexes of 4-methylbenzylidenepyruvate with heavier trivalent lanthanides and yttrium (III) [23]. Tests with hydrochloric acid solution on sample heated up to the temperature of formation of this intermediate, as indicated by the

The last step corresponding to an endothermic peak is attributed to the thermal decomposition of derivative of carbonate (Calcd. = 3.61%) together with carbonaceous residue (TG = 4.23%). The total mass loss up to 710 °C is in agreement with the formation of lanthanum oxide, as final residue (Calcd. = 73.31%; TG = 73.25%).

3.2. Cerium compound

The simultaneous TG–DTA curves are shown in Fig. 4b. The thermal decomposition of the anhydrous compounds occurs in three steps corresponding to exothermic peaks attributed to oxidation of the organic matter and oxidation reaction of Ce(III) to Ce(IV). The profiles of TG–DTA curves corresponding to the second step show that the oxidation of organic matter occurs with combustion. The total mass loss up to 490 °C is in agreement with the formation of cerium (IV) oxide, CeO₂, as final residue (Calcd.=71.00%; TG=71.14%).



Fig. 6. IR spectra of the gaseous products evolved during the thermal decomposition of lanthanum compound.

3.3. Praseodymium compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4c and 5b. The first two steps up to $165 \,^{\circ}$ C, corresponding to endothermic peaks at 100 and $155 \,^{\circ}$ C (DTA) or 106 and 160 $\,^{\circ}$ C (DSC) are due to dehydration with losses of 0.5 and $1.5H_2$ O, respectively (Calcd. = 1.31 and 4.47%; TG = 1.43 and 4.29%).

The thermal decomposition of the anhydrous compound occurs in five steps corresponding to exothermic peaks attributed to the oxidation of the organic matter and due to the oxidation reaction of Pr(III) to Pr_6O_{11} . The profiles of TG–DTA curves corresponding to the fourth step also show that the oxidation of the organic matter occurs with combustion. No thermal event corresponding to the last mass loss is observed in the DTA curve and this is probably because the small mass loss occurs slowly that the heat involved is not sufficient to produce a thermal event.

The total mass loss up to $650 \circ C$ is in agreement with formation of praseodymium oxide, Pr_6O_{11} , as final residue (Calcd. = 72.99%; TG = 72.79%).

3.4. Neodymium compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4d and 5c. The first two steps up to $170 \,^{\circ}$ C, corresponding to endothermic peaks at 110 and 160 $\,^{\circ}$ C (DTA) or 114 and 165 $\,^{\circ}$ C (DSC) are due to dehydration with losses of 0.5 and 1.5H₂O (Calcd. = 1.32% and 4.62%; TG = 1.42 and 4.27%).

The thermal decomposition of the anhydrous compound occurs in five steps, corresponding to exothermic peaks attributed to the oxidation of the organic matter. As already observed in the praseodymium compound, no thermal event corresponding to the last step is also observed in the DTA curve.

The total mass loss up to $700 \degree C$ is in agreement with the formation of neodymium oxide, Nd₂O₃, as final residue (Calcd. = 73.45%; TG = 73.52%).

3.5. Samarium compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4e and 5d. The first mass loss between 110 and 180 °C, corresponding to an endothermic peak at 175 °C (DTA) and 176 °C (DSC) is due to dehydration with loss of $2H_2O$ in a single step (Calcd.=5.63%; TG=5.82%). The thermal decomposition of the anhydrous compound occurs in four steps, corresponding to exothermic peaks attributed to the oxidation of the organic matter, except for the last step in which the mass loss occurs slowly and no thermal event is observed in the DTA curve.

The total mass loss up to 770 °C is in agreement with the formation of samarium oxide, Sm_2O_3 , as final residue (Calcd. = 72.75%; TG = 72.34%).

3.6. Europium compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4f and 5e. The first mass loss observed between 90 and 180 °C, corresponding to endothermic peak at 175 °C (DTA) and 177 °C (DSC) is due to dehydration with loss of $2H_2O$ in a single step (Calcd. = 5.62%; TG = 5.87%).

The thermal decomposition of the anhydrous compound occurs in five steps corresponding to endothermic and exothermic peaks attributed to the thermal decomposition and oxidation of the organic matter, except for the last step. The total mass loss up to 750 °C is in agreement with the formation of europium oxide, Eu_2O_3 , as final residue (Calcd. = 72.56%; TG = 73.02%).

3.7. Gadolinium compound

The simultaneous TG–DTA and DSC curves are shown in Figs. 4g and 5f. The first mass loss observed between 90 and 181 °C, corresponding to an endothermic peak at 175 °C (DTA) and 180 °C (DSC) is due to dehydration with loss of $2H_2O$ in a single step (Calcd. = 5.57%; TG = 6.07%).

The thermal decomposition of the anhydrous compound occurs in three steps, corresponding to exothermic peaks attributed to the oxidation of the organic matter, except for the last step. The total mass loss up to $600 \,^{\circ}$ C is in agreement with the formation of gadolinium oxide, Gd_2O_3 , as final residue (Calcd. = 71.97%; TG = 72.37%).

The mass losses, temperature ranges and the peak temperatures observed in each step of the TG–DTA curves are shown in Table 5.

Table 5

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

Compounds		TG–DTA steps						
		First	Second	Third	Fourth	Fifth	Sixth	Seventh
$La(L)_3 \cdot 1H_2O$	θ (°C) Peak (°C) Loss (%)	150–215 200 (endo) 3.08	215–335 270 (exo) 26.38	335–450 415 (exo) 10.02	450–490 480 (exo) 12.13	490–525 515 (exo) 17.41	645–710 685 (endo) 4.23	
Ce(L) ₃	θ (°C) Peak (°C) Loss (%)	80–220 195 (exo) 48.33	220–360 360 (exo) 15.55	360–490 – 7.26				
$Pr(L)_3 \cdot 2H_2O$	θ (°C) Peak (°C) Loss (%)	75–110 100 (endo) 1.43	110–165 155 (endo) 4.29	180–285 275 (exo) 22.95	285–315 305 (exo) 8.97	315–370 – 2.64	370–485 485 (exo) 31.36	485-650 - 1.09
$Nd(L)_3 \cdot 2H_2O$	θ (°C) Peak (°C) Loss (%)	75–125 110 (endo) 1.42	125–170 160 (endo) 4.27	180–290 280 (exo) 28.95	290–350 320 (exo) 7.24	350-460 450 (exo) 17.11	460–500 500 (exo) 11.52	500–700 - 2.96
Sm(L) ₃ ·2H ₂ O	θ (°C) Peak (°C) Loss (%)	110–180 175 (endo) 5.82	190–380 300 (exo) 34.92	380–460 450 (exo) 18.29	460–520 495 (exo) 11.31	520–770 – 2.0		
$Eu(L)_3 \cdot 2H_2O$	θ (°C) Peak (°C) Loss (%)	90–180 175 (endo) 5.87	190–255 240 (exo) 14.09	255–390 350 (exo) 19.33	390–455 445 (exo) 13.76	455–490 480 (exo) 17.03	490–750 – 2.94	
Gd(L)₃·2H₂O	θ (°C) Peak (°C) Loss (%)	90–181 175 (endo) 6.07	181–348 303 (exo) 33.69	348–486 458 (exo) 30.61	486-600 - 2.00			

L: mandelate.

From DSC curves, the dehydration enthalpies found for the compounds were: 61.7 (La); 9.9, 93.5 (Pr); 7.9, 89.3 (Nd); 135.5 (Sm); 120.5 (Eu) and 124.2 (Gd) kJ mol⁻¹. These results show that no correlation is observed between the increase of the dehydration peak temperatures and the dehydration enthalpies. The increase of dehydration peak temperatures (I) as well as dehydration enthalpies (II) follows the order:

(I) $Pr < Nd < Sm \cong Eu < Gd < La$

(II) La < Nd < Pr < Eu < Gd < Sm

The gaseous products evolved during the thermal decomposition of the compounds studied in this work were monitored by FTIR and it has benzaldehyde, carbon monoxide and carbon dioxide as main products due to the decarboxylation and oxidation of the organic matter. The IR spectra of the gaseous products evolved during the thermal decomposition of lanthanum, as representative of all the compounds, are shown in Fig. 6.

4. Conclusion

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

The theoretical and experimental infrared spectroscopic data suggest that the mandelate compounds should be formed by contribution of both structures, as shown in Fig. 1. The similarity between the experimental infrared spectra suggests that all the compounds are coordinated in a similar way.

The TG–DTA curves also provided previously unreported information concerning the thermal stability and thermal decomposition.

The monitoring of evolved gases during the thermal decomposition of lanthanide mandelates showed that they have benzaldehyde, carbon monoxide and carbon dioxide as main products.

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