

Thermal studies on solid 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene of lighter trivalent lanthanides

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Abstract Solid-state compounds of general formula $\text{Ln}_2\text{L}_3 \cdot n\text{H}_2\text{O}$, where L represents 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene and $\text{Ln} = \text{La, Ce, Pr, Nd, Sm}$, were synthesized. Complexometric titrations with EDTA, thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, elemental analysis and infrared spectroscopy have been employed to characterize and to study the thermal behavior of these compounds in dynamic air atmosphere. The results led to information about the composition, dehydration, crystallinity, and thermal decomposition of the synthesized compounds.

Keywords 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene · Lighter lanthanides · Thermal behavior

Introduction

Several metal–ion complexes of phenyl-substituted derivatives of benzylidenepyruvate, ($\text{C}_6\text{H}_5\text{--CH=CH--COCOO--}$

(BP)), have been investigated in aqueous solutions [1]. These works reported the thermodynamic stability (β_1), and spectroscopic parameters ($\epsilon_{1\text{max}}$, λ_{max}), associated with 1:1 complex species, as well as analytical applications of sodium 4-dimethylamino-BP for gravimetric determination of Cu(II), or as indicator in the complexometric titrations of Th(IV) and Al(III), with EDTA [2, 3].

The works reported the synthesis and characterization of the compounds by means of thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), X-ray powder diffractometry, and other methods of analysis. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies [1–8].

In the present article, solid compounds of lighter trivalent lanthanides (i.e., La, Ce, Pr, Nd, and Sm) with 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene (L) were prepared.

The compounds were investigated by means of complexometry, X-ray powder diffractometry, infrared spectroscopy, differential scanning calorimetry (DSC) and simultaneous thermogravimetry and differential thermal analysis (TG-DTA). The results allowed us to acquire information concerning these compounds in the solid state including their thermal behavior.

Experimental

Sodium 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene (L) and its corresponding acid were synthesized following the same procedure described in the literature [9].

Aqueous solution of $\text{Na}_2(\text{L})$, 0.1 mol L^{-1} was prepared by direct weighting of the salt. Lanthanide chlorides were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid.

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The obtained chlorides were 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 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. Cerium (III) was used as its nitrate and 0.1 mol L⁻¹ aqueous solutions of this ion were prepared by direct weighing of the salt.

The solid-state compounds Ln₂L₃ (Ln = lanthanides) 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 Whatman no. 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In solid-state compounds, hydration water, ligand, and metal contents were determined from the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solutions, using xylenol orange as indicator [10].

X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer, employing Cu K α radiations ($\lambda = 1.541 \text{ \AA}$) and setting of 40 kV and 20 mA.

The attenuate total reflectance infrared spectra for 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene (sodium salt) as well as for its trivalent lanthanide compounds were run on a Nicolet iS10 spectrophotometer (Thermo Scientific).

Simultaneous TG-DTA were performed in a SDT 2960 apparatus from TA Instruments. All the TG-DTA curves were obtained under dynamic dried air atmosphere (gas flow of 100 mL min⁻¹) and at a heating rate of 20 °C min⁻¹. The sample masses were about 5 mg. Alumina crucibles were used in the TG-DTA experiments.

DSC curves were recorded using a DSC Q10 modulus (TA instruments) under an air flow of 50 mL min⁻¹ and at a heating rate of 20 °C min⁻¹. The sample masses were about 2 mg and covered aluminum crucibles with a pin hole ($\phi = 0.7 \text{ mm}$) in the center of the lid were employed during the analysis. DSC modulus was calibrated using indium metal (99.99+%) for temperature and enthalpy.

Results and discussion

The analytical results are shown in Table 1. These data permitted to establish the stoichiometry of the compounds, which is in agreement with general formula Ln₂L₃·nH₂O, where Ln represents lighter lanthanides (La, Ce, Pr, Nd, and Sm), L is 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene and $n = 5$ (La), 7 (Ce, Pr, Sm), and 7.5 (Nd).

The X-ray powder patterns showed that all the compounds were obtained in with low crystallinity degree and without evidence for the formation of an isomorphous series.

Table 1 Analytical data for Ln₂L₃·nH₂O

Compounds	Metal/%			ΔL /%		Water/%		Final residue/%		
	Calc.	TG	EDTA	Calc.	TG	Calc.	TG	Calc.	TG	Oxide
La ₂ L ₃ ·5H ₂ O	23.45	22.94	23.71	64.89	65.65	7.68	7.40	27.50	26.90	La ₂ O ₃
Ce ₂ L ₃ ·7H ₂ O	22.90	22.59	22.42	62.85	62.15	10.42	10.10	28.15	27.75	CeO ₂
Pr ₂ L ₃ ·7H ₂ O	23.01	23.45	22.76	62.77	61.33	10.40	10.34	27.80	28.33	Pr ₆ O ₁₁
Nd ₂ L ₃ ·7.5H ₂ O	23.26	23.50	24.33	61.97	61.91	11.01	10.85	27.13	27.41	Nd ₂ O ₃
Sm ₂ L ₃ ·7H ₂ O	24.18	23.59	23.78	61.81	62.69	10.24	9.95	28.04	27.36	Sm ₂ O ₃

Table 2 Spectroscopic data for sodium salt of 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene and for its compounds with lanthanum (III) and lighter trivalent lanthanides

Compound	$\nu_{\text{O-H}}$ H ₂ O	$\nu_{\text{as.}}$ (COO ⁻)	ν_{sym} (COO ⁻)	$\nu_{\text{C=O}}$
Na ₂ (L)	–	1594	1423	1671, 1640, 1620,
La ₂ L ₃ ·5H ₂ O	3414	–	1429, 1413	1671, 1629
Ce ₂ L ₃ ·7H ₂ O	3372	1590	1416	1664, 1637
Pr ₂ L ₃ ·7H ₂ O	3368	1589	1416	1665, 1639, 1626
Nd ₂ L ₃ ·7.5H ₂ O	3350	1591	1416, 1405	1665, 1638, 1624
Sm ₂ L ₃ ·7H ₂ O	3375	1587, 1596	1417	1700, 1663, 1635, 1610

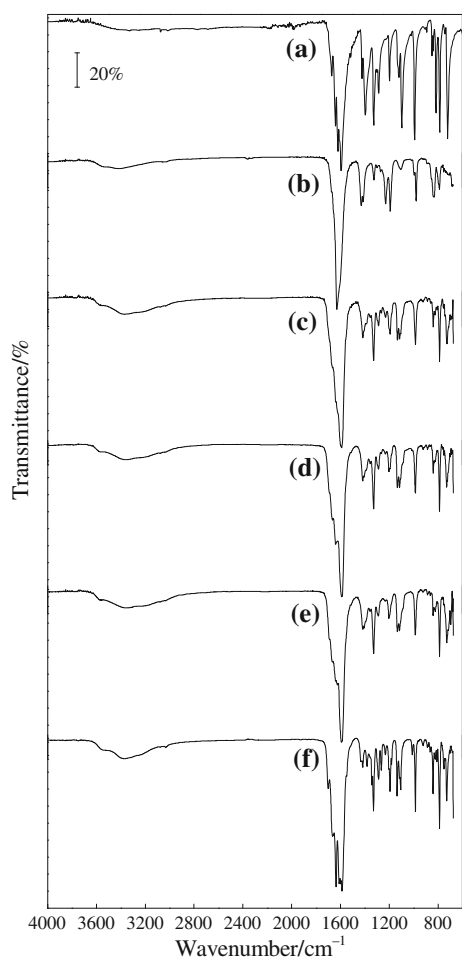


Fig. 1 Reflectance infrared spectra of *a* Na₂L, *b* La₂L₃·5H₂O, *c* Ce₂L₃·7H₂O, *d* Pr₂L₃·7H₂O, *e* Nd₂L₃·7.5H₂O, and *f* Sm₂L₃·7H₂O

Infrared spectroscopic data on 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene and its compounds with La, Ce, Pr, Nd, and Sm are shown in Table 2 and Fig. 1.

The bands found for 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene (sodium salt) are centered at 1671 cm⁻¹, 1640 cm⁻¹, 1620 cm⁻¹ (ketonic carbonyl stretches), 1594 cm⁻¹ (anti-symmetrical carboxylate vibration), and 1423 cm⁻¹ (symmetrical carboxylate vibration). The ketonic carbonyl stretches vibrations frequency is unchanged in the compounds, namely, La (1671, 1629 cm⁻¹), Ce (1664, 1637 cm⁻¹), Pr (1665, 1639, 1626 cm⁻¹), Nd (1665, 1638, 1624 cm⁻¹), and Sm (1700, 1663, 1635, 1610 cm⁻¹). These data suggest that the ketonic carbonyl does not participate in coordination with the metal centers. The anti-symmetrical carboxylate stretches vibrations both shifted to lower frequencies in the compounds, namely, La (is not observed), Ce (1590 cm⁻¹), Pr (1589 cm⁻¹), Nd (1591 cm⁻¹), and Sm (1587, 1596 cm⁻¹) for the vibration. These data suggest that

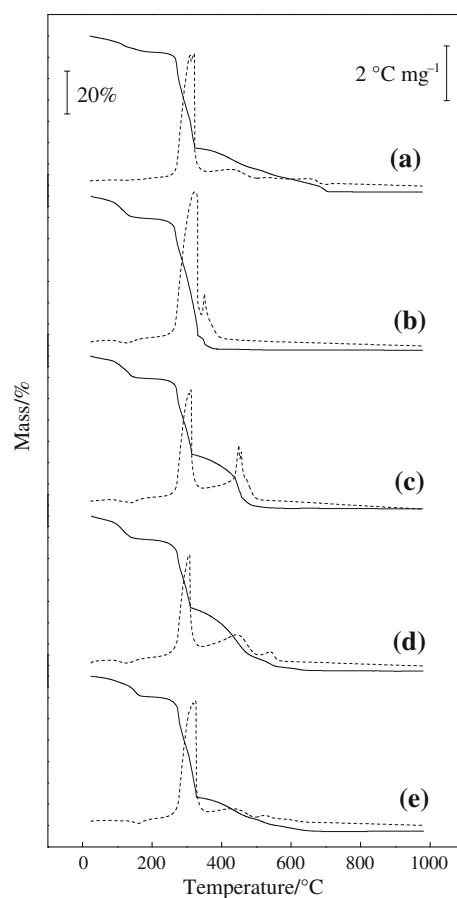


Fig. 2 TG-DTA curves of the compounds *a* La₂L₃·5H₂O (*m* = 5.0808 mg), *b* Ce₂L₃·7H₂O (*m* = 5.1760 mg), *c* Pr₂L₃·7H₂O (*m* = 5.0352 mg), *d* Nd₂L₃·7.5H₂O (*m* = 5.0265 mg), and *e* Sm₂L₃·7H₂O (*m* = 5.1541 mg)

1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene acts as a bidentate ligand by the carboxylate groups [11].

The simultaneous TG-DTA curves of the compounds are shown in Fig. 2. These curves exhibit mass losses in three (Ce and Pr) and four (La, Nd, and Sm) steps and thermal events corresponding to these losses.

The first mass loss of the compounds that occurs in the range of 22–209 °C is attributed to dehydration, which occurs in a single step. This mass loss is associated to an endothermic peak in the range of 124–160 °C in the DTA curve.

For the anhydrous cerium and praseodymium compounds the thermal decomposition occurs in two steps between 200–330 °C and 330–426 °C (Ce) or 200–313 °C and 313–600 °C (Pr), corresponding to the exothermic peaks at 324 and 352 °C (Ce) or 312, 449, and 457 °C (Pr), attributed to decomposition/oxidation of the organic matter. For the cerium compound, the profiles of the TG curve

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

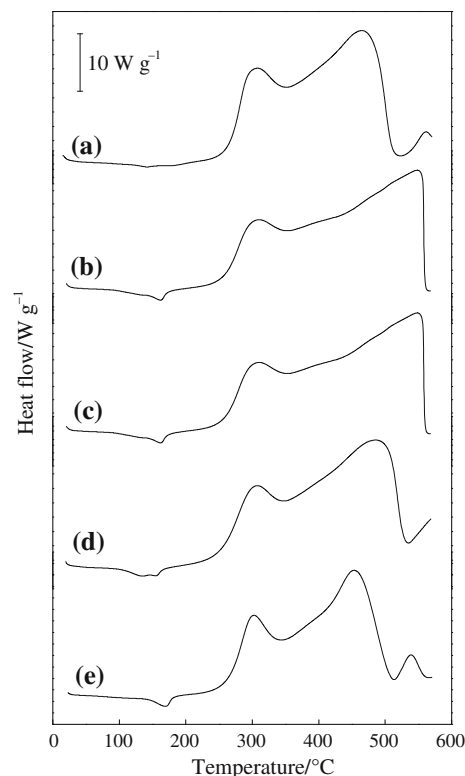
Compounds	Steps			
	First	Second	Third	Fourth
$\text{La}_2\text{L}_3 \cdot 5\text{H}_2\text{O}$				
θ / °C	22–183	183–323	323–497	497–750
Loss/%	7.40	45.15	9.82	10.73
Peak/ °C	124 (endo)	310/321 (exo)	440 (exo)	550 (exo)
$\text{Ce}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$				
θ / °C	24–157	200–330	330–426	–
Loss/%	10.10	55.22	6.93	–
Peak/ °C	128 (endo)	324 (exo)	352 (exo)	–
$\text{Pr}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$				
θ / °C	24–165	200–313	313–600	–
Loss/%	10.34	35.69	25.64	–
Peak/ °C	140 (endo)	312 (exo)	449/457 (exo)	–
$\text{Nd}_2\text{L}_3 \cdot 7.5\text{H}_2\text{O}$				
θ / °C	25–170	200–311	311–500	500–650
Loss/%	10.85	32.16	23.77	5.81
Peak/ °C	126 (endo)	306 (exo)	444 (exo)	541 (exo)
$\text{Sm}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$				
θ / °C	24–209	209–329	329–500	500–670
Loss/%	9.81	46.96	10.22	5.65
Peak/ °C	160 (endo)	324 (exo)	436 (exo)	525 (exo)

in the first step suggest that the oxidation of the organic matter occurs with combustion. For the praseodymium compound, the TG-DTA curves show that the last step occurs thought an overlapping one.

For the anhydrous lanthanum, neodymium, and samarium compounds, the thermal decomposition occurs in three steps between 183–323 °C, 323–497 °C, and 497–750 °C (La) or 200–311 °C, 311–500 °C, and 500–650 °C (Nd) or 209–329 °C, 329–500 °C, and 500–670 °C (Sm), corresponding to the exothermic peaks at 310, 321, 440, 550 °C (La), 306, 444, and 541 °C (Nd) or 324, 436, and 525 °C (Sm), attributed to oxidation of the organic matter. The mass losses, temperature ranges, and the peak temperatures observed in each step in the TG-DTA curves are shown in Table 3.

The X-ray powder patterns showed that the residues heated up 1,000 °C are Ln_2O_3 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$), CeO_2 , and Pr_6O_{11} .

The DSC curves of the compounds are shown in Fig. 3. These curves show endothermic and exothermic peaks and that all are in accordance with the mass losses observed in the TG curves. The endothermic peaks at 140.7 °C (La), 143.4 °C (Ce), 162.0 °C (Pr), 134.8 °C (Nd), and 170.0 °C (Sm) are assigned to the dehydration. The dehydration enthalpies found for these compounds (La, Ce, Pr, Nd, and

**Fig. 3** DSC curves of the compounds *a* $\text{La}_2\text{L}_3 \cdot 5\text{H}_2\text{O}$ ($m = 2.102$ mg), *b* $\text{Ce}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$ ($m = 2.197$ mg), *c* $\text{Pr}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$ ($m = 2.279$ mg), *d* $\text{Nd}_2\text{L}_3 \cdot 7.5\text{H}_2\text{O}$ ($m = 2.277$ mg), and *e* $\text{Sm}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$ ($m = 2.460$ mg)

Sm) were 22.7, 156.5, 158.1, 169.8, and 156.7 J g^{-1} , respectively.

Conclusions

Based on the TG curves and the results of complexometric titration, a general formula could be established for the synthesized compounds. TG-DTA and DSC provided previously unreported information concerning the thermal behavior and thermal decomposition of these compounds. The spectroscopic infrared data suggest that 1,4-bis(3-carboxy-3-oxo-prop-1-enyl)benzene acts as a bidentate ligand by the carboxylate groups.

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