THERMAL STUDIES OF SOLID 2-METHOXYBENZYLIDENEPYRUVATE OF LIGHTER TRIVALENT LANTHANIDES

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Solid-state compounds with a general formula of $LnL_3 \cdot nH_2O$, where *Ln* stands for lighter trivalent lanthanides (lanthanum to samarium), *L* is 2-methoxybenzylidenepyruvate and *n*=1.5, 2, 2, 1.5 and 2, respectively, have been synthesized.

On heating these compounds are decompose in two or three steps. They lose their hydration water in the first step and the thermal decomposition of the anhydrous compounds occurs with the formation of the respective oxide, CeO_2, Pr_6O_{11} and Ln_2O_3 (*Ln*=La, Nd, Sm) as final residue. The dehydration enthalpies found for these compounds (La to Sm) were: 222.7, 163.6, 497.7, 513.9 and 715.4 kJ mol^{-1}, respectively.

Keywords: lighter lanthanides, 2-methoxybenzylidenepyruvate, thermal behaviour

Introduction

Several metal-ion complexes of phenyl-substituted derivatives of benzylidenepyruvate, $C_6H_5–CH=CH–COCOO^-$ (BP), have been investigated in aqueous solutions [1–5]. These works reported the thermodynamic stability (β_1), and spectroscopic parameters (ε_{1max}, 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. In the solid-state, the works reported the synthesis and investigation of the compounds by means of thermogravimetry, derivative thermogravimetry (TG, DTG), differential thermal analysis (DTA), X-ray powder diffractometry and other analytical methods. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies [6–15].

In the present paper, solid-state compounds of lighter trivalent lanthanides (i. e. La, Ce, Pr, Nd and Sm) with 2-methoxybenzylidenepyruvate (2-MeO-BP) were prepared.

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

Experimental

The sodium salt of 2-methoxybenzylidenepyruvic acid was prepared following the same procedure as described in [16]. Aqueous solutions of 0.1 mol L^{-1} Na 2-MeOBP were prepared by direct weighing of the corresponding metal oxides (except for cerium) and by their treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to obtain an almost dry substance. The residues were dissolved again in distilled water and the solutions have been evaporated again almost completely to eliminate the excess of hydrochloric acid. Then 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, with adjusting their pH to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. Cerium(III) was used as its nitrate and ca. 0.1 mol L^{-1} aqueous solution were prepared by direct weighing of the salt.

The solid-state compounds were prepared by adding slowly, with continuous stirring, the solutions of the ligand to the respective metal chloride or nitrate solutions, 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 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In solid-state compounds, the hydration water, ligand and metal contents were determined from the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [17].

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X-ray powder patterns were obtained by using Siemens D-500 X-ray diffractometer, applying CuK_α radiations (λ=1.541 Å) and setting 40 kV and 20 mA as operating parameters.

Infrared spectra of 2 MeO-BP (sodium salt) as well as for its trivalent lanthanide compounds were recorded on the Nicolet mod. Impact 400 FT-IR instrument, in the range of 4000–400 cm^{-1}, using KBr pellets.

Simultaneous TG-DTA and DSC curves were obtained using two thermoanalytical systems, TA Instruments SDT 2960 and DSC 2010. The purge gas was flowing air with a flow rate of 100 mL min^{-1}. The heating rates were 20 K min^{-1} and the initial sample masses were about 7 mg. Alumina and aluminum crucibles, the latter one with perforated covers, were used for TG-DTA and DSC experiments, respectively.

Results and discussion

The analytical results of the synthesized compounds are shown in Table 1. Based on these results the stoichiometry of the compounds was calculated which was in a good agreement with the general formula of $Ln(2\text{-MeO-BP})_3 \cdot n H_2O$, where *Ln* represents lanthanides, 2-MeO-BP is 2-methoxybenzylidene-pyruvate and *n*=1.5 for La and Nd; 2 for Ce, Pr and Sm.

The X-ray powder patterns showed that all the compounds were obtained in amorphous state and in disagreement with the 4-methoxybenzylidenepyruvate

with the same metal ions that were obtained in crystalline state [6]. The amorphous state is undoubtedly related to the low solubility of these compounds, as it has already observed for the lanthanides and yttrium compounds with other phenyl substituted derivatives of BP [7, 10].

Infrared spectroscopic data on 2-methoxybenzylidenepyruvate (sodium salt) and its compounds with lighter trivalent lanthanides are shown in Table 2. The bands for 2-MeO-BP (sodium salt) centered at 1776 cm^{-1} (ketonic carbonyl stretching) and 1651 cm^{-1} (anti-symmetrical carboxylate vibration) are both shifted to lower frequencies in the compounds, namely, 1703–1709 and 1632–1640 cm^{-1}, respectively, suggesting lanthanides co-ordination by the α-ketonic carbonyl and carboxylate groups of the ligand [18, 19]. This behaviour is in agreement with some bivalent metal ions and lanthanide compounds with other phenyl substituted derivatives of BP [12, 14, 15].

The simultaneous TG-DTA curves of the compounds are shown in Fig. 1. These curves exhibit mass losses in two or three steps. The TG-DTA profiles of the lanthanum, cerium and neodymium compounds are very similar, as it can be seen in Figs 1a, b and d. On the other hand, praseodymium and samarium compounds display another set of TG-DTA profiles, Figs 1c and e which are very similar together.

The first mass loss is in the range of 40–110ºC for all the compounds and ascribed to dehydration, which occurs in a single step. After dehydration, the

Table 1 Analytical data for $Ln(L)_3 \cdot n H_2O$

Compounds	*Ln*/%			Ligand lost/%		Water/%	
	calc.	TG	EDTA	calc.	TG	calc.	TG
La(L)$_3$·1.5H$_2$O	17.77	17.92		75.70	75.48	3.46	3.50
Ce(L)$_3$·2H$_2$O	17.70	17.88	17.43	73.71	73.57	4.55	4.47
Pr(L)$_3$·2H$_2$O	17.78	17.58		73.97	74.21	4.55	4.55
Nd(L)$_3$·1.5H$_2$O	18.34	18.60	17.58	75.20	74.90	3.44	3.40
Sm(L)$_3$·2H$_2$O	18.75	18.56		73.77	74.10	4.49	4.37

Ln – lanthanides, *L* – 2-methoxybenzylidenepyruvate.

Table 2 1R spectroscopic data for sodium 2-methoxybenzylidenepyruvate and for its compounds with lighter trivalent lanthanides

Compounds	$\upsilon_{(O-H)}H_2O$	$\upsilon_{s(COO^-)}$	$\upsilon_{as(COO^-)}$	$\upsilon_{(C=O)}$
NaL·1.5H$_2$O	3488 m	1556 m	1651 s	1776 s
La(L)$_3$·1.5H$_2$O	3437 m	1557 m	1634 s	1704 s
Ce(L)$_3$·2H$_2$O	3437 m	1557 m	1634 s	1709 s
Pr(L)$_3$·2H$_2$O	3420 m	1555 m	1640 s	1705 s
Nd(L)$_3$·1.5H$_2$O	3453 m	1554 m	1632 s	1703 s
Sm(L)$_3$·2H$_2$O	3409 m	1557 m	1634 s	1705 s

L=2-methoxybenzylidenepyruvate; s – strong, m – medium, $\upsilon_{as(O-H)}$ – hydroxyl group stretching frequency, $\upsilon_{s(COO^-)}$ and $\upsilon_{as(COO^-)}$ – symmetrical and anti-symmetrical vibrations of the COO$^-$ structure; $\upsilon_{s(C=O)}$ – ketonic carbonyl stretching frequency.

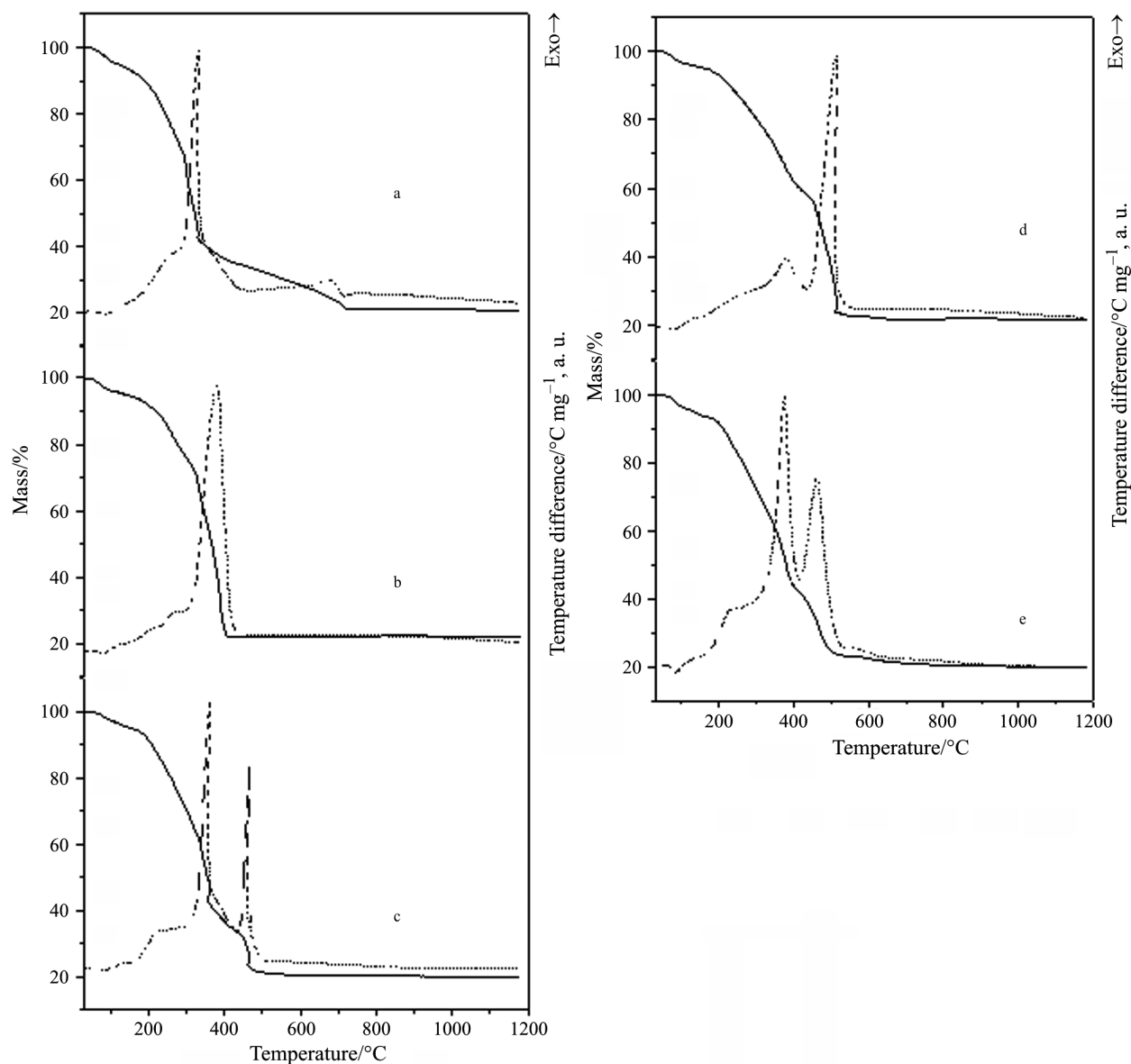**Fig. 1** Simultaneous TG-DTA curves of the compounds: a – La(2-MeO-BP)·1.5H$_2$O, b – Ce(2-MeO-BP)·2H$_2$O, c – Pr(2-MeO-BP)·2H$_2$O, d – Nd(2-MeO-BP)·1.5H$_2$O and e – Sm(2-MeO-BP)·2H$_2$O

mass loss observed above 110ºC for all compounds is due to the thermal decomposition of the anhydrous compounds; that takes place in consecutive and/or overlapping steps with partial mass losses which are characteristic for each compound.

For cerium compound, the thermal decomposition occurs up to 420ºC with the formation of cerium(IV) oxide, CeO$_2$, as final residue. The less thermal stability of the cerium compound is attributed to the oxidation reaction of Ce(III) to Ce(IV) together with the oxidation of the organic matter. This behaviour concerning to the thermal stability of the cerium compound had already been observed for other cerium compounds [6, 7, 12].

For the other compounds, the mass losses up to 740ºC (La), 500ºC (Pr) and 660ºC (Nd, Sm), corresponding to the exothermic peaks, are attributed to the oxidation of the organic matter, with the probable formation of dioxycarbonate, Ln$_2$O$_2$(CO$_3$)$_2$, accompanied by the formation of small quantities of carbonaceous residue, except for praseodymium compound. Tests with hydrochloric acid solutions on samples heated up a given temperature indicated by the TG curves, i.e. 650ºC (La), 550ºC (Nd, Sm), confirmed the elimination of CO$_2$ and the presence of carbonaceous residue.

In the final step of the thermal decomposition, only lanthanum compound exhibits a small exothermic peak at 683°C, followed by and endothermic one at 717°C. It corresponds to the oxidation of the carbonaceous residue and the thermal decomposition of the intermediate $Ln_2O_2(CO_3)_2$, leading to the lanthanum oxide, La_2O_3. For the other compounds, only the samarium compound exhibits a small exotherm, corresponding to the last mass loss, and only for the praseodymium and neodymium compounds the final mass loss from TG-DTA curves show that the sample temperature exceed the oven's one, suggesting that the oxidation of the organic matter is accompanied by

combustion. The final thermal decomposition residues of these compounds are the respective oxides, i.e. Pr_6O_{11}, Nd_2O_3 and Sm_2O_3.

The DSC curves of the compounds are shown in Fig. 2. These curves indicate endothermic and exothermic peaks that all are in accordance with the mass losses observed in the TG curves. The endothermic peak at 100°C, for all compounds is ascribed to the dehydration. The dehydration enthalpies for these compounds (La to Sm) were: 222.7, 163.6, 497.7, 513.9 and 715.4 kJ mol^{-1}, respectively.
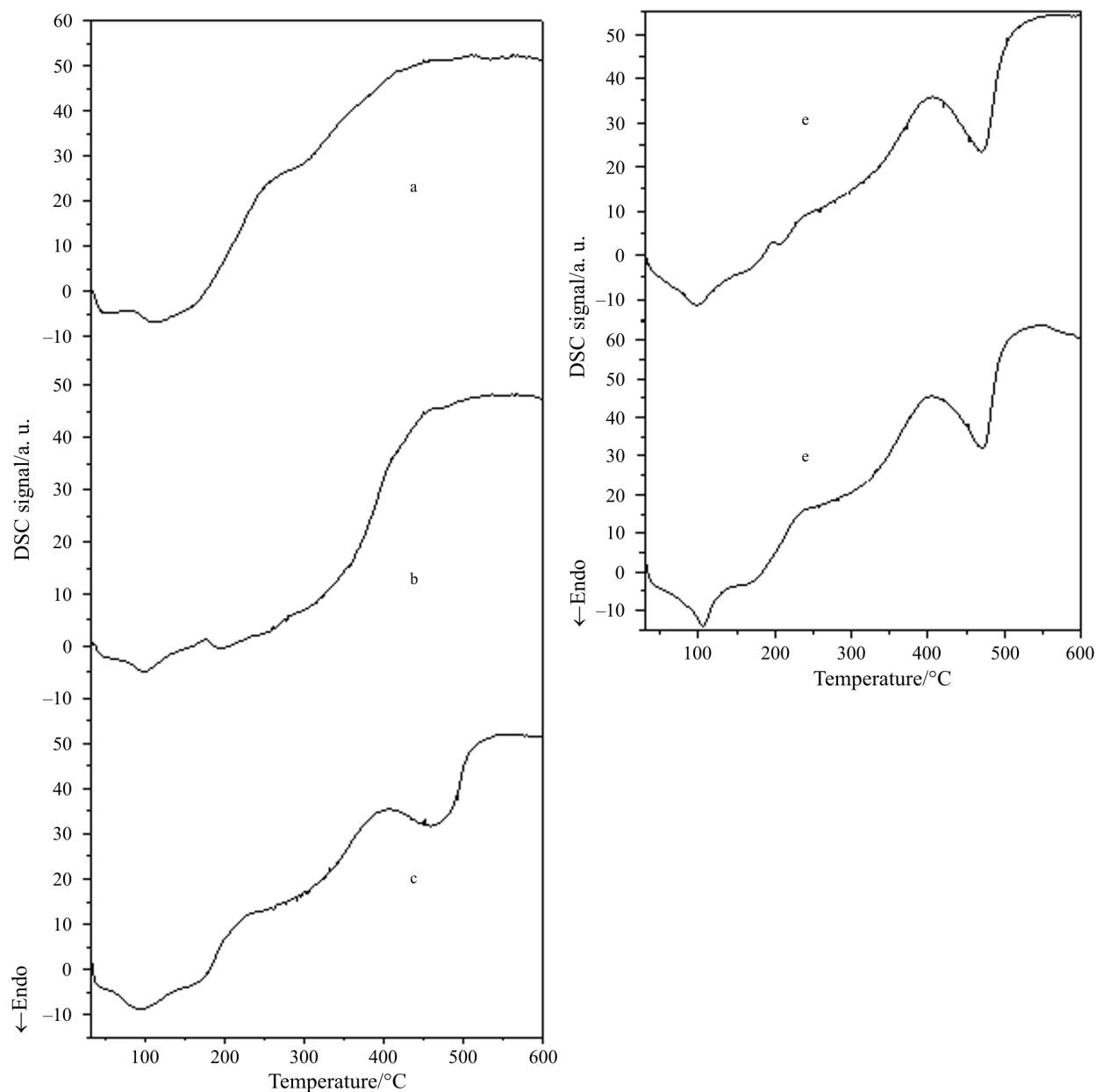

Fig. 2 DSC curves of the compounds: a – La(2-MeO-BP)·1.5H$_2$O, b – Ce(2-MeO-BP)·2H$_2$O, c – Pr(2-MeO-BP)·2H$_2$O, d – Nd(2-MeO-BP)·1.5H$_2$O and e – Sm(2-MeO-BP)·2H$_2$O

Table 3 Temperature ranges (θ/°C), mass losses (%) and peak temperatures (°C) observed for each step of the TG-DTA curves of Ln(L)$_3 \cdot n$H$_2$O compounds, where *Ln* – lanthanides, *L* – 2-methoxybenzylidenepyruvate

Compound		Steps		
		first	second	third
LaL$_3 \cdot$1.5H$_2$O	θ/°C mass loss/% peak temperature/°C	40–110 3.50 90 (endo)	110–336 54.30 336 (exo)	336–740 21.18 683 (exo), 717 (endo)
CeL$_3 \cdot$1.5H$_2$O	θ/°C mass loss/% peak temperature/°C	40–110 4.47 90 (endo)	110–320 25.76 274 (exo)	320–420 47.81 380 (exo)
PrL$_3 \cdot$1.5H$_2$O	θ/°C mass loss/% peak temperature/°C	40–110 4.55 90 (endo)	110–400 45.97 357 (exo)	400–500 28.24 491 (exo)
NdL$_3 \cdot$1.5H$_2$O	θ/°C mass loss/% peak temperature/°C	40–110 3.40 90 (endo)	110–450 41.20 380 (exo)	450–660 33.70 511 (exo)
SmL$_3 \cdot$1.5H$_2$O	θ/°C mass loss/% peak temperature/°C	40–110 4.37 90 (endo)	110–395 51.15 375 (exo)	395–660 22.95 463 (exo), 575 (exo)

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

Conclusions

From TG curves and complexometry results, a general formula could be established for these compounds in the solid-state.

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

Acknowledgements

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