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Synthesis, characterization and thermal behaviour of solid state compounds of 4-methylbenzylidenepyruvate with lighter trivalent lanthanides

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Abstract

Solid state Ln-4-Me-BP compounds, where Ln stands for lighter trivalent lanthanides (lanthanum to europium) and 4-Me-BP is 4-methylbenzylidenepyruvate, have been synthesized. Elemental analysis, complexometry, X-ray powder diffractometry, infrared spectroscopy and simultaneous thermogravimetry-differential thermal analysis (TG-DTA), have been used to characterize and to study the thermal behaviour of these compounds. The results provided information concerning the stoichiometry, crystallinity, thermal stability and thermal decomposition.

Keywords: Lighter trivalent lanthanides; 4-Methylbenzylidenepyruvate; Characterization; Thermal behaviour

1. 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] and in the solid state [6–12]. In aqueous solutions these works reported the thermodynamic stability (β_1), and spectroscopic parameters ($\varepsilon_{1\max}$, $\lambda_{\max}$), associated with 1:1 complex species, as well as analytical applications of sodium 4-dimethylamino-BP for the gravimetric determination of Cu(II), or as indicator in the complexometric titration 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), differential scanning calorimetry (DSC), 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.

In the present paper, solid state compounds of lighter trivalent lanthanides (i.e. La, Ce, Pr, Nd, Sm and Eu) with 4-methylbenzylidenepyruvate (4-Me-BP) were prepared. The compounds were investigated by means of complexometry, elemental analysis, X-ray powder diffractometry, infrared spectroscopy and simultaneous TG-DTA. The results allowed us to acquire information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

2. Experimental

The sodium salt of 4-methylbenzylidenepyruvic acid, was prepared following the same procedure described in the literature [13]. Aqueous solutions of 0.10 M Na-4-Me-BP were prepared by direct weighing of the salt.

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, the residues redissolved in distilled water, and the solutions again evaporated to near dryness to eliminate the excess of hydrochloric acid. The residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.10 M 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 M 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 or nitrate solutions, until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of the chlo-

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ride (or nitrate) ions, filtered through and dried on Whatman no. 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 the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [14]. Carbon and hydrogen microanalysis were performed using an EA 1110, CHNS-O Elemental Analyser (CE Instruments).

X-ray powder patterns were obtained by using a Siemens D-500 X-ray diffractometer, employing Cu Kα radiation (λ=1.541 Å) and settings of 40 kV and 20 mA. Infrared spectra for 4-Me-BP (sodium salt) as well as for its trivalent lanthanide compounds, were run on a Nicolet mod. 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 recorded on a model SDT 2960 thermal analysis system from TA Instruments. The purge gas was an air flow of 150 ml min^{-1}. A heating rate of 20 °C min^{-1} was adopted, with samples weighing about 7–8 mg. Alumina crucibles were used for recording the TG-DTA curves.

3. Results and discussion

The analytical results of the synthesized compounds are shown in Table 1. These results permitted to establish the stoichiometry of the compounds, which is in agreement with the general formula $Ln(4\text{-Me-BP})_3 \cdot nH_2O$, where Ln represents lanthanides, 4-Me-BP is 4-methylbenzylidenepyruvate and n=1, except for Eu where n=1.5.

The X-ray powder patterns showed that all the compounds were obtained in amorphous state. The amorphous state is undoubtedly related to the low solubility of these compounds, as already observed for the lanthanides and yttrium compounds with other phenyl-substituted derivatives of BP [6,7].

Infrared bands found for 4-Me-BP (sodium salt), centered at 1670 cm^{-1} (ketonic carbonyl stretching) and 1635 cm^{-1} (anti-symmetrical carboxylate vibration) are both shifted to lower frequencies in the complexes, namely 1643–1635 and 1593–1585 cm^{-1}, respectively, suggesting lanthanides coordination both by the α-ketonic carbonyl and carboxylate groups of the ligand. This behaviour is in line with that observed for the 1:1 complexes of the same ligand with lanthanides in aqueous solution, where linear-free energy relationships, as applied to oxygen donor substances, also suggest the $-COCOO^-$ moiety as the bidentate metal binding site of 4-Me-BP [5].

The simultaneous TG-DTA curves of the compounds are shown in Fig. 1. These curves show mass losses in two (Ce), four (Eu), five (La, Pr, Sm) and six (Nd) steps between 55 and 725 °C. The first mass loss in the range 70–125 °C (La-Sm) and 55–140 °C (Eu) is ascribed to dehydration, which occurs in a single step.

After dehydration, the mass losses observed above 145 °C for the cerium compound (Fig. 1b), above 155 °C for the samarium and europium compounds (Fig. 1e,f) and above 170 °C for the lanthanum, praseodymium and neodymium compounds (Fig. 1a,c,d), are due to the thermal decomposition of the anhydrous compounds; these take place in consecutive and/or overlapping steps with partial losses which are characteristic for each compound.

For the cerium compound, the thermal decomposition occurs up to 375 °C, with the formation of cerium(IV) oxide, CeO_2, as the final residue. The smaller 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 the thermal stability of the cerium compound, had already been observed for other cerium compounds [6,7].

For the other compounds, the mass losses up to 570 °C (La, Sm), 445 °C (Pr, Eu) and 600 °C (Nd), corresponding to exothermic peaks, are attributed to the oxidation of the organic matter, with the probable formation of dioxycarbonates, $Ln_2O_2CO_3$, accompanied by small quantities of

Table 1
Analytical data for the $LnL_3 \cdot nH_2O$ compounds

Compound	Lanthanides (%)			Ligand lost (%)		Water (%)		Carbon (%)		Hydrogen (%)	
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd.	E.A.	Calcd.	E.A.
$LaL_3 \cdot H_2O$	19.17	19.32	19.38	75.03	74.80	2.49	2.55	54.70	53.96	4.04	4.17
$CeL_3 \cdot H_2O$	19.31	19.54	19.54	73.80	73.70	2.48	2.30	54.61	54.80	4.04	4.13
$PrL_3 \cdot H_2O$	19.39	19.29	19.29	74.09	74.16	2.48	2.54	54.58	54.59	4.03	4.11
$NdL_3 \cdot H_2O$	19.76	19.75	20.04	74.47	74.48	2.47	2.50	54.30	53.88	4.01	4.17
$SmL_3 \cdot H_2O$	20.43	20.33	20.58	73.86	73.91	2.45	2.51	53.85	53.33	3.98	4.15
$EuL_3 \cdot 1.5H_2O$	20.35	20.22	20.59	72.81	72.86	3.62	3.73	53.08	53.98	4.05	4.12

Ln, lanthanides; L, 4-methylbenzylidenepyruvate.

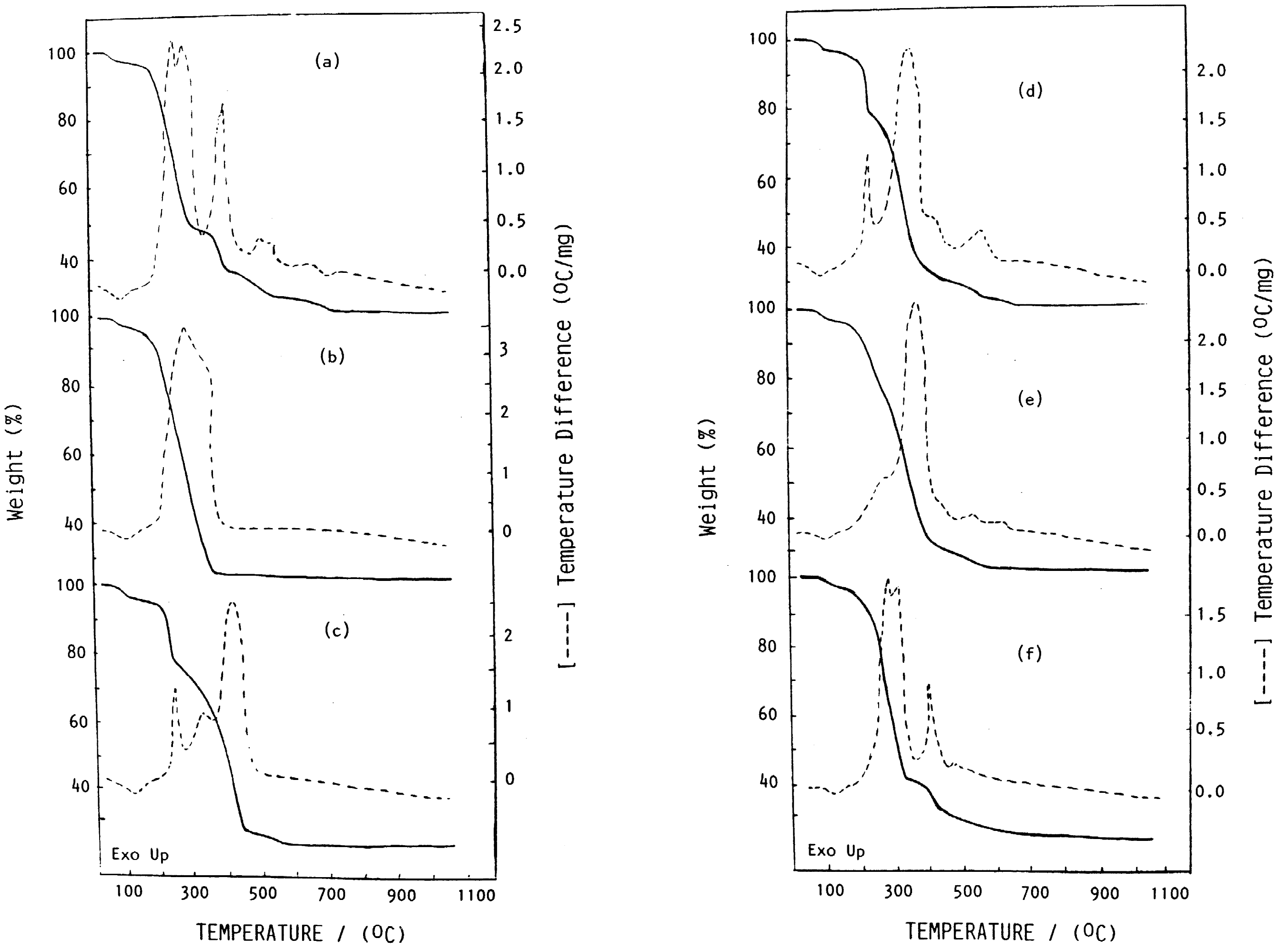

Fig. 1. Simultaneous TG-DTA curves of the compounds: (a) La(4-Me-BP)$_3$·H$_2$O (8.052 mg); (b) Ce(4-Me-BP)$_3$·H$_2$O (7.930 mg); (c) Pr(4-Me-BP)$_3$·H$_2$O (8.189 mg); (d) Nd(4-Me-BP)$_3$·H$_2$O (8.132 mg); (e) Sm(4-Me-BP)$_3$·H$_2$O (8.062 mg) and (f) Eu(4-Me-BP)$_3$·1.5 H$_2$O (8.732 mg).

carbonaceous residues. Tests with hydrochloric acid solution on samples heated up to the temperature indicated by the TG curves confirmed the elimination of CO_2 and the presence of carbonaceous residues.

In the final step of the thermal decomposition, only the lanthanum compound exhibits a small exothermic peak at 660 °C, followed by an endothermic peak at 710 °C, in agreement with the oxidation of the carbonaceous residue and thermal decomposition of the intermediate, leading to the lanthanum oxide, La_2O_3. For the other compounds, only the samarium compound exhibits a small exothermic peak at 635 °C, corresponding to the last mass loss; nevertheless no peak is observed due to the simultaneous oxidation of the carbonaceous residue (exothermic) and the thermal decomposition of the intermediate derivative of carbonate (endothermic); the resulting heat in this step is insufficient to produce a thermal event. The final thermal decomposition residues of these compounds are the respective oxides, i.e. Ln_2O_3, CeO_2 and Pr_6O_{11}, as proven by their X-ray powder diffraction patterns, compared with those associated with the corresponding authentic oxides.

The mass losses, temperature ranges and the peak temperatures observed in each step of the TG-DTA curves are shown in Table 2.

4. Conclusions

From the TG curves and elemental analysis, a general formula could be established for these compounds in the solid state.

The TG-DTA curves and X-ray powder patterns provided previously unreported information concerning the thermal stability and thermal decomposition of these compounds.

Table 2
Mass losses, temperature ranges and peak temperatures observed in each step of the TG-DTA curves

Compound	TG		DTA
	T range (°C)	Mass loss (%)	Peak (°C)
$LaL_3\cdot H_2O$	70–125	2.55	100 (endo)
	170–320	49.10	230, 300 (exo)
	320–440	14.27	410 (exo)
	440–570	6.29	510, 545 (exo)
	570–725	5.14	660 (exo), 710 (endo)
$CeL_3\cdot H_2O$	70–125	2.30	100 (endo)
	145–375	73.70	280 (exo)
$PrL_3\cdot H_2O$	70–125	2.54	100 (exo)
	170–260	18.83	250 (exo)
	260–380	19.40	330 (exo)
	380–455	31.95	420 (exo)
	455–600	3.98	–
$NdL_3\cdot H_2O$	70–125	2.50	100 (endo)
	170–260	18.19	250 (exo)
	260–400	44.75	360 (exo)
	400–480	5.20	440 (exo)
	480–600	4.90	575 (exo)
	600–670	1.44	–
$SmL_3\cdot H_2O$	70–125	2.51	100 (endo)
	155–325	27.14	270 (exo)
	325–405	36.38	380 (exo)
	405–570	8.66	530 (exo)
	570–670	1.73	635 (exo)
$EuL_3\cdot 1.5H_2O$	55–140	3.73	100 (endo)
	155–330	55.90	285, 310 (exo)
	330–445	9.67	400 (exo)
	445–700	7.29	–

L, 4-methylbenzylidenepyruvate.

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