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SOLID-STATE COMPOUNDS OF 4-CHLOROBENZYLIDENEPYRUVATE WITH LANTHANIDES

Preparation and thermal studies

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Abstract

Solid-state compounds Ln-4Cl-BP, where *Ln* represents lighter trivalent lanthanides and 4Cl-BP is 4-chlorobenzylidenepyruvate, were prepared. Thermogravimetry, derivative thermogravimetry (TG and DTG), differential scanning calorimetry (DSC) and other methods of analysis were used to characterize and to study the thermal behaviour of these compounds.

Keywords: 4-chlorobenzylidenepyruvate, lighter trivalent lanthanides, thermal behaviour

Introduction

Various metal ion complexes of benzylidenepyruvate, C_6H_5–CH=CH–$COCOO^-$ (BP), and of five phenyl-substituted derivatives of BP, i.e. 4-dimethylamino- (DMBP), 2-chloro-4-dimethylamino- (2Cl-DMBP), 4-methoxy- (4MeO-BP), 2-chloro- (2Cl-BP) and 4-chlorobenzylidenepyruvate (4Cl-BP), were earlier investigated in aqueous solution [1–4].

In connection with the solution studies, solid-state compounds of DMBP and 4-MeO-BP with several metal ions have also been prepared and investigated by means of TG, DTG, DTA, DSC. X-ray powder diffractometry and other methods of analysis [5–9]. Establishment of the stoichiometry and the details of the thermal decomposition was the main objective of those studies. In an endeavour to extend the previous work, the present paper deals with solid-state compounds of 4Cl-BP (Cl–C_6H_4–CH=CH–$COCOO^-$) with lighter trivalent lanthanides, studied via thermoanalytical techniques and other methods of analysis. The results on these compounds are mainly discussed in connection with those found in the previously reported studies.

Experimental

The sodium salt of 4Cl-BP was prepared as described in the literature [10]. Lighter lanthanides chlorides were prepared as described in [11]. The solid-state compounds of

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Table 1 Analytical data on the compounds $ML_3 \cdot nH_2O$

Compounds	Lanthanides/%			ΔL/%		Water/%		Carbon/%		Hydrogen/%	
	Theor.	TG	EDTA	Theor.	TG	Theor.	TG	Theor.	E.A	Theor.	E.A
$LaL_3 \cdot 1.8H_2O$	17.36	19.08	18.60	72.17	69.63	4.05	4.04	45.03	43.30	2.72	2.49
$CeL_3 \cdot 1.5H_2O$	17.60	18.15	17.50	74.94	74.26	3.40	3.44	45.26	43.83	2.66	2.44
$PrL_3 \cdot 2.0H_2O$	17.49	17.29	17.97	71.74	72.05	4.47	4.36	44.71	44.58	2.75	2.48
$NdL_3 \cdot 1.9H_2O$	17.87	17.50	17.99	71.64	72.19	4.24	4.18	44.63	44.49	2.72	2.50
$SmL_3 \cdot 2.0H_2O$	18.44	18.74	18.77	70.57	70.10	4.42	4.75	44.19	43.32	2.72	2.50

L – 4-chlorobenzylidenepyruvate and ΔL means ligand loss these lighter trivalent lanthanides with 4Cl-BP were prepared by reaction of an aqueous solution of the ligand with an aqueous solution of the corresponding lanthanide chloride. The precipitates obtained were washed until elimination of chloride ions, filtered and dried in Whatman no. 42 filter papers, and stored in a desiccator over anhydrous calcium chloride.

After ignition of the compounds, the metal ion contents were determined by complexometric titration with standard EDTA solution, xylenol orange being used as indicator [12], and from the TG curves. The water and the ligand contents were determined from the TG curves.

The TG, DTG and DSC curves were obtained with a Mettler TA-4000 thermal analysis system, with an air flow of about 150 ml min^{-1}, a heating rate of 10°C min^{-1} and samples of about 7 mg. An alumina crucible was used for the TG and DTG curves, and an aluminium crucible with a perforated cover for the DSC curves.

Diffraction patterns were obtained with Siemens D-500 X-ray diffractometer equipment, using CuK$_\alpha$ radiation (λ=1.541 Å) and settings of 40 kV and 30 mA.

Carbon and hydrogen contents were determined by microanalytical procedures on a Perkin Elmer Elemental Analyzer.

Results and discussion

Table 1 presents the analytical and thermoanalytical (TG) results on the prepared compounds, from which the general formula $Ln(4Cl\text{-}BP)_3{\cdot}nH_2O$ can be established, where *Ln*=La, Ce, Pr, Nd or Sm, 4Cl-BP=4-chlorobenzylidenepyruvate, and *n*=1.5–2.0.

The X-ray powder diffraction patterns of these compounds indicate amorphous structures.

The TG and DTG curves are presented in Fig. 1. Although the TG curves reveal mass losses in three steps between 30 and 550°C, the DTG curves suggest four steps, and with the same thermal decomposition mechanism, except for the cerium compound. In all the curves, the first mass loss observed up to 120°C is due to loss of the hydration water; after the dehydration, the TG curves indicate mass losses in two consecutive steps.

For the anhydrous La, Pr, Nd and Sm compounds (Fig. 1a, c–e), the step observed between 180 and 400°C corresponds respectively to a mass loss of 43.96, 43.46, 43.58 and 42.64%. The final thermal decomposition that occurs up to 550°C corresponds to a mass loss of 25.57, 27.99, 27.97 and 27.13%, and gives rise to a mixture of lanthanide oxide and oxychloride in no simple stoichiometric relation. The formation of the mixture, as suggested by calculations based on the mass losses observed in the TG curves, was confirmed by the X-ray powder diffraction patterns, and the presence of chloride ion in the final residue of the thermal decomposition was also confirmed by qualitative tests. The disagreement between the theoretical and TG data relating to the ligand loss (Table 1) is due to the mixture of the oxide and oxychloride being formed as final residue of the thermal decomposition; the theoretical calculation was based on lanthanide oxychloride as final residue.

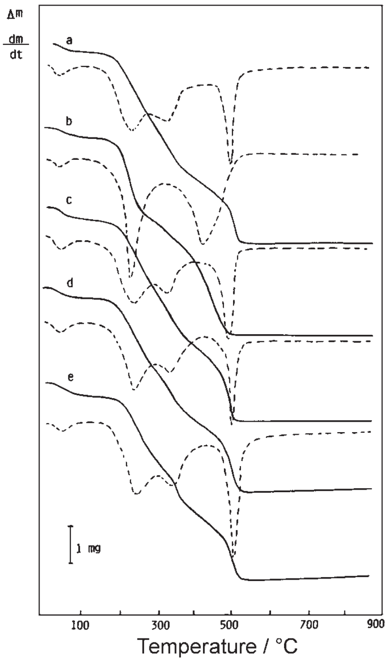

Fig. 1 TG and DTG curves of the compounds: a – $La(4Cl\text{-}BP)_3{\cdot}1.8H_2O$ (7.3160 mg); b – $Ce(4Cl\text{-}BP)_3{\cdot}1.5H_2O$ (7.2110 mg); c – $Pr(4Cl\text{-}BP)_3{\cdot}2H_2O$ (7.4800 mg); d – $Nd(4Cl\text{-}BP)_3{\cdot}1.9H_2O$ (7.2790 mg); e – $Sm(4Cl\text{-}BP)_3{\cdot}2H_2O$ (7.2250) mg

The formation of oxy- or dioxycarbonate, $Ln_2O_2CO_3$, as intermediate, as reported in the thermal decompositions of lanthanide compounds with DMBP and 4MeO-BP [5, 6], was not observed during the thermal decompositions of the compounds studied in this work. The formation of oxychloride as residue, without any indication of the formation of intermediate, oxy- or dioxycarbonate, is undoubtedly related to the influence of the chloro group in this substituted derivative of BP.

For the anhydrous cerium compound (Fig. 1b), the mass loss also occurs in two steps, between 180 and 550°C. The first step, observed up to 350°C, corresponds to a mass loss of 35.63, and the last step to the loss of 37.79%, with the formation of cerium oxide, CeO_2, as residue, in agreement with earlier data [5, 6]. The absence of chloride ion from the final residue was confirmed by qualitative tests. The formation of CeO_2 as final residue is due to the oxidation of Ce(III) to Ce(IV) that occurs during the thermal decomposition of the compound in air atmosphere, where this latter oxide is the more stable form. The oxidation of Ce(III) probably rules out the formation of the mixture of oxide and oxychloride as final residue, as observed for the other compounds.

The fact that the final temperature of thermal decomposition of the cerium compound is practically the same as for the other compounds is in contrast with the situation for the other lanthanide compounds previously studied, where the final thermal decomposition of the cerium compounds occurred at lower temperature (about

100°C) [5, 6, 13–15]. This behaviour suggests the influence of the chloro group of the ligand during the thermal decompositions of these compounds.

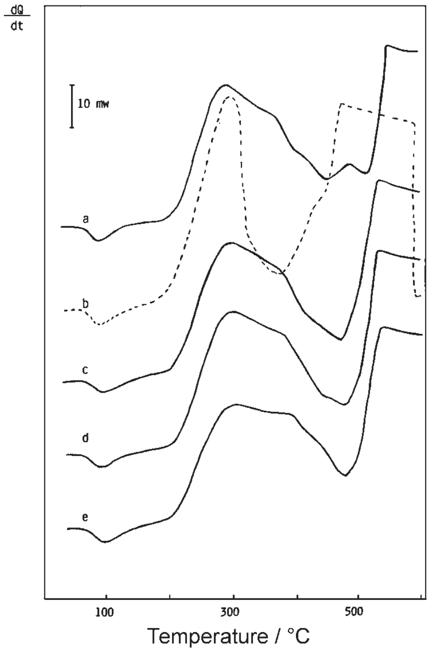

Fig. 2 DSC curves of the compounds: a – La(4Cl-BP)$_3$·1.8H$_2$O (7.150 mg); b – Ce(4Cl-BP)$_3$·1.5H$_2$O (7.628 mg); c – Pr(4Cl-BP)$_3$·2H$_2$O (7.268 mg); d – Nd(4Cl-BP)$_3$·1.9H$_2$O (7.568 mg); e – Sm(4Cl-BP)$_3$·2H$_2$O (7.555) mg

The DSC curves are depicted in Fig. 2. These curves exhibit endothermic and exothermic peaks that all accord with the mass losses observed in the TG curves. The broad endotherms that occur for all the compounds between 50 and 150°C, with peaks at 100°C, are due to the loss of hydration water. The dehydration enthalpies found for these compounds were 60.4, 42.6, 54.1, 57.1 and 60.8 kJ mol^{-1}, respectively. The broad exotherms observed for all the compounds, with two or three peaks between 200 and 600°C, are attributed to the thermal decompositions of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive stages; this is in agreement with the TG and DTG curves.

Conclusions

The X-ray powder patterns verified that the compounds display amorphous structures.

The TG, DTG and DSC curves allowed establishment of the stoichiometries of these compounds in the solid-state and also provided information about the thermal stabilities and thermal decompositions.

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