

## **THERMAL STUDIES OF SOLID 4-CHLOROBENZYLIDENEPYRUVATES OF HEAVY LANTHANIDES(III) AND YTTRIUM(III)**

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### **Abstract**

Solid-state compounds of general formula  $\text{LnL}_3 \cdot 2\text{H}_2\text{O}$ , where Ln is heavier trivalent lanthanides and yttrium, L is 4-chlorobenzylidenepyruvate have been synthesised.

On heating these compounds decompose in steps. They lose the hydration water in the first step and the thermal decomposition of the anhydrous compounds occurs with the formation of oxochloride (Eu, Gd); mixture of oxide and oxochloride that decrease with increasing of atomic number of metal (Tb–Tm); or oxide (Yb, Lu, Y) as final residue, up to 900°C. The dehydration enthalpies found for terbium, holmium, ytterbium and yttrium compounds were: 34.93, 42.40, 57.39 and 62.24 kJ mol<sup>-1</sup>, respectively.

**Keywords:** 4-chlorobenzylidenepyruvate, heavier lanthanide, thermal decomposition

### **Introduction**

Preparation and investigation of several metal-ion complexes of benzylidenepyruvate,  $\text{C}_6\text{H}_5\text{--CH=CH--COCOO}^-$  (BP), as well as those associated with five phenyl-substituted derivatives of BP, i.e., 4-dimethylamino (DMBP), 2-chloro-4-dimethylamino (2-Cl-DMBP), 4-methoxy (4-MeO-BP), 2-chloro (2-Cl-BP) and 4-chloro (4-MeO-BP), 2-chloro (2-Cl-BP) and 4-chloro (4-Cl-BP), have been investigated in aqueous solutions [1–4]. These papers report the thermodynamic stability ( $\beta_1$ ) and spectroscopic parameters ( $\epsilon_{1\text{max}}$ ,  $\lambda_{\text{max}}$ ) of the 1:1 species.

In the solid-state, several metal-ion complexes with DMBP, 4-MeO-BP and 4-Cl-BP, have also been investigated using thermoanalytical techniques, X-ray powder diffractometry and other methods of analysis [5–14]. The establishment of the stoichiometry of these compounds, as well as, their thermal behavior have been the main objective of these studies. As an extension of the works of [5–14], the sodium salt of 4-chlorobenzylidenepyruvic acid,  $(\text{Cl--C}_6\text{H}_4\text{--CH=CH--COCOONa})$ , as well as, compounds of this ligand with heavier trivalent lanthanides and yttrium have been

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prepared. The compounds were investigated by using complexometric analysis, TG, DTG, DSC, X-ray powder diffractometry, elemental analysis and energy dispersive X-ray microanalysis (EDX). The results associated with these compounds are discussed in connection with those found for previously reported studies.

## Experimental

The sodium salt of 4-chlorobenzylidenepyruvic acid (4-Cl-BP) was prepared following the same procedure described in the literature [15].

Solid-state compounds of heavier trivalent lanthanides and yttrium with 4-Cl-BP were prepared by mixing solutions of the corresponding lanthanide and yttrium chlorides with aqueous solution of the ligand, until total precipitation of the metal ions. The precipitates were washed until elimination of chloride ions, filtered and dried in Whatman n° 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In the solid-state compounds, water and 4-Cl-BP contents were determined from TG curves, and the metal-ions were determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [16], after samples of the compounds have been ignited to the metal oxide and dissolved in hydrochloric acid solution, and also from TG curves.

TG, DTG and DSC curves were obtained by using a Mettler TA-4000 thermal analysis system, with air flowing at  $150 \text{ mL min}^{-1}$  and a heating rate of  $10^\circ\text{C min}^{-1}$  and with samples weighing about 7 mg. An alumina crucible was used to obtain the TG, DTG curves and an aluminium crucible with perforated cover was used to obtain the DSC curves.

Carbon and hydrogen contents were determined by microanalytical procedures using an Elemental Analyser EA 1110 CHNS-O, CE Instruments.

IR spectra of the ligand and of the prepared compounds were recorded on a Spectrophotometer Nicolet, Impact 400-FT, in the range  $4000\text{--}400 \text{ cm}^{-1}$ . The samples were prepared as KBr discs.

X-ray powder patterns were obtained using a Siemens D-500 X-ray diffractometer equipment using  $\text{CuK}_\alpha$  radiation ( $\lambda=1.5441 \text{ \AA}$ ) and a setting of 40 kV and 20 mA. The thermogravimetry residues were characterized by an energy dispersive X-ray microanalysis (EDX) system (Noran).

## Results and discussion

Table 1 presents the analytical, thermoanalytical (TG) and elemental analysis data for the prepared compounds from which the general formula  $\text{LnL}_3 \cdot 2\text{H}_2\text{O}$  can be established, where  $\text{Ln}$  represents heavier trivalent lanthanides and yttrium and  $L$  is 4-chlorobenzylidenepyruvate.

X-ray powder patterns showed that all compounds are amorphous. The amorphous structure is undoubtedly related to the low solubility of these compounds, as al-

**Table 1** Analytical, thermoanalytical (TG) and elemental analysis data of the compounds, Ln(L<sub>3</sub>)·2H<sub>2</sub>O

Compound	Metal/%			<i>L</i> loss/%		Water/%		Carbon/%		Hydrogen/%		Residue
	Theor.	EDTA	TG	Theor.	TG	Theor.	TG	Theor.	E.A.	Theor.	E.A.	
EuL <sub>3</sub> ·2H <sub>2</sub> O	18.60	18.77	18.74	70.68	71.80	4.41	4.32	44.00	43.63	2.71	2.66	EuOCl
GdL <sub>3</sub> ·2H <sub>2</sub> O	19.13	19.53	18.46	70.23	70.66	4.38	4.84	43.72	43.32	2.70	2.69	GdOCl
TbL <sub>3</sub> ·2H <sub>2</sub> O	19.29	19.31	18.70	72.93	73.57	4.37	4.44	43.63	43.92	2.69	2.57	Tb <sub>4</sub> O <sub>7</sub> *
DyL <sub>3</sub> ·2H <sub>2</sub> O	19.64	19.50	19.92	73.10	72.72	4.36	4.41	43.44	43.42	2.68	2.59	Dy <sub>2</sub> O <sub>3</sub> *
HoL <sub>3</sub> ·2H <sub>2</sub> O	19.88	19.84	21.05	72.89	71.59	4.34	4.34	43.31	43.51	2.67	2.69	Ho <sub>2</sub> O <sub>3</sub> *
ErL <sub>3</sub> ·2H <sub>2</sub> O	20.10	19.96	19.92	72.68	72.87	4.33	4.35	43.30	43.16	2.65	2.56	Er <sub>2</sub> O <sub>3</sub> *
TmL <sub>3</sub> ·2H <sub>2</sub> O	20.26	19.72	19.92	72.54	72.79	4.32	4.46	43.21	42.61	2.66	2.59	Tm <sub>2</sub> O <sub>3</sub> *
YbL <sub>3</sub> ·2H <sub>2</sub> O	20.65	20.65	20.82	72.18	71.97	4.30	4.33	43.00	42.93	2.65	2.60	Yb <sub>2</sub> O <sub>3</sub>
LuL <sub>3</sub> ·2H <sub>2</sub> O	20.79	20.73	20.55	72.06	72.31	4.29	4.36	42.93	42.22	2.65	2.61	Lu <sub>2</sub> O <sub>3</sub>
YL <sub>3</sub> ·2H <sub>2</sub> O	11.79	11.44	11.89	80.24	80.01	4.78	4.88	47.80	46.23	2.95	2.87	Y <sub>2</sub> O <sub>3</sub>

Key: *L* means 4-chlorobenzylidenepyruvate;

\* mixture of oxide and a small quantity of oxochloride

ready observed for lanthanides and yttrium compounds with DMBP and for the heavier lanthanides and yttrium with 4-MeO-BP [5, 6].

Table 2 presents the symmetric and asymmetric stretching frequencies of the carboxylate group and the stretching frequency of ketonic carbonyl group.

The infrared spectrum of the ligand shows a relative intensity band at  $1403\text{ cm}^{-1}$  and a strong band at about  $1622\text{ cm}^{-1}$  attributed to the symmetric and asymmetric stretching frequencies of the carboxylate group, respectively. The strong band at  $1675\text{ cm}^{-1}$  is attributed to the stretching frequency of the ketonic carbonyl group.

For the prepared compounds, the infrared spectra show a broad band in the range of  $3200$  and  $3500\text{ cm}^{-1}$  attributed to hydration water. The symmetric and asymmetric stretching frequencies of the carboxylate group are observed between  $1403$ – $1406$  and  $1593$ – $1601\text{ cm}^{-1}$ , respectively and the stretching frequency of the ketonic carbonyl, between  $1642$ – $1655\text{ cm}^{-1}$ . These data show that the bands due to the asymmetric stretching frequency of the carboxylate and the stretching frequency of the ketonic carbonyl groups are moved to the lower frequencies in comparison with the ligand frequencies, suggesting that the metal-ions are coordinate by carboxylate and ketonic carbonyl groups.

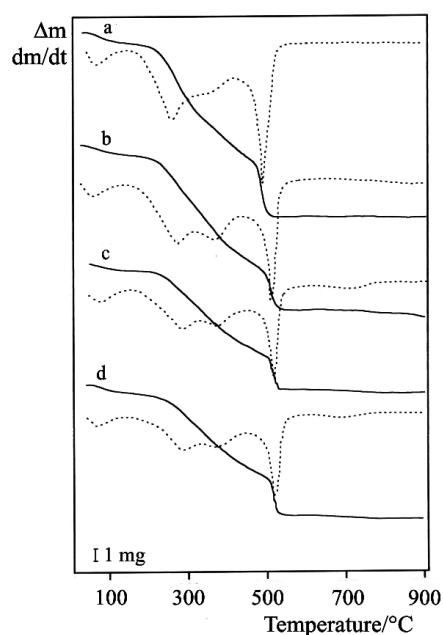
TG and DTG curves of the europium, dysprosium, thulium and lutetium compounds, as representative of the studied compounds, are shown in Fig. 1. These curves show mass losses in steps, and between  $30$  and  $560^\circ\text{C}$  a great similarity of these curves suggest that the thermal decompositions occur in the same way.

The mass loss due to the dehydration, that begins at  $30^\circ\text{C}$ , the beginning undoubtedly is provoked by air flux used ( $150\text{ mL min}^{-1}$ ) as already observed in the dehydration of other compounds [5, 7, 11]. This behavior seems to be characteristic of amorphous compounds. The dehydration of these compounds occurs in one step up to  $130^\circ\text{C}$  with loss of  $2\text{H}_2\text{O}$ .

**Table 2** IR spectra / $\text{cm}^{-1}$

Compounds	OH( $\text{H}_2\text{O}$ )	$\nu_{\text{asym. COO}^-}$	$\nu_{\text{asym. COO}^-}$	CO=O
Na-4ClBP	3459 br	1403 m	1622 s	1675 s
Eu(4-ClBP) $_3$ ·2H $_2$ O	3384 br	1406 m	1599 s	1652 s
Gd(4-ClBP) $_3$ ·2H $_2$ O	3367 br	1406 m	1594 s	1644 s
Tb(4-ClBP) $_3$ ·2H $_2$ O	3385 br	1405 m	1599 s	1642 s
Dy(4-ClBP) $_3$ ·2H $_2$ O	3370 br	1406 m	1593 s	1655 s
Ho(4-ClBP) $_3$ ·2H $_2$ O	3398 br	1405 m	1596 s	1654 s
Er(4-ClBP) $_3$ ·2H $_2$ O	3413 br	1406 m	1595 s	1643 s
Tm(4-ClBP) $_3$ ·2H $_2$ O	3364 br	1406 m	1593 s	1652 s
Yb(4-ClBP) $_3$ ·2H $_2$ O	3315 br	1406 m	1598 s	1652 s
Lu(4-ClBP) $_3$ ·2H $_2$ O	3365 br	1403 m	1597 s	1649 s
Y(4-ClBP) $_3$ ·2H $_2$ O	3378 br	1405 m	1601 s	1650 s

br – broad; m – medium; s – strong



**Fig. 1** TG and DTG curves of dihydrated compounds of 4-chlorobenzylidene-pyruvate with: a – Eu (7.470 mg); b – Dy (7.486 mg); c – Tm (6.989 mg) and d – Lu (7.182 mg)

The thermal decomposition of the anhydrous compounds occurs above 150°C. Although the DTG curves show mass losses in three consecutive or simultaneous steps, the TG curves suggest two consecutive steps up to 560°C, which begins with a slow process followed by a fast process. The mass losses observed in each step of the TG curves, between 150–500 and 500–560°C correspond to: 41.80 and 30.00% (Eu); 43.76 and 26.90% (Gd); 43.68 and 29.89% (Tb); 43.56 and 29.16% (Dy); 43.79 and 27.80% (Ho); 43.30 and 29.57% (Er); 42.75 and 30.04% (Tm); 42.37 and 29.60% (Yb); 42.40 and 29.91% (Lu); 47.00 and 30.01% (Y). These results and a close similarity concerning the TG and DTG profiles, suggests that the thermal decomposition mechanism seem to be the same. Above 560°C no mass loss is observed in the TG and DTG curves of europium and gadolinium compounds, however for the other compounds, a small mass loss is observed above 600°C.

Calculations based on the mass losses observed in the TG curves up to 900°C, suggest the formation of oxychloride as residue for the europium and gadolinium compounds (EuOCl, GdOCl), and the respective oxide for the other compounds (Tb<sub>4</sub>O<sub>7</sub>, Ln<sub>2</sub>O<sub>3</sub>). Tests with AgNO<sub>3</sub> solution on sample heated up to 900°C, after dissolution in nitric acid solution, confirmed the presence of chloride ions only for europium and gadolinium compounds. However the presence of chloride ions in the thermal decomposition residue, except for ytterbium lutetium and yttrium compounds, was verified by EDX (Energy Dispersive X-ray Microanalysis), Fig. 2. The EDX data

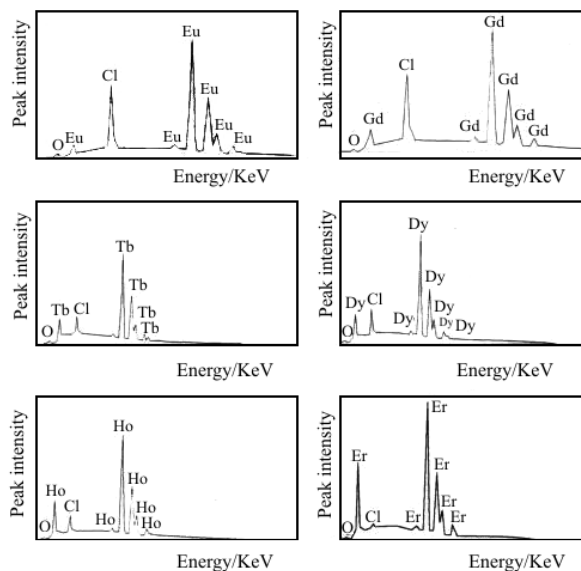


Fig. 2 EDX data of the thermal decomposition residues up to 900°C

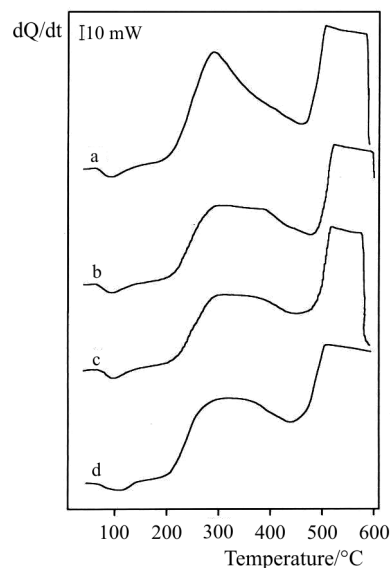
also show that the presence of chloride ions decrease with the increase of the atomic number of the lanthanides.

Tests with nitric acid solution on sample heated up to 560°C, did not indicate the formation of intermediate, oxy- or dioxycarbonate as observed in the thermal decomposition of lanthanides and yttrium compounds with DMBP and 4-MeO-BP [5, 6]. The non formation of these intermediates undoubtedly is due to the influence of the chloro- as phenyl-substituted derivative of BP during the thermal decomposition.

Thus, based on the EDX data, the last step observed above 600°C in the TG and DTG curves of terbium, dysprosium and holmium compounds, where the mass losses are still being observed up to 900°C and the last step observed between 600 and 900°C for erbium and thulium compounds are attributed to elimination of chloride ions with formation of the respective oxide ( $Tb_4O_7$ ,  $Ln_2O_3$ ) accompanied yet by a small quantity of chloride ions. The presence of the chloride ions verified by EDX, and no identified by qualitative tests, did not prejudiced the establishment of the stoichiometry of these compounds by using the TG data.

For the ytterbium, lutetium and yttrium compounds, the last step between 600 and 900°C observed in the TG and DTG curves, is due to elimination of chloride ions with formation of the respective oxide ( $Ln_2O_3$ ).

The DSC curves of the europium, dysprosium, thulium and lutetium compounds, as representative of the studied compounds are shown in Fig. 3. These curves show endothermic and exothermic peaks that all accord with the mass losses observed in the TG curves. The broad endothermic peak in the range 50–130°C, for all compounds is ascribed to the dehydration. The dehydration enthalpies found for terbium, holmium, ytterbium and yttrium compounds were: 34.93; 42.40; 57.39 and 62.25  $\text{kJ mol}^{-1}$ , respectively.



**Fig. 3** DSC curves of dihydrated compounds of 4-chlorobenzylidenepyruvate with:  
a – Eu (7.264 mg); b – Dy (7.308 mg); c – Tm (7.206 mg) and d – Lu (7.589 mg)

The exotherms observed for all compounds with evidence of two or three peaks between 200 and 600°C, are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive steps; this is in agreement with the DTG curves.

## Conclusions

The X-ray powder patterns verified that the heavier lanthanides compounds with 4-Cl-BP have an amorphous structure.

The TG and DTG curves permitted to establish the stoichiometry of these compounds in the solid-state and also provided information about the thermal stability and thermal decomposition.

EDX data showed the presence of chloride ion in the final residue up to 900°C, except for ytterbium, lutetium and yttrium compounds.

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