

## **THERMAL DECOMPOSITION OF HYDRATED LANTHANIDE PICRATES BY TG/DTG AND DSC ANALYSES**

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### **Abstract**

Hydrated lanthanide picrates with a composition of:  $\text{Ln}(\text{pic})_3 \cdot x\text{H}_2\text{O}$  ( $\text{Ln}=\text{La-Lu, Y}$ ) were synthesized and characterized. Thermal decomposition of the picrates by TG/DTG and DSC techniques are reported.

**Keywords:** DSC, lanthanide, picrates, TG/DTG

### **Introduction**

There is a great deal of interest in the coordination chemistry of lanthanide complexes as a research area. This research is motivated by a wide range of applications of these compounds as luminescent probes, solid-state lasers, catalytic processes, NMR shift reagents, electroluminescent devices, and other uses [1–3]. Hydrated lanthanide picrates have been used in the synthesis of complexes with different ligands that contain oxygen atoms as coordination sites [4–8]. Their preparation and some properties of lanthanide picrates have already been described [9–13], but their thermal behavior has not been fully explored. In this paper the thermal behavior of hydrated lanthanide picrates is presented using TG/DTG and DSC techniques.

### **Experimental**

Hydrated lanthanide picrates were prepared by the reaction of lanthanide hydroxycarbonates and picric acid in aqueous solution. The preparation of hydrated lanthanide hydroxycarbonates consisted basically of dissolution of the corresponding oxides in diluted hydrochloric acid, followed by heating to boiling and further addition of small amounts of urea to reach a pH of about 7. The precipitates were separated by filtration and washed with distilled water until total elimination of chloride ions. The presence of chloride ions in wash water was verified by testing with  $\text{Ag}^+$  ions.

To an aqueous suspension of lanthanide hydroxycarbonate under heating at 80°C, picric acid was slowly added, under stirring, until almost complete hydroxycarbonate dissolution and keeping pH of the solution in about 5. The unreacted metallic hydroxycarbonate was filtered and the solution was concentrated. After 24 h at room temperature, the yellow crystals formed were washed with distilled water and dried in air.

Lanthanide ions were determined by complexometric titration with EDTA using xylenol-orange as indicator. Analyses of carbon, hydrogen and nitrogen were performed using a Perkin Elmer Model 240 elemental analyzer. IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets. X-ray powder patterns were recorded on a Miniflex-Rigaku Denke instrument, using  $\text{CuK}_\alpha$  radiation.

TG/DTG experiments were performed in a TGA-50 Shimadzu instrument under dynamic air atmosphere ( $50 \text{ mL min}^{-1}$ ). Due to easy explosion of the picrates, that occurs in temperatures above 250°C, it was studied a heating program that allowed such experiments, so resulting in a programming in three heating stages: heating rate of  $20^\circ\text{C min}^{-1}$  up to 250°C,  $2^\circ\text{C min}^{-1}$  up to 450°C and  $20^\circ\text{C min}^{-1}$  up to 900°C. In all essays a Pt crucibles with perforated lid was used.

DSC measurements were performed in a dynamic nitrogen atmosphere ( $50 \text{ mL min}^{-1}$ ) at heating rate of  $10^\circ\text{C min}^{-1}$ , using a cell DSC-50 Shimadzu. For  $\Delta H$  measurements, DSC system was calibrated with indium ( $m.p.=156.6^\circ\text{C}$ ;  $\Delta H_m=28.54 \text{ J g}^{-1}$ ). For TG/DTG and DSC experiments, a small amount of material (1–1.5 mg) was used in this study.

## Results and discussion

Table 1 presents a summary of the analytical results. Experimental and calculated values are in good agreement.

Different numbers of hydration water molecules were obtained as shown in Table 2. The same behavior was observed by some authors. Nakagawa *et al.* [9] found eleven for light lanthanides (La–Gd) and eight for Dy and Yb. Yongchi and Yingqiu [10] found four for the light lanthanides and five for the heavy lanthanides. Zhou *et al.* [11] found four. Harrowfield *et al.* [12] found twelve. Delboni *et al.* [13] found twelve for Ce. These differences suggest that the synthesis route and storage of those salts are factors directly linked to the salt compositions and structures.

The coordination between the picrate ion and lanthanides(III) can happen in three different ways: monodentate through the phenolic oxygen, bidentate through the phenolic and one oxygen of an ortho nitrogroup and through a net of hydrogen bonding. Studies of structures by X-ray single-crystal reveal the coordination of the Ln(III) ions and picrate anions. Yongchi and Yingqiu [10] determined the structures of Yb(III) and Y(III) picrate pentahydrates, showing that they are eight-coordinated to five water molecules and two picrate anions differently, bonded by a phenolic oxygen of the first picrate and a phenolic oxygen and a nitro oxygen from a second picrate and the third picrate is associated by hydrogen bonding. Delboni *et al.* [13] determined two structures of Ce(III) picrate dodecahydrate showing that they are

nine-coordinated to six water molecules and two picrates; the third picrate ion and six additional water molecules complete the crystal packing through a complex network of hydrogen bonds.

**Table 1** Analytical data (%) for the compounds of formula  $\text{Ln(pic)}_3 \cdot x\text{H}_2\text{O}$

<i>Ln</i>	Ln/%		C/%		H/%		N/%	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
La	14.1	14.3	21.9	21.7	2.5	2.6	12.8	12.7
Ce	14.0	13.9	21.5	21.3	2.6	2.6	12.6	12.4
Pr	14.3	14.2	21.9	21.9	2.5	2.4	12.8	12.6
Nd	14.1	14.1	21.1	21.0	2.8	2.7	12.3	12.3
Sm	15.1	15.0	21.7	21.6	2.4	2.4	12.7	12.5
Eu	16.7	16.8	23.8	23.9	1.6	1.5	13.9	14.0
Gd	17.2	17.1	23.7	23.6	1.5	1.6	13.8	13.7
Tb	17.4	17.1	23.6	23.7	1.5	1.6	13.8	13.7
Dy	17.7	17.8	23.5	23.4	1.5	1.6	13.7	13.6
Ho	16.9	17.0	22.2	21.2	2.1	2.2	12.9	12.9
Er	17.1	17.2	22.1	21.2	2.1	2.1	12.9	12.8
Tm	17.3	17.3	22.1	22.0	2.1	2.1	12.9	12.7
Yb	17.6	17.5	22.0	22.8	2.1	2.0	12.8	12.8
Lu	17.4	17.6	21.6	21.7	2.2	2.3	12.6	12.3
Y	9.8	9.9	23.8	23.9	2.3	2.3	13.9	13.9

According to IR spectra, the bands  $\nu_{\text{as}}\text{NO}_2$ ,  $\nu_{\text{s}}\text{NO}_2$  and  $\nu\text{CO}$  in picric acid were shifted to higher frequencies in the picrates, suggesting coordination through the phenolic and one oxygen of an ortho nitrogroup [10, 14–16]. OH stretching around  $3400\text{ cm}^{-1}$  indicates the presence of coordinated water molecules. The spectra of all lanthanide picrates are similar, suggesting that all compounds belong to the same spectral serie.

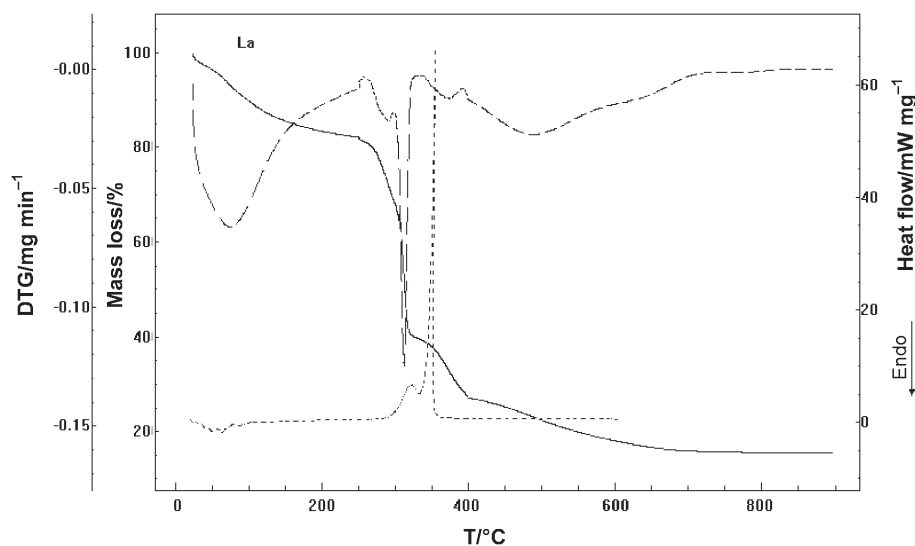
X-ray diffraction powder patterns show only two isomorphous series; one composed by Eu(III), Gd(III), Tb(III) and Dy(III) picrates and another by Er(III), Tm(III) and Yb(III) picrates. For the other picrates, no isomorphism was found.

Figures 1 to 4 show TG/DTG and DSC curves for some representative picrates, those of La(III), Eu(III), and Tm(III).

When analyzing TG/DTG and DSC curves, different behaviors in the thermal decomposition of the picrates and three similar groups were detected: (A) La–Sm; (B) Eu–Dy and (C) Ho–Lu and Y. Table 2 reports percentages of mass losses in TG curves and the peaks of those events in DTG curves.

**Table 2** Percentage of mass loss in TG curves and the temperature peaks in DTG curves of the  $\text{Ln}(\text{pic})_3 \cdot x\text{H}_2\text{O}$ 

<i>Ln</i>	$x\text{H}_2\text{O}$	1 <sup>st</sup> step			2 <sup>nd</sup> step		3 <sup>rd</sup> step			
		$\text{H}_2\text{O}/\%$		$T/^\circ\text{C}$	%	$T/^\circ\text{C}$	%	$T/^\circ\text{C}$	$\text{Ln}_2\text{O}_3/\%$	
		calc.	exp.						calc.	exp.
La	9	16.5	15.5	57	43.1	316	22.6	456	16.5	15.8
Ce*	10	17.9	17.6	58	62.8	296	–	–	17.1	19.3
Pr*	9	16.4	16.6	47	43.3	316	22.0	468	17.2	18.1
Nd	11	19.3	18.8	48	40.1	319	21.2	450	16.4	19.9
Sm	9	16.3	16.9	51	42.4	317	21.2	456	17.5	19.5
Eu	4	7.9	7.7	129	47.0	320	24.8	476	19.4	20.6
Gd	4	7.9	8.5	136	47.7	323	23.0	452	19.8	20.7
Tb*	4	7.9	7.8	137	47.8	325	23.8	455	20.4	20.5
Dy	4	7.8	7.9	136	47.6	318	23.4	459	20.3	21.2
Ho	7	12.9	13.2	72	45.5	325	20.8	454	19.4	20.4
Er	7	12.9	12.8	71	46.1	337	19.0	460	19.6	22.0
Tm	7	12.9	13.2	81	47.9	353	19.1	472	19.7	19.7
Yb	7	12.8	14.8	74	46.5	335	18.9	461	20.0	19.8
Lu	8	14.4	14.3	77	47.4	356	15.3	482	19.8	23.0
Y	7.5	14.9	14.9	72	49.2	326	23.1	457	12.4	12.8

\*CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub> and Tb<sub>4</sub>O<sub>7</sub>**Fig. 1** TG/DTG and DSC curves of  $\text{La}(\text{pic})_3 \cdot 9\text{H}_2\text{O}$  (solid line: TG; dashed line: DTG; dotted line: DSC)

The first event corresponds to the loss of hydration water, beginning at room temperature in A and C groups. Group B has a different behavior, since the compounds are thermally stable until about 100°C, when the water loss occurs. It is also

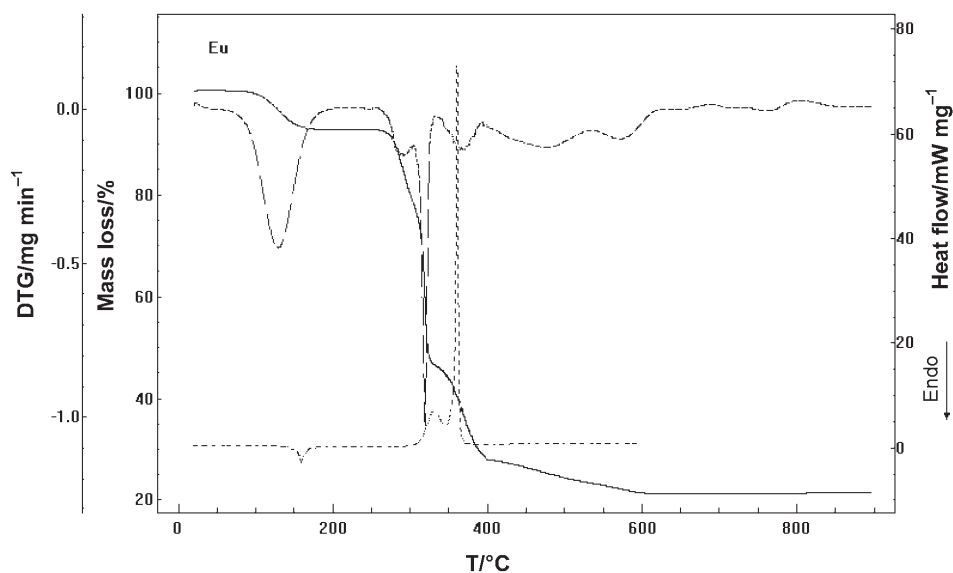


Fig. 2 TG/DTG and DSC curves of Eu(pic)<sub>3</sub>·4 H<sub>2</sub>O (solid line: TG; dashed line: DTG; dotted line: DSC)

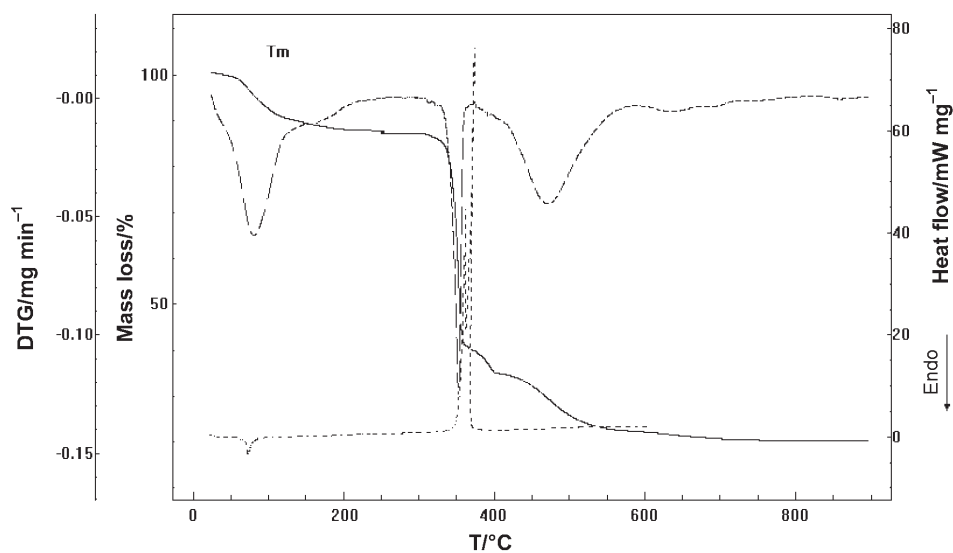


Fig. 3 TG/DTG and DSC curves of Tm(pic)<sub>3</sub>·7 H<sub>2</sub>O (solid line: TG; dashed line: DTG; dotted line: DSC)

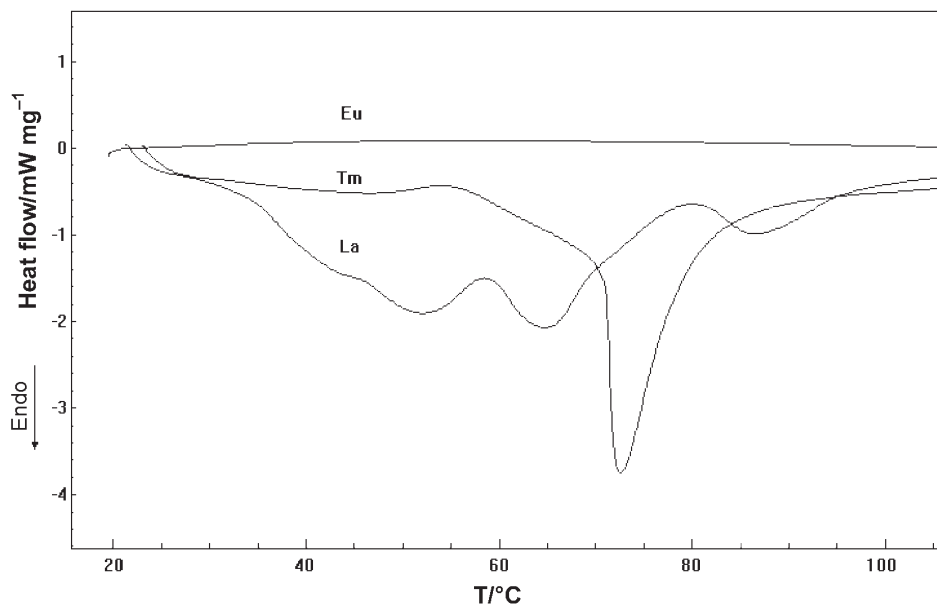


Fig. 4 Part of DSC curves of La, Eu and Tm picrates

verified that in group A the mass loss is continuous up to about 250°C, while in the groups B and C, where mass loss ends at lower temperatures, it was observed a more defined plateau after dehydration, which practically was not verified in the group A.

Second and third events correspond to thermal decomposition of the picrates. The separation of those events is not very defined. In the second event the mass loss is accentuated and it happens in a lower temperature range, causing the corresponding peak in the DTG curve to be quite sharp and intense. Thermal decomposition begins at approximately 250°C for almost all picrates, except for Tm, Yb, and Lu, for which it begins at about 300°C.

The third event happens in a larger range of temperatures and the corresponding peak in DTG curve is wide and not so defined. Thermal decomposition ends at about 600°C with formation of the respective oxide. In the case of Ce(III) picrate, the process is different from the others, occurring in only one stage and forming the oxide at a lower temperature (350°C). The formation of Pr and Tb oxides also occurs at lower temperatures: 525 and 540°C, respectively; the formation of La, Tm and Lu oxides occurs at higher temperatures, 700, 735 and 760°C respectively.

Table 1 also relates the calculated and experimental percentages of hydration water and the respective oxides. Different numbers of hydration water molecules are verified, and such fact confirms the results of elemental analyses. Some picrates show residual mass higher than the calculated, indicating the presence of non-burnt carbon.

DSC curves are in agreement with TG/DTG curves and indicate that the decomposition of the picrates occurs in two simultaneous highly exothermic events with corresponding intense and sharp peaks. The thermal decomposition begins above

250–300°C and ends below 380°C. Regular increase in the thermal decomposition temperatures with the decrease of the ionic radii of the lanthanides(III) ions were not observed, while the involved energy, in general, is found to decrease. Observation of endothermic peaks due to dehydration is masked due to the high intensity of the exothermic peaks. Figure 4 shows part of the DSC curves, up to 100°C, where it is possible to see the difference in dehydration for La, Eu and Tm(III) picrates.

The temperature and dehydration energy calculated for picrates are shown in Table 3. DSC curves of La, Ce, Pr, Nd, and Sm compounds showed 2 to 3 peaks, and other compounds only one peak. For the compounds of the second group, it is observed a higher temperature of the peak compared to other compounds. The dehydration energies are higher for La–Sm picrates. The different temperature and energy of dehydration indicate that there are different kinds of hydration water; one weakly bonded, non-coordinated to lanthanide ion and, another stronger coordinated to the central ion.

**Table 3** Temperature of the peaks and energy at DSC curves of the  $\text{Ln}(\text{pic})_3 \cdot x\text{H}_2\text{O}$

<i>Ln</i>	Dehydration				Decomposition		
	<i>T</i> /°C	<i>T</i> /°C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	<i>T</i> /°C	<i>T</i> /°C	$\Delta H/\text{kJ mol}^{-1}$
La	52	87	261	23	323	356	–2936
Ce	47	95	299	89	297	331	–3265
Pr	53	97	270	134	318	354	–3357
Nd	50	99	329	103	314	354	–3080
Sm	53	138	267	123	317	355	–3000
Eu	159	–	172	–	331	361	–2670
Gd	135	–	182	–	321	359	–3115
Tb	135	–	211	–	319	360	–3139
Dy	137	–	170	–	316	360	–3041
Ho	72	–	168	–	316	361	–2874
Er	72	–	158	–	354	368	–2689
Tm	73	–	140	–	363	375	–2918
Yb	75	–	119	–	360	372	–2183
Lu	72	–	218	–	364	378	–2749
Y	72	–	149	–	318	363	–2798

## Conclusions

The results showed that the thermal decomposition of hydrated lanthanide picrates occurs in three similar groups, allowing the study of the thermal stability and the determination of the different number of hydration water molecules, contributing to the

knowledge of thermal behavior of this complexes. These compounds are explosives and their thermal decomposition occurs in highly exothermic events.

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## References

- 1 J.-C. G. Bünzli, in *Lanthanides Probes in Life, Chemical and Earth Sciences Theory and Practice*, (J.-C. G. Bünzli and G. R. Choppin Eds) Elsevier, New York 1989.
- 2 M. Leskelä and L. Niinistö, *Mat. Chem. Phys.*, 31 (1992) 7.
- 3 A. Abrão in *Química e Tecnologia das Terras Raras*, CETEM/CNPq, Rio de Janeiro, Brazil 1994.
- 4 P. Miranda Jr., C. C. Carvalho, J. Zukerman-Schpector, P. C. Isolani, G. Vicentini and L. B. Zinner, *J. Alloys Comp.*, 303–304 (2000) 162.
- 5 G. Vicentini, L. B. Zinner and K. Zinner, *Koord. Khim.*, 17 (1991) 422.
- 6 J. R. Matos, L. B. Zinner and G. Vicentini, *Thermochim. Acta*, 214 (1993) 361.
- 7 J. D. Ayala, L. B. Zinner, G. Vicentini, A. Del Pra and G. Bombieri, *Inorg. Chim. Acta*, 211 (1993) 161.
- 8 L. B. Zinner, J. R. Matos, M. A. Andrade da Silva and J. E. X. Matos, *Thermochim. Acta*, 242 (1994) 253.
- 9 K. Nakagawa, K. Amita, H. Mizuno, Y. Inoue and T. Hakushi, *Bull. Chem. Soc. Jpn.*, 60 (1987) 2037.
- 10 T. Yongchi, L. Yingqui and N. Jiazan, *J. Mol. Sci. (China)*, 5 (1987) 83.
- 11 Z.-X. Zhou, W.-C. Zheng and Y.-Z. Li, *Polyhedron*, 15 (1996) 3525.
- 12 J. M. Harrowfield, W. M. Lu, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 47 (1994) 321.
- 13 L. F. Delboni, G. Oliva, E. E. Castellano, L. B. Zinner and S. Braun, *Inorg. Chim. Acta*, 221 (1994) 169.
- 14 L. K. Dyllal, *Australian J. Chem.*, 14 (1961) 493.
- 15 A. M. Hindawey, A. L. El-Ansary, Y. A. Marghalani and Y. Issa, *M. Egypt. J. Chem.*, 23 (1980) 251.
- 16 R. M. Issa, A. F. Shoukry, A. M. Hindawey and A. L. El-Ansary, *Egypt. J. Chem.*, 24 (1981) 39.