

Study of the thermal decomposition of the Nd(III), Eu(III) and Tb(III) scorpionates

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Abstract

The thermal behavior of the compounds $[\kappa^3\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3]_3\text{Ln}$ (Ln=Nd, Eu and Tb) was investigated through TG/DTG and DSC analyses. TG/DTG experiments were performed in a TGA-50 Shimadzu instrument under dynamic air atmosphere (50 ml min^{-1}). DSC measurements were performed in a dynamic nitrogen atmosphere (50 ml min^{-1}) at $10 \text{ }^\circ\text{C min}^{-1}$ heating rate using a DSC-50 Shimadzu differential calorimeter. For the TG/DTG and DSC analyses, an amount of 1.5–2.0 mg was used. From the TG curves, it was possible to show that all compounds are anhydrous, a one-step mass loss occurring between 200 and $450 \text{ }^\circ\text{C}$, yielding a residual stable up to $900 \text{ }^\circ\text{C}$. From the DTG curves it was found that decomposition temperatures decrease as the Ln(III) ionic radius decreases. DSC curves indicate that the compounds do not melt before the decomposition. For all three compounds, the decomposition process is exothermic.

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1. Introduction

The poly(pyrazolyl)-borates (Tp^*), also known as scorpionates, formula $\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3$, are chelating monovalent anions, containing nitrogen as donor atoms. Such compounds have lately found numerous applications in inorganic, organometallic and bioinorganic chemistry [1,2]. The Tp^* ligand behaves as a six-electron donor and, with regard to rare earth ions, they fulfil the electronic and steric requirements of the central ion, saturating its coordination sphere and therefore providing anhydrous stable compounds, $[\kappa^3\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3]_3\text{Ln}$, even when prepared from aqueous solution, with unusual chemical environments and molecular structures [3]. A formula drawing of a $\text{Ln}(\text{Tp}^*)_3$ compound is shown in Fig. 1.

As the $\text{Ln}(\text{Tp}^*)_3$ are very unusual water-free non-hydro-

sopic compounds, the investigation of their thermal behavior was undertaken in order to understand and correlate it with the structure of the compounds along the lanthanide series.

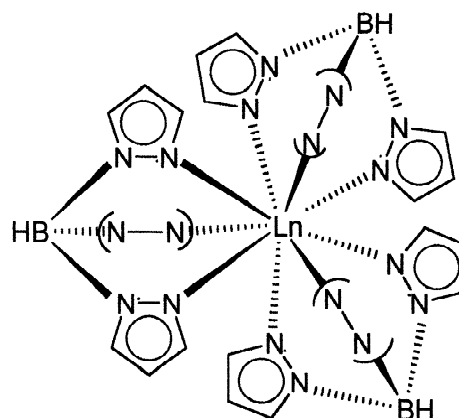


Fig. 1. Formula drawing of $\text{Ln}(\text{Tp}^*)_3$.

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2. Experimental

The $\text{Ln}(\text{Tp}^*)_3$ ($\text{Tp}^*=\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3$, $\text{Ln}=\text{Nd}$, Eu and Tb) compounds were synthesized through the reaction of hydrated lanthanide chlorides with excess of KTp^* in aqueous solution [3]. The resulting solid compounds were separated and washed with distilled water and dried under vacuum over anhydrous calcium chloride.

The thermal decomposition of the compounds was performed by TG/DTG and DSC analyses, using a small amount of material (1.5–2.0 mg). TG/DTG experiments were performed in a TGA-50 Shimadzu instrument under dynamic air atmosphere (50 ml min^{-1}) at a $10 \text{ }^\circ\text{C min}^{-1}$ heating rate. DSC measurements were performed in a dynamic nitrogen atmosphere (50 ml min^{-1}) at $10 \text{ }^\circ\text{C min}^{-1}$ heating rate, using a differential calorimeter DSC-50 Shimadzu.

The resulting residual, obtained at $600 \text{ }^\circ\text{C}$ heating, was characterized by elemental analysis of Ln , C , H and N and IR spectroscopy. Lanthanide ions were determined by titration with EDTA using a buffer (pH 5.8) and xylenol-orange as indicator. CHN microanalytical procedures were performed in a Perkin-Elmer 240 instrument. IR spectra were recorded on a Bomem MB-100 spectrometer using KBr pellets.

3. Results and discussion

The solid $\text{Ln}(\text{Tp}^*)_3$ compounds obtained by precipitation from aqueous solutions were stable in air. Their colors are those of lanthanide chlorides. $\text{Nd}(\text{Tp}^*)_3$ is pale mauve, while $\text{Eu}(\text{Tp}^*)_3$ and $\text{Tb}(\text{Tp}^*)_3$ are white. The Ln ,

C , H and N contents found in the compounds are in agreement with the proposed stoichiometry, $[\kappa^3\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3]_3\text{Ln}$, by Apostolidis et al. [3]. The IR spectra of the $\text{Ln}(\text{Tp}^*)_3$ compounds were very similar, evidencing the isomorphism among them. A previous work reported that $\text{Ln}(\text{Tp}^*)_3$ ($\text{Ln}=\text{La}$ to Dy) compounds are isostructural, having the same structure as $\text{Pr}(\text{Tp}^*)_3$, determined by single-crystal X-ray analysis, where the lanthanide ion is nine-coordinated to three nitrogen atoms from each ligand and displays tricapped trigonal prismatic geometry [3].

TG, DTG and DSC curves are shown in Figs. 2–4. In the TG curves the anhydrous character of the compounds was evidenced. The mass loss occurs in a single stage, corresponding to 61.7% for the Nd compound, 60.0% for Eu , and 50.2% for Tb , in the interval from 200 to $450 \text{ }^\circ\text{C}$, generating a stable residual until $900 \text{ }^\circ\text{C}$.

In the DTG curves, it was observed that the values of decomposition peak temperatures decrease with the decrease of the ionic radius of lanthanide ions: 313, 303 and $287 \text{ }^\circ\text{C}$ for Nd , Eu and Tb compounds, respectively.

The DSC curves showed peaks related to the decomposition that occurs in endothermic and exothermic events. The first peak appears at 372, 318 and $321 \text{ }^\circ\text{C}$ for the Nd , Eu and Tb compounds, respectively. These peaks correspond to endothermic events and are not related to the melting, since the TG curves show a mass loss in the same temperature range. This observation indicates that the melting and decomposition processes occur simultaneously in endothermic and exothermic events.

Above $400 \text{ }^\circ\text{C}$, in the DSC curves, it was verified that the thermal decomposition occurs in exothermic events, with maximum peaks at 474, 464 and $489 \text{ }^\circ\text{C}$ for Nd , Eu

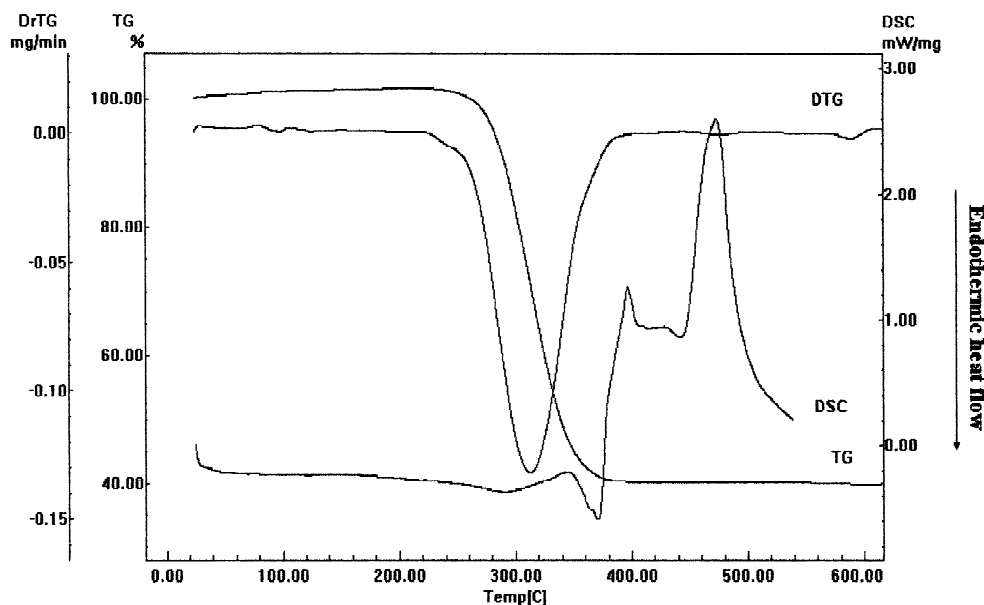
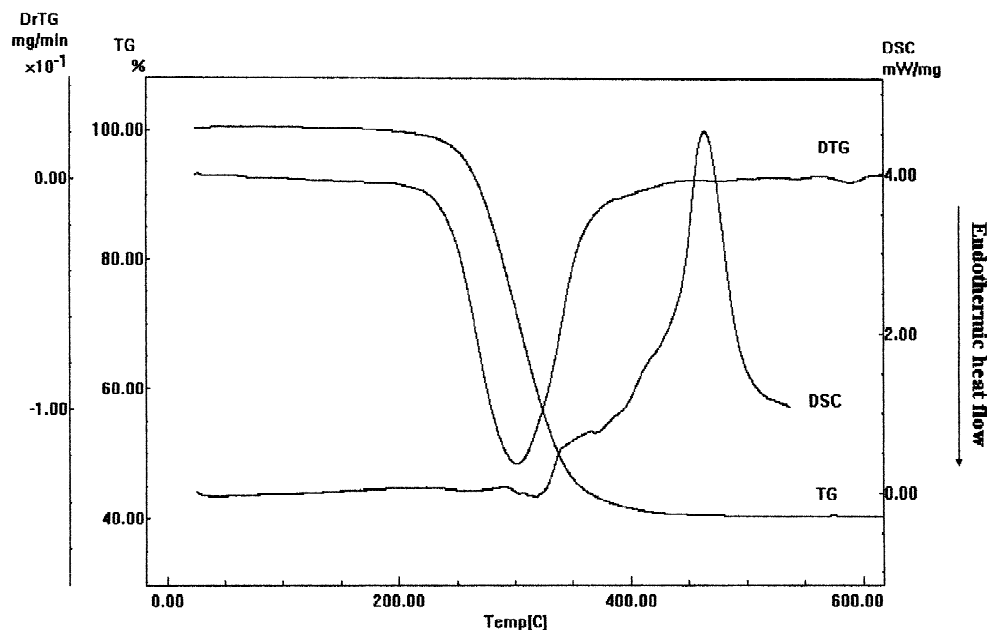


Fig. 2. TG/DTG and DSC curves for $\text{Nd}(\text{Tp}^*)_3$.

Fig. 3. TG/DTG and DSC curves for $\text{Eu}(\text{Tp}^*)_3$.

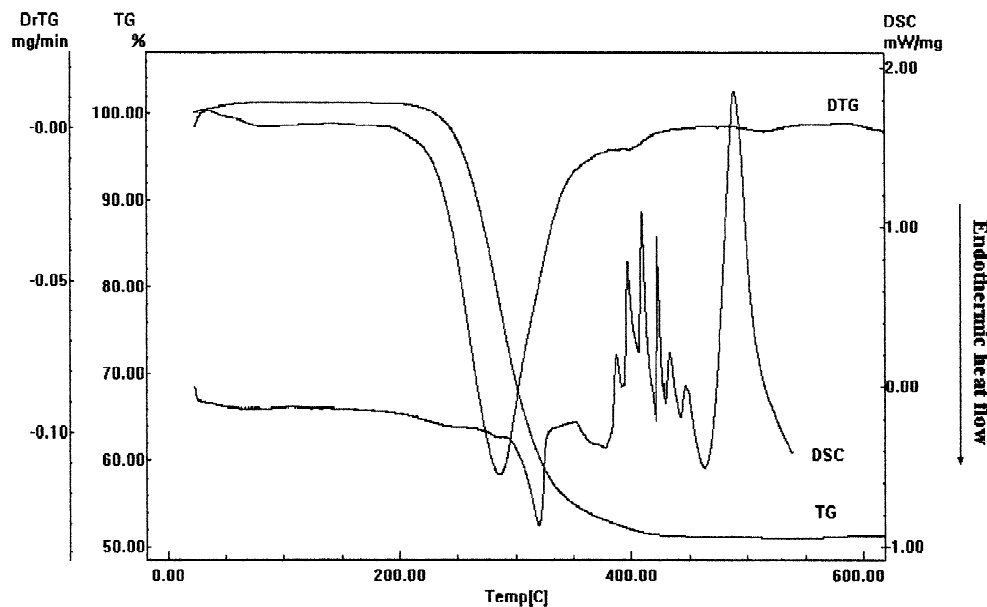
and Tb compounds, respectively. Some similarity was observed between the peaks of Nd and Eu compounds. The Tb compound presented different behavior, showing several peaks.

Fig. 5 shows the TG/DTG and DSC curves for KTp^* , which is the starting salt for the synthesis of $\text{Ln}(\text{Tp}^*)_3$ compounds. The decomposition behavior for KTp^* differs significantly from that of the $\text{Ln}(\text{Tp}^*)_3$.

It was found that KTp^* contains hydration water, which corresponds to the 6.5% mass loss and to the 73 °C peak in

the DTG curve; with further heating, the compound curve initially shows a plateau; after 200 °C until 650 °C the mass loss reaches 63.5%, related to several events in the DTG curve, whose most intense peak occurs at 380 °C.

The DSC curve for KTp^* showed one endothermic event related to dehydration, corresponding to one peak at 79 °C. It was also possible to verify that the melting of this compound corresponds to one peak at 190 °C. The decomposition occurred above 270 °C in several exothermic events, whose most intense peak occurs at 452 °C.

Fig. 4. TG/DTG and DSC curves for $\text{Tb}(\text{Tp}^*)_3$.

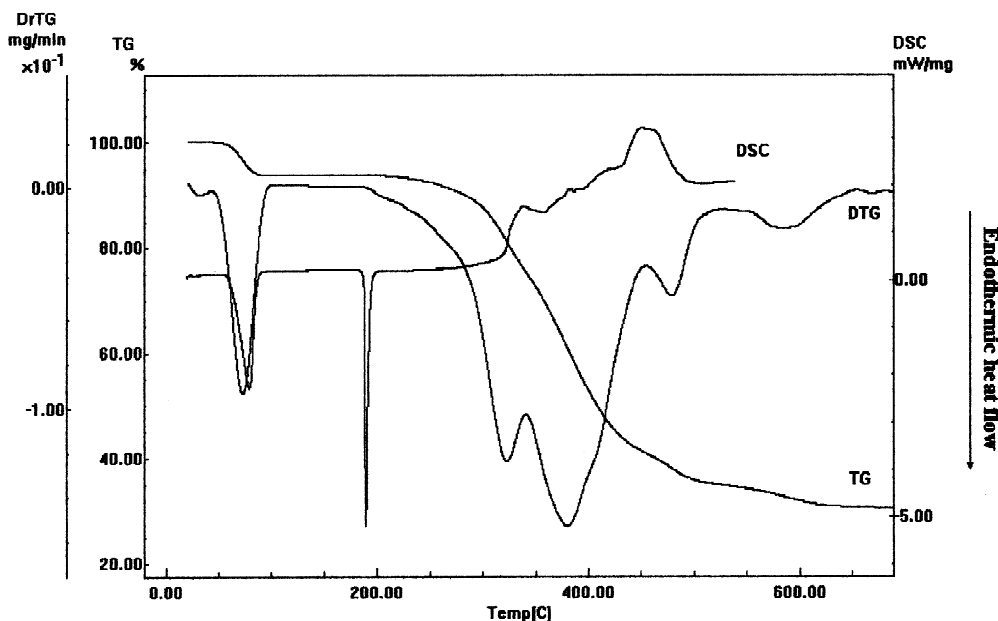


Fig. 5. TG/DTG and DSC curves for KTp*.

CHN analyses results of the residual at 600 °C of three lanthanide compounds did not indicate the presence of C, H and N elements. The IR spectra (Fig. 6) for those samples showed absorption bands characteristic of borate ion. The four bands corresponding to the vibrational mode of the planar borate ion [4], ν_1 (around 900 cm^{-1}), ν_2 (around 700 cm^{-1}), ν_3 (around 1400 cm^{-1}) and ν_4 (around 600 cm^{-1}), could be observed. These results are in agreement with the data of the infrared spectrum of the lanthanum borate [5].

The monocrystal structure of $\text{Nd}(\text{Tp}^*)_3$ was elucidated [3]. By using indirect structural determination in the

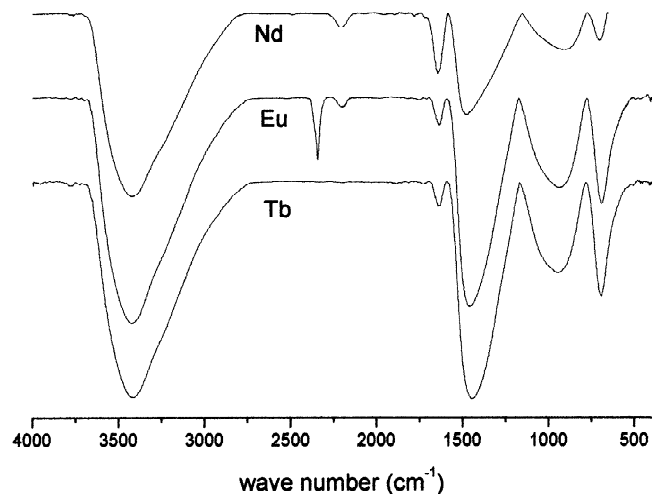


Fig. 6. IR spectra for residuals at 600 °C.

distant IR, it was found that Nd and Eu compounds are isostructural [3]. Structural information for the $\text{Tb}(\text{Tp}^*)_3$ is not known, but according to the differences of its thermal behavior in comparison with those of Nd and Eu, one may suppose that the Tb compound should not be isostructural with $\text{Nd}(\text{Tp}^*)_3$ and $\text{Eu}(\text{Tp}^*)_3$, but instead with the $\text{Yb}(\text{Tp}^*)_3$, which have a Tp^* as bidentate and two Tp^* as tridentate, resulting in octa-coordinated compounds [6].

4. Summary

This paper reports the study of the thermal behavior of the $\text{Ln}(\text{Tp}^*)_3$ ($\text{Ln}=\text{Nd}$, Eu and Tb). In the TG curves the anhydrous character of the compounds was evidenced. The mass loss occurs in a single stage in the interval from 200 to 450 °C, generating a stable residual up to 900 °C. In the DTG curves, it was observed that the values of decomposition peak temperatures decrease with the decrease of the ionic radius of lanthanide ions. The DSC curves showed peaks related to the decomposition that occurs in endothermic and exothermic events, the melting and decomposition processes occurring simultaneously. The IR spectra of the residual at 600 °C showed absorption bands characteristic of borate ion. Structural information for the $\text{Tb}(\text{Tp}^*)_3$ is not known, but according to the differences of its thermal behavior in comparison with those of Nd and Eu, one may suppose that the Tb compound should not be isostructural with $\text{Nd}(\text{Tp}^*)_3$ and $\text{Eu}(\text{Tp}^*)_3$, but instead with the $\text{Yb}(\text{Tp}^*)_3$, which have a Tp^* as bidentate and two Tp^* as tridentate, resulting in octa-coordinated compounds.

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