Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 77–82

SYNTHESIS, CHARACTERIZATION, SPECTROSCOPY AND THERMAL ANALYSIS OF RARE EARTH PICRATE COMPLEXES WITH *L*-LYSINE

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Rare earth picrate (RE) complexes with *L*-lysine (Lys) were synthesized and characterized. Elemental analysis (CHN), EDTA titrations and thermogravimetry data suggest a general formula $RE(pic)_3\cdot 2Lys\cdot 2H_2O$, where *RE*=La–Lu (without Pm) and Y, *pic*=picrate). IR spectra suggest that Lys is coordinated to the central ion through the nitrogen of the α-amino group. Parameters obtained from the absorption spectrum of the Nd compound indicated that the metal-ligand bonds are essentially electrostatic. Emission spectrum and biexponential behavior of the luminescence decay of the Eu compound suggest the existence of polymeric species. Thermogravimetric/derivative thermogravimetric (TG/DTG) and differential scanning calorimetry (DSC) curves of all complexes are very similar, with five events. The final products are the corresponding rare earth oxides and their X-ray diffraction patterns are identical to the calcinated oxides.

Keywords: *L-lysine, luminescence, rare earths picrates, synthesis and characterization, thermal analysis*

Introduction

Interest in the study of the coordination chemistry of rare earth ions with amino acids is increasing, since this interaction is of enormous importance in biological systems. Rare earth ions are often used as spectroscopic probes in studies of these systems. These ions, however, interact with biological materials in specific ways, which along with their unique magnetic and spectroscopic properties make them very interesting substitution probes for calcium-containing biological materials [1, 2].

Complexes containing picrates have been investigated systematically in our laboratories. Several lanthanide picrate complexes with a series of different organic neutral ligands (including the amino acids glycine and arginine), involving synthesis, characterization, studies of properties and structures have been reported [3–11]. The presence of the picrate anion (2,4,6-trinitrophenolate) in these coordination compounds is expected to enhance the luminescence properties of these materials, because this anion acts as a luminescence antenna, absorbing and transferring energy efficiently to the rare earth ions and consequently increasing their luminescence.

Since amino acids participate in many biochemical processes essential to living systems, their interaction with metals have been the center of attention of many investigations, inclusive with rare earths [3, 4, 12–16]. However, in the literature no complexes of *L*-lysine with rare earth picrates have been reported.

Studies of thermal behavior of several lanthanide compounds have been reported [17–20]. Some ones described the thermal stability investigation enable to evaluate of water molecule in the outer or inner coordination spheres and other works the study is about the only dehydration and thermal decompositon of the lanthanide compounds. In these studies, the thermal behavior of the lanthanide compounds is not similar.

Thermal decomposition of hydrated lanthanide picrates was reported by Miranda *et al*. [19]. The results showed that the thermal decomposition of hydrated lanthanide picrates occurs in three similar groups: La–Sm, Eu–Dy and Ho–Lu and Y with different numbers of hydration water molecules.

In this paper, we describe the synthesis, characterization, spectroscopic study and thermal analysis of rare earth picrate complexes with *L*-lysine. *L*-lysine (2,6-diaminohexanoic acid, $NH_2(CH_2)_4CH-(NH_2)COOH$) is an essential amino acid and is characterized by having an amino group at ε-C, which exists as an inner salt or in the zwitterionic form $NH_3^+(CH_2)_4CH-(NH_2)COO^-$ [21–23].

Experimental

After extensive preliminary tests it was developed a preparation route for the new complexes. They were prepared according to the following: *L*-lysine (Fluka, purity above 98%, used without purification) in a molar ratio 1:2 (salt:ligand) was dissolved in ethanolic

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1388–6150/$20.00

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solution (50%) and the rare earth picrate (solid) was added to this solution. The solution containing salt and ligand was stirred and heated (~60°C) until dissolution of the salt. Immediately it was observed the formation of a yellow precipitate. The adducts were filtered and dried under vacuum over anhydrous calcium chloride.

The compounds were characterized by complexometric titration of the rare earth ion with standardized EDTA solutions using xylenol orange as indicator (the complexes were dissolved in nitric acid and the pH value was adjusted to 6.5 by adding ammonium hydroxide) [24]. Carbon, hydrogen and nitrogen contents of the complexes were obtained by microanalytical procedures using a Perkin-Elmer analyzer (model 240). Infrared absorption spectra were recorded in the range 4000–400 cm^{-1} in KBr pellets, using a BOMEM MB-100 spectrometer. The absorption spectrum of the neodymium compound was obtained in a Zeiss DMR-10 spectrophotometer in the solid state at room temperature using a silicone mull. Excitation and luminescence spectra of the europium, gadolinium and terbium compounds were recorded with a SPEX-Fluorolog-1681 spectrofluorimeter and the luminescence decay profiles were measured with a SPEX 1934D phosphorimeter accessory coupled to a SPEX-Fluorolog FL 212 spectrofluorimeter at room temperature (298 K) and in liquid N_2 (77 K). X-ray diffraction powder patterns were obtained on a Miniflex Rigaku diffractometer, with CuK_{α} (λ=1.5418 Å) radiation, in the interval of 5 to 50° (2θ).

Thermogravimetric/derivative thermogravimetric (TG/DTG) curves of the complexes and ligand were obtained on a Shimadzu TGA-50 thermobalance in the temperature range 25–900°C (complexes) and 25–650°C (ligand) with a heating rate of 2 and 10°C min^{-1}, under dynamic air and nitrogen atmospheres (50 mL min^{-1}), using platinum crucibles with ca. 1.5 mg of samples (complexes) and 2.5 mg (ligand). Differential scanning calorimetry (DSC) curves were obtained on a Shimadzu DSC-50 cell using partially closed aluminum crucibles with ca. 1.5 mg for the complexes and 2.5 to 5.3 for the ligand, under dynamic nitrogen atmosphere (100 mL min^{-1}) in the temperature range 25–400°C (complexes) and 25–550°C (ligand), with a heating rate of 10°C min^{-1}. The DSC cell was calibrated with indium (m.p. 156.6°C and ΔH_{fusion} =28.54 J g^{-1}) and zinc (m.p. 419.6°C).

Results and discussion

According to CHN analyses, EDTA titrations (% RE^{3+}) and thermal analyses (% H_2O and % RE_2O_3) data (Table 1) it was possible to establish the composition $RE(pic)_3{\cdot}2Lys{\cdot}2H_2O$ for all compounds. The yellow compounds present the characteristic hues of the respective rare earth (III) ions. They are crystalline powders, odorless, slightly hygroscopic and slightly soluble in water and acetone. X-ray diffraction power patterns results indicate that all the compounds are isomorphous. Several attempts to obtain single crystals were unsuccessful.

All infrared spectra are similar and present as a general characteristic a shift of *n*NH (α-amine group) band of the *L*-lysine to lower frequencies (3250, 3200, 3030 cm^{-1}) with relation to the free ligand (3396, 3306, 3062 cm^{-1}). The disappearance of the bands associated with the zwitterion structure (combination bands at ca. 2090 cm^{-1}, characteristic of NH_3^+ groups of the α-amino group of free lysine) in the complexes, suggest that *L*-lysine is coordinated to the central ion through the nitrogen of the α-amine group. The free lysine side chain amino group (NH_3^+ group of ε-C) presents $\delta_{as}(NH_3^+)$ and $\delta_s(NH_3^+)$ vibrations at ca. 1626 and 1519 cm^{-1} respectively. These vibrations in the complexes [$\delta_{as}(NH_3^+)$ ~1622 cm^{-1} and $\delta_s(NH_3^+)$ ~1517 cm^{-1}] do not show changes with relation to free lysine, suggesting that this group is not involved in coordination [25]. The infrared absorption spectrum of free lysine shows the asymmetric ($\nu_{as}COOH$) and symmetric stretching (ν_sCOOH) bands, located at 1580 and 1409 cm^{-1}, respectively. These vibrations in the complexes do not present major changes with relation to the free ligand, suggesting that the oxygen atom of the carboxylic group is not used in the ligand-metal ion bonding and that it is possibly bonded to water molecules through hydrogen bonds [3, 4, 26–30]. Bands due to the picrate ion at ~1268 cm^{-1} (νCO), ~1558 and 1492 cm^{-1} ($\nu_{as}NO_2$), ~1365 and 1330 cm^{-1} (ν_sNO_2), indicate that at least in part they are coordinated as bidentate ligands through the phenoxo group and one oxygen of an ortho-nitro group [5, 8, 31]. Bands near 3430 cm^{-1} are attributed to H_2O (ν_1 and ν_2), indicating the presence of water molecules in these complexes [3, 4, 5–11].

The absorption spectrum of the neodymium complex was registered in the solid state at room temperature for the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition. The calculated nephelauxetic parameter (β=0.992), covalent factor ($b^{1/2}$=0.060) and Sinha's parameter (δ=0.731) indicated that the metal-ligand bonds are essentially electrostatic.

The luminescence spectrum of the $Gd(pic)_3{\cdot}2Lys{\cdot}2H_2O$ complex at 77 K was recorded under excitation at 350 nm. This emission spectrum shows a wide phosphorescence emission band centered around 609 nm and was attributed to the picrate anion. Owing to the large energy gap (ca. 32000 cm^{-1}) between the $^8S_{7/2}$ ground estate and first $^6P_{7/2}$ excited of the Gd^{3+} ion, this trivalent ion cannot accept any energy from the excited triplet estate of the organic ligand; for that reason, this spectrum was used to calculate the value of the lowest

Table 1 Analytical data for $RE(pic)_3{\cdot}2Lys{\cdot}2H_2O$ compounds

RE	*RE*/%			C/%		H/%		N/%		H_2O/%		$RE_2O_3{}^c$/%	
	calc.	exp.[a]	exp.[b]	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.[b]	calc.	exp.[b]
La	12.1	12.4	13.5	31.3	31.2	3.3	3.3	15.3	15.8	3.1	3.2	14.2	15.9
Ce	12.2	12.1	13.5	31.2	30.8	3.3	3.0	15.8	14.8	3.1	3.1	14.9	16.4
Pr	12.2	12.4	12.4	31.2	29.2	3.3	2.7	15.8	14.2	3.1	3.2	14.8	15.0
Nd	12.5	12.5	12.4	31.1	30.3	3.3	3.0	15.7	15.2	3.1	3.2	14.5	14.5
Sm	12.9	13.0	13.5	31.0	31.1	3.3	3.6	15.6	14.9	3.1	3.3	15.0	15.5
Eu	13.0	13.0	13.3	30.9	30.3	3.3	3.2	15.6	15.0	3.1	3.0	15.1	15.0
Gd	13.5	14.0	13.5	30.8	30.0	3.3	4.4	15.6	14.7	3.1	3.1	15.5	15.5
Tb	13.6	13.9	13.1	30.8	30.9	3.3	3.3	15.5	14.9	3.1	3.1	15.9	15.4
Dy	13.8	14.0	14.2	30.7	29.3	3.3	3.0	15.5	14.7	3.1	3.1	15.9	16.3
Ho	14.0	14.4	14.4	30.6	31.0	3.2	3.3	15.5	16.0	3.1	2.2	16.0	16.5
Er	14.2	14.5	13.6	30.5	29.3	3.2	3.1	15.4	14.7	3.0	3.5	16.2	15.5
Tm	14.3	14.8	14.1	30.5	29.8	3.2	3.2	15.4	15.0	3.0	3.4	16.3	15.7
Yb	14.6	14.7	14.2	30.4	30.3	3.2	3.2	15.4	15.5	3.0	3.1	16.6	16.1
Lu	14.7	14.8	13.2	30.3	29.8	3.2	2.8	15.3	14.9	3.0	3.0	16.8	15.0
Y	8.1	8.1	7.3	32.7	33.6	3.5	3.7	16.5	16.9	3.3	3.1	10.2	9.2

[a]complexometric titration with EDTA, [b]TG data analysis for dehydration and residues and [c]CeO_2, Pr_6O_{11} and Tb_4O_7

triplet state of the picrate ligand. The energy level of the triplet state of this ligand is around 16447 cm^{-1}. For the terbium complex no luminescence is observed for Tb^{3+} ion at room temperature and 77 K; this can be due to the lowest excited energy levels of Tb^{3+} ion ($^5D_4$~20400 cm^{-1}) to be located above the excited triplet energy level of the ligand. As a consequence, energy transfer from the ligands to trivalent terbium ion is not possible. In the spectral range 420 to 720 nm at room temperature only a wide emission band attributed to picrate anion phosphorescence is observed.

The excitation spectrum for solid $Eu(pic)_3{\cdot}2Lys{\cdot}2H_2O$ complex was recorded at room temperature and with the emission monitored on the $^5D_0\rightarrow{}^7F_2$ transition at 611 nm. This spectrum shows a very broad band (like in all picrate complexes) in the region 300–550 nm, attributed to the picrate anions that act as luminescence antennas, indicating that the picrate anion is a good sensitizer for the Eu^{3+} luminescence.

Emission spectra of the europium compound in the solid state at 298 and 77 K are similar, but at low temperature it is better resolved (Fig. 1). The number of peaks for a single complex is given by 2 J+1. For the $^5D_0\leftarrow{}^7F_0$ transition only one peak may be observed; for $^5D_0\rightarrow{}^7F_1$ three peaks; for $^5D_0\rightarrow{}^7F_2$ a maximum of five peaks, etc. In the spectrum obtained at 77 K in the region of the $^5D_0\rightarrow{}^7F_0$ transitions two peaks were observed (576.6 and 578.4 nm); for $^5D_0\rightarrow{}^7F_1$ transitions were observed three broad peaks (588.0, 590.7 and 594.3 nm); for $^5D_0\rightarrow{}^7F_2$ five peaks (609.9, 611.1, 611.7, 614,7 and 624.3 nm) and two shoulders (617.1 and 618.7 nm) were observed and for $^5D_0\rightarrow{}^7F_4$ five peaks (692.7, 693.6, 697.3, 702.0 and 704.4 nm) were observed too. The existence of a $^5D_0\rightarrow{}^7F_0$ transition indicates that only C_{nv}, C_n and C_s symmetries are possible around the central Eu^{3+} ion. As more than one peak for $^5D_0\rightarrow{}^7F_0$ transition and broad bands for $^5D_0\rightarrow{}^7F_J$ (J=1, 2 and 4) transitions were observed, this suggests the probable existence of polymeric species that is in agreement with the biexponential behavior of this luminescence. The luminescence decay curve of the $^5D_0$ excited state of Eu^{3+} ion for solid $Eu(pic)_3{\cdot}2Lys{\cdot}2H_2O$ complex was obtained at 77 K. This curve fits very well to a double-exponential curve. Values of τ_1 and τ_2 were calculated to be 240.5 and 1157.8 μs, respectively.

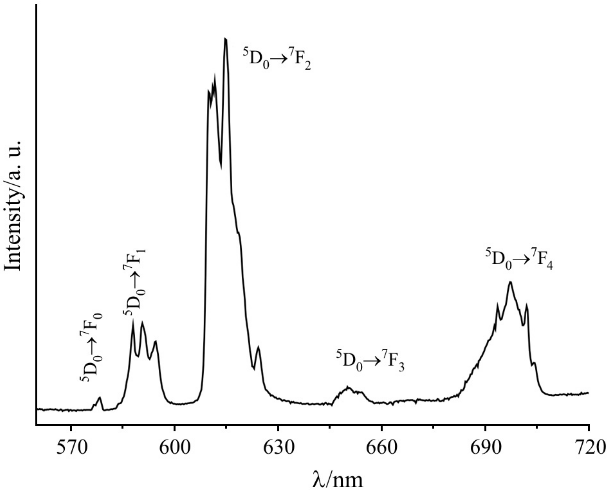

Fig. 1 Emission spectra of $Eu(pic)_3{\cdot}2Lys{\cdot}2H_2O$ at 77K

Figure 2 shows TG/DTG and DSC curves of *L*-lysine. In the temperature range 25 to 166°C there are two events of mass loss. The first event occurs between 27 and 90°C (Δm=5.0%) and the second between 90 and 166°C (Δm=0.7%). These events correspond to the release of 0.5 water molecule. This result indicated that the formula of *L*-lysine is $NH_2(CH_2)_4CH–(NH_2)COOH·1/2H_2O$ (%H_2O, calc. 5.8% and exp. 5.7%). The thermal decomposition of anhydrous species occurs in three steps between 166–650°C (T_{onset}=212°C to first step) with 97% of mass loss. The DSC curve shows five endothermic peaks in the temperature range 25 to 300°C and one exothermic peak in the temperature range 300 to 550°C. The first (T_{peak}=71°C) and second peaks (T_{peak}=97°C) corresponding to release 0.5 water molecule and phase transition, respectively. This results is confirmed by DSC curves obtained with heating and cooling down cycles according to Fig. 3. It can be observed that the first peak disappears during the second heating while the second endothermic peak is exothermic in the cooling down showing that phase transition in reversible. During the second heating this event occur equal confirming the reversibility of the process. It was observed that the endothermic peaks of *L*-lysine at 97, 225 and 234°C disappear in the complexes $RE(pic)_3·2Lys·2H_2O$. This modification of DSC peaks confirms that new compounds were formed, in other words the prepared complexes are not a simple mixture of $RE(pic)_3·xH_2O$ and *L*-lysine (compare with Fig. 4).

All complexes exhibit a similar thermoanalytical profile, in good agreement with the powder X-ray results. Table 2 reports percentages of mass losses in TG curves and the temperature peaks of those events in DTG curves. Figure 4 shows TG/DTG and DSC curves in the temperature range 25 to 900°C and 25 to 400°C, respectively, for $Lu(pic)_3·2Lys·2H_2O$ as a representative of the series. These curves show two events of mass loss relative to the elimination of two water molecules in the temperature range 25 to 155°C. The decompositions of the anhydrous complexes in the temperature range 155 to 900°C occur in three steps, as also shown in the DTG curves, as can be seen in Fig. 4. These steps correspond to simultaneous decomposition of the picrate anions and *L*-lysine. These data are corroborated by microanalytical CHN analyses.

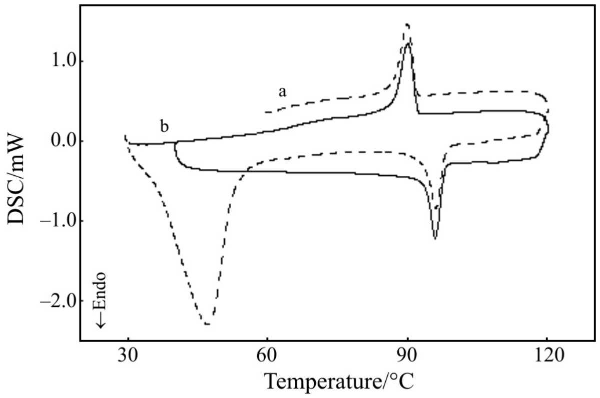

Fig. 3 DSC curves of the *L*-lysine obtained with heating and cooling down in dynamic nitrogen atmosphere (100 mL min^{-1}), heating rate 2°C min^{-1} and ca. 5.3 mg of sample. a – first heating and b – second heating

The residues after thermal decomposition of the complexes at 900°C were characterized by X-ray diffraction patterns (powder method) as rare earth oxides, RE_2O_3 (*RE*=La, Nd, Sm–Gd, Dy–Lu and Y), CeO_2, Pr_6O_{11} and Tb_4O_7. These X-ray patterns are identical to the ones of the respective oxides calcinated at 900°C.

All thermal events between 25 and 400°C observed in DSC curves are in accord with those observed in TG/DTG curves. DSC curves show two endothermic events and two exothermic events.

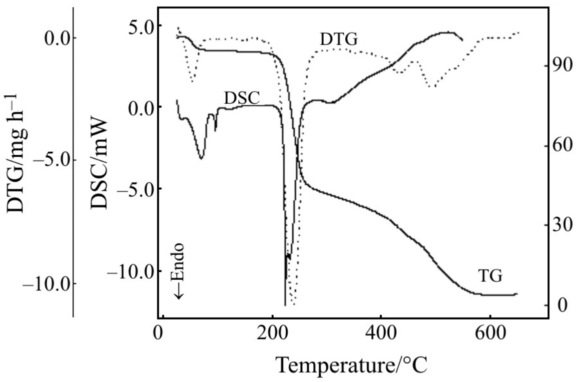

Fig. 2 TG/DTG and DSC curves of the *L*-lysine obtained in dynamic air (50 mL min^{-1}) and dynamic nitrogen atmosphere (100 mL min^{-1}), respectively, heating rate 10ºC min^{-1} and ca. 2.5 mg of sample for both

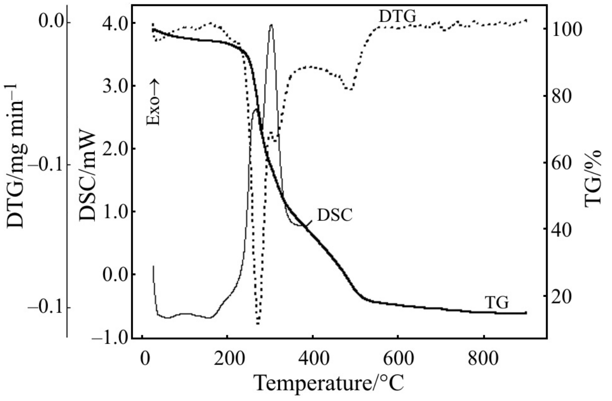

Fig. 4 TG/DTG and DSC curves of the $Lu(pic)_3·2Lys·2H_2O$ complex obtained in dynamic air (50 mL min^{-1}) and nitrogen atmospheres (100 mL min^{-1}), respectively, heating rate 10ºC min^{-1} and 1.5 mg of sample for both

Table 2 Result from TG/DTG and DSC curves for RE(pic)$_3$·2Lys·2H$_2$O compounds. Curves obtained in the temperature range 25–900ºC (TG) and 25–400ºC (DSC) with a heating rate of 10ºC min^{-1}, under dynamic air (50 mL min^{-1}) (TG) and N$_2$ (100 mL min^{-1}) (DSC) atmospheres, using ca. 1.5 mg of samples

	Step 1 25–155°C				Step 2 155–290°C			Step 3 290–370°C			Steps 2+3	Step 4^a 370–900°C	
RE	TG	DTG	DSC	DSC	TG	DTG	DSC	TG	DTG	DSC	DSC	TG	DTG
	Δ*m*/%	*T*/°C	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*m*/%	*T*/°C	*T*/°C	Δ*m*/%	*T*/°C	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*m*/%	*T*/°C
La	3.2	46/148	45/124	157.9	30.6	260	246	20.1	299	292	–1311.4	30.1	435
Ce	3.1	48/71	57/127	124.0	40.8	262	255	12.5	320	284	–1166.2	27.2	340
Pr	3.2	50/131	60/146	137.3	24.2	268	254	40.0	303	294	–1390.0	17.6	483
Nd	3.2	27/132	61/150	129.0	27.3	265	253	32.8	291	294	–1548.5	22.2	440
Sm	3.3	29/132	38/157	146.6	30.6	270	263	18.2	303	290	–1531.4	32.4	444
Eu	3.0	51/91	64/156	166.9	34.7	264	250	18.9	306	291	–2047.9	28.4	431
Gd	3.1	27/130	54/153	110.5	35.8	270	270	18.2	308	296	–1235.0	27.4	456
Tb	3.1	55/98	65/144	144.6	29.8	266	256	21.2	307	297	–1738.2	30.5	464
Dy	3.1	37/127	54/150	178.0	35.2	270	259	18.8	309	298	–1357.7	26.6	458
Ho	2.2	56/143	44/155	155.7	34.1	255	250	22.0	316	306	–1625.0	25.2	431
Er	3.5	30/129	37/151	188.3	37.1	273	271	18.1	308	295	–1350.9	25.8	464
Tm	3.4	28/131	38/150	106.4	35.0	267	256	17.6	309	296	–1370.1	28.3	453
Yb	3.1	63/138	38/153	178.8	29.3	254	245	22.3	313	308	–1729.2	29.2	450
Lu	3.0	36/129	59/155	180.2	38.0	274	267	21.5	313	303	–1565.9	22.5	486
Y	3.1	52/130	65/150	136.7	37.7	266	258	28.1	288	305	–1578.3	21.9	450

T=peak temperature, Δ*m*=mass loss, ^{a}The last peak was not observed in DSC

TG/DTG and DSC curves for all RE(pic)$_3$·2Lys·2H$_2$O presented similar profiles. DSC results for all complexes are summarized in Table 2.

It is important to mention that small amounts of material were used in thermal analysis experiments due to the explosive properties of the picrates. It was observed that the furnace atmosphere (N$_2$ and air) and heating rate (2 and 10°C min^{-1}) do not influence the thermal decomposition processes of the compounds.

Acknowledgements

The authors acknowledge Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. One of us (TMS) is much indebted to FAPESP for a doctoral fellowship (process 01/06684-1). The authors thank Prof. Dr. Hermi F. Brito and Dr. Ercules E. S. Teotonio for the recording of luminescence spectra.

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Received: January 3, 2005
In revised form: March 18, 2005

DOI: 10.1007/s10973-005-6828-z