

Synthesis, characterization and thermal behavior of some trivalent lanthanide 4-amino-benzenesulfonate salts

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Abstract The lanthanide 4-amino-benzenesulfonate salts (or sulfanilates) were obtained by the reaction of lanthanide carbonates (La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} and Gd^{3+}) and 4-amino-benzenesulfonic (or sulfanilic) acid in aqueous solution. Simultaneous thermogravimetry, differential thermal analysis and differential scanning calorimetry, elemental analysis, X-ray powder diffractometry and infrared spectroscopy (FTIR) were used to characterize and to study the thermal behavior of these compounds. The general formula could be established as $\text{LnL}_3 \cdot n\text{H}_2\text{O}$, where Ln represents trivalent lanthanide ions (La–Gd), L is the 4-amino-benzenesulfonate anion ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$) and $n = 8$ (La–Gd) and $n = 7$ only for Ce. The thermal behavior indicates that dehydration occurs in a single step up to 443 K, characterized by an endothermic peak, and the enthalpy of dehydration was evaluated by DSC. Thermal decomposition takes place above 523 K producing a stable intermediate $\text{Ln}_2\text{O}_2\text{SO}_4$ characterized by X-ray diffraction, which in the sequence decomposed to the respective oxides. For the La^{3+} , Nd^{3+} and Pr^{3+} sulfanilates, the residual oxide formation occurs only after 1573 K.

Keywords Lanthanides · Sulfanilates · 4-Amino-benzenesulfonates · Thermal behavior

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Introduction

The molecular formula of sulfanilic acid ($\text{pK}_a = 3.232$) or 4-amino-benzenesulfonic acid may be represented by ($\text{C}_6\text{H}_7\text{NO}_3\text{S}$) or ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$). It is an organic synthetic compound obtained from aniline and sulfuric acid. It is a zwitterion, in other words, a dipolar ion having opposite charges on different atoms. In the complex compound formation, the sulfonic group ($-\text{SO}_3^-$) can act as a monodentate, bidentate or tridentate ligand for different metallic ions. In some cases, both the amine ($-\text{NH}_2$) and sulfonic groups participate in the metal coordination [1].

Rare earths are a group of metallic elements which contain, in addition to the lanthanides ($_{58}\text{Ce}$ to $_{71}\text{Lu}$), the elements $_{21}\text{Sc}$, $_{39}\text{Y}$ and $_{57}\text{La}$ [2]. In coordination chemistry, the lanthanide ions (Ln^{3+}) are classified as hard acid by Pearson's theory. Among the electron donor species, namely bases, the preference to form a bond follows the $\text{O} > \text{N} > \text{S} > \text{F}$ order, with ionic nature interactions. The sulfanilate ion ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$) has suitable chemical characteristics to act as a ligand with lanthanide ions.

In the literature, some studies report the synthesis and the structure determination of some sulfanilates with alkali metal, ammonium and transition metals [3–11]. Gunderman [7] described the synthesis of the two complexes, bis(4-amino-benzenesulfonate)diaquocopper(II) dihydrate, $[\text{Cu}(\text{C}_6\text{H}_6\text{NO}_3\text{S})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and bis(4-amino-benzenesulfonate)diaquomanganese(II) $[\text{Mn}(\text{C}_6\text{H}_6\text{NO}_3\text{S})_2(\text{H}_2\text{O})_2]$. Vinciguerra et al. [8] studied the magnetic moment, infrared and optical spectra of ortho-, meta- and para-amino-benzenesulfonates of copper (II). Shakeri and Haussuhl [9] studied the crystal structure of the cobalt sulfanilate tetrahydrate $[\text{Co}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_2(\text{H}_2\text{O})_4]$. Zhao et al. [12] studied the structure of 4-amino-benzenesulfonates of some lanthanide metals (La, Nd, Sm, Eu,

Tb, Dy and Er) by means of FTIR and X-ray diffraction. In most of these studies, the main goal was the structure determination of the synthesized compound, and a few of them have reported the thermal behavior of the compounds derivatives from sulfonic acid.

Experimental

Synthesis

The 4-amino-benzenesulfonic acid, $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$, with 99.6% was obtained from Sigma. Carbonates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) were prepared by adding slowly, with continuous stirring, the saturated sodium hydrogen carbonate solution to the corresponding metal chlorides or nitrate solutions until total precipitation of the metal ions. The precipitates were washed with distilled water until the elimination of chloride or nitrate ions (qualitative test with $\text{AgNO}_3/\text{HNO}_3$ solution for chloride ions or diphenylamine in sulfuric acid solution for nitrate ions) and maintained in aqueous suspension.

Solid-state Ln^{3+} sulfanilates were prepared by mixing the aqueous solution of 4-amino-benzenesulfonic acid with the corresponding metallic carbonate suspension, in slight excess. The aqueous suspension was heated slowly up to near boiling until the total neutralization of the acid occurs. The carbonates in excess were filtered, and the aqueous solutions of the respective metallic sulfanilates were slowly evaporated. The compounds were dried in air and kept in a desiccator over anhydrous calcium chloride.

Experimental equipment and conditions

In solid-state compounds, hydration water, ligand and metal contents were determined from the TG curves. All TG, DTA and DSC curves were recorded using a SDT-Q600 simultaneous TG-DTA-DSC thermal analysis controlled by Thermal Advantage (4.2.1) software, both from TA Instruments, under dynamic dry air atmosphere (gas flow of 100 mL min^{-1}), heating rate of 10 K min^{-1} in the range of 303–1573 K, with sample masses of ca. 5 mg in a sample holder of alumina. The dehydration enthalpy was evaluated using SDT Q600 from TA Instruments under dynamic dry air atmosphere (100 mL min^{-1}), heating rate of 10 K min^{-1} in the range of 303–473 K and sample masses of ca. 4 mg in a platinum sample holder.

Elemental analysis for C, H, N and S was performed using a Leco CHNS Analyzer. X-ray powder patterns were obtained using a BRUKER system D8 Advance diffractometer, employing $\text{CuK}\alpha$ radiations ($\lambda = 1.54184 \text{ \AA}$) and setting of 40 kV and 20 mA. Each run was performed with

2θ values between 10 and 70 at a step size of 0.010 and a count time of 0.5 s per step.

The attenuated total reflectance (ATR) spectra for 4-amino-benzenesulfonic acid as well as for its trivalent lanthanide compounds were run on a Spectrum system 100 ATR FTIR spectrophotometer (Perkin-Elmer), using an ATR accessory with Ge windows. The FTIR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm^{-1} .

Results and discussion

The FTIR spectra are shown in Fig. 1. The main absorption bands observed are those associated with the stretches ($\nu \text{ O-H}$, $\nu \text{ N-H}$ and $\nu \text{ SO}_3$) and deformations ($\delta \text{ H-S-H}$ and $\delta \text{ H-C-H}$), and all absorptions are in agreement with Zhao et al. [12]. Significant differences are noted between the spectra of the sulfanilic acid and its compounds suggesting the complex formation. The absorption bands found between 3700 and 3000 cm^{-1} are related with the presence of water molecules of hydration, which are not observed in the IR spectrum of sulfanilic acid. The absorption bands of $\nu \text{ N-H}$ were not observed, associated

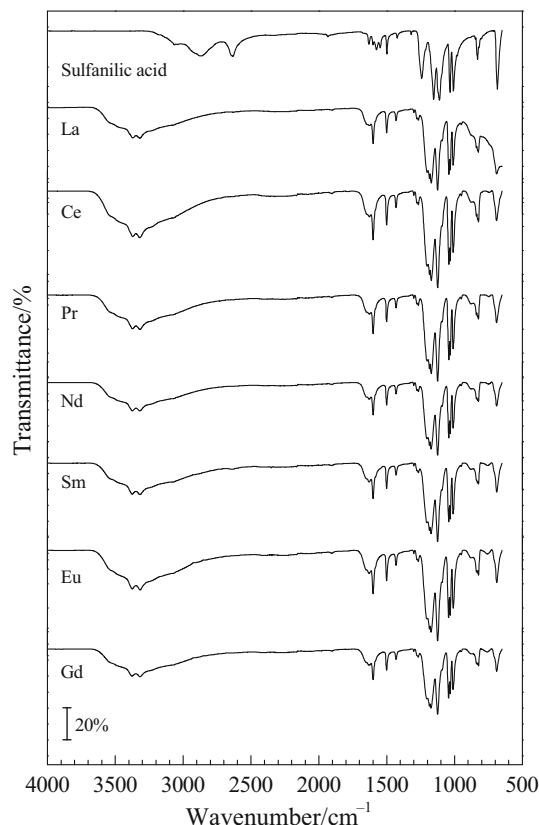


Fig. 1 FTIR spectra of the sulfanilic acid and its trivalent lanthanide compounds

with the $-\text{NH}_2$ group in the sulfanilic acid spectrum, while the spectra of lanthanide sulfanilates presented a broad band attributed to absorption of H_2O and $-\text{NH}_2$ ($1650\text{--}1631\text{ cm}^{-1}$) overlapped.

The elemental analysis results are presented in Table 1 and are in agreement with the proposed general formula.

The X-ray powder patterns presented in Fig. 2 showed that all compounds were obtained with good crystallinity degree and with evidence for the formation of an isomorphous series. Zhao et al. [12] reported that in these compounds, the metallic ion is coordinated by two oxygen atoms of two sulfonate groups and seven oxygen atoms from water molecule.

The simultaneous TG–DTA curves of the compounds are shown in Fig. 3. These curves exhibit mass losses in three main steps and thermal events corresponding to these losses (endothermic and exothermic peaks). The thermal analytical data from TG curves are shown in Table 2.

The first mass loss in the range of 323–433 K is attributed to dehydration, which occurs in a single step with formation of anhydrous compounds (stable up to 533 K). The anhydrous compounds decompose above 533 K, and the TG curves profile suggests that the oxidation occurs at least with three overlapping events, producing $\text{Ln}_2\text{O}_2\text{SO}_4$ as a stable intermediate. After this event, the stable intermediates decomposed to the respective oxides as a final residue (La_2O_3 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 and Gd_2O_3). For the cerium compound, the decomposition of organic matter occurs directly to the CeO_2 without the formation of the stable intermediate. These results indicate that the stability of the compounds decreases with the decreasing ionic radius of the lanthanide ions.

$\text{La}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$

The TG–DTA curves are shown in Fig. 3a. The dehydration process occurs between 330 and 449 K, with mass loss

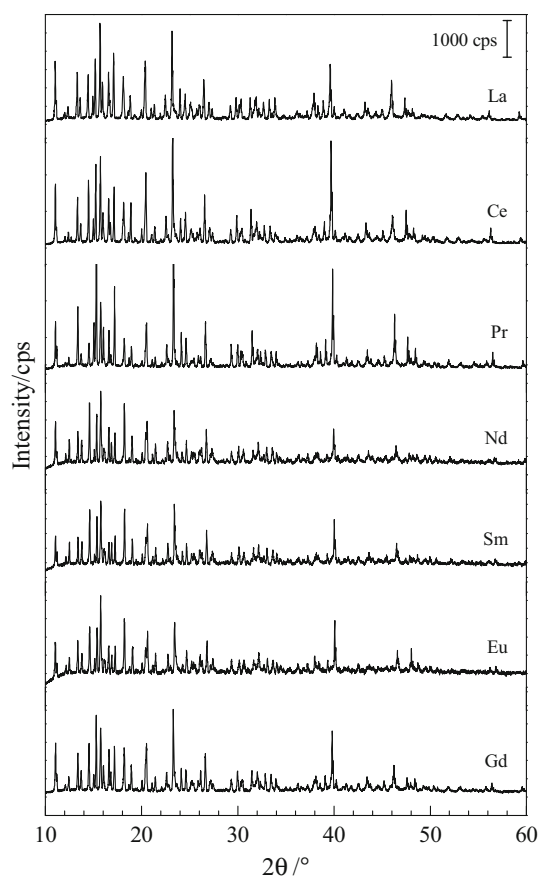


Fig. 2 X-ray diffraction pattern of the trivalent lanthanide compounds

of 18.8% ($\approx 8\text{ H}_2\text{O}$) associated with an endothermic peak at 389 K in DTA curve. In DSC curve, this event was evaluated and an enthalpy of 539 kJ mol^{-1} was calculated (Fig. 4). The anhydrous compound is stable up to 529 K and after this temperature the thermal decomposition of organic material occurs until 1083 K, with the formation of $\text{La}_2\text{O}_2\text{SO}_4$ as stable intermediate (Fig. 3a) and X-ray diffraction patterns (Fig. 5). In these steps were observed

Table 1 Elemental analysis of the solid Ln^{3+} sulfanilates

Compound	% C		% H		% N		% S	
	Calc.	EA	Calc.	EA	Calc.	EA	Calc.	EA
$\text{La}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	27.17	28.07	4.30	4.06	5.26	5.65	12.03	12.36
$\text{Ce}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 7\text{H}_2\text{O}$	27.62	28.34	4.13	4.08	5.37	5.59	12.29	12.83
$\text{Pr}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	26.97	27.59	4.28	4.11	5.24	5.40	12.00	12.36
$\text{Nd}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	26.86	27.29	4.26	4.09	5.22	5.46	11.95	12.39
$\text{Sm}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	26.66	27.50	4.23	4.14	5.18	5.46	11.86	12.42
$\text{Eu}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	26.60	26.99	4.23	4.08	5.17	5.47	11.84	12.21
$\text{Gd}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$	26.43	26.98	4.20	4.08	5.14	5.45	11.76	12.24

two exothermic peaks at 723 and 843 K. The $\text{La}_2\text{O}_2\text{SO}_4$ is stable up to 1483 K °C when its decomposition takes place to produce La_2O_3 . At 1573 K, the final residue is a mixture of $\text{La}_2\text{O}_2\text{SO}_4$ and La_2O_3 .

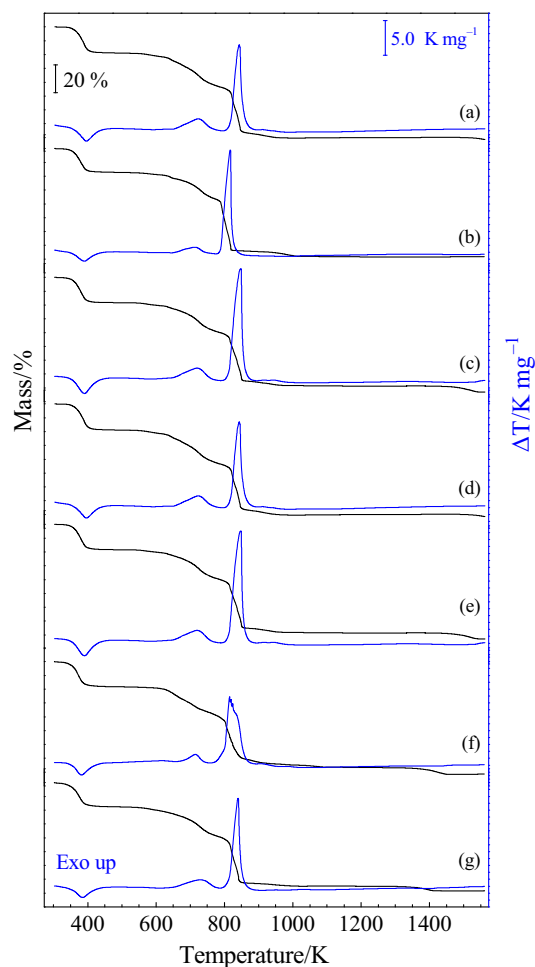


Fig. 3 TG–DTA curves: (a) $\text{LaL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 4.304$ mg), (b) $\text{CeL}_3 \cdot 7\text{H}_2\text{O}$ ($m = 3.426$ mg), (c) $\text{PrL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 5.343$ mg), (d) $\text{NdL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 4.299$ mg), (e) $\text{SmL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 5.342$ mg), (f) $\text{EuL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 4.207$ mg) and (g) $\text{GdL}_3 \cdot 8\text{H}_2\text{O}$ ($m = 4.005$ mg)

$\text{Ce}(\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3)_3 \cdot 7\text{H}_2\text{O}$

The TG–DTA curves are shown in Fig. 3b. The dehydration occurs between 325 and 441 K, with mass loss of 16.8% ($\approx 7 \text{H}_2\text{O}$) characterized by an endothermic peak in DTA curve at 390 K, as can be seen in Fig. 3b. From DSC data, this event was evaluated with dehydration enthalpy of 495 kJ mol^{-1} (Fig. 4) and the anhydrous compound remains stable up to 809 K. The thermal decomposition of organic material occurs between 536 and 1013 K, with the formation of the respective oxide CeO_2 (Fig. 5). Two exothermic peaks are observed in DTA and DSC curves for

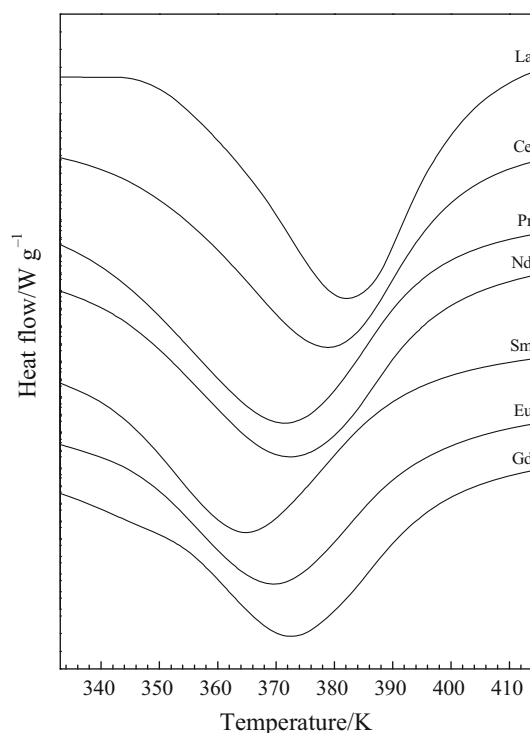


Fig. 4 DSC curves of all compounds showing the dehydration step

Table 2 Thermal analytical data from TG, DTA and DSC curves

Sample	M.M./g mol ⁻¹		% H ₂ O		$\Delta H_{(\text{dehydr})}$ kJ mol ⁻¹	% metal		% Ln ₂ O ₂ SO ₄		% residue	
	Calc.	TG	Calc.	TG		Calc.	TG	Calc.	TG	Calc.	TG
$\text{LaL}_3 \cdot 8\text{H}_2\text{O}$	799.53	806.71	18.02	18.75	539	17.37	17.22	25.38	23.38	20.38	19.56*
$\text{CeL}_3 \cdot 7\text{H}_2\text{O}$	782.73	789.35	16.11	16.81	495	17.90	17.75	–	–	21.99	22.50
$\text{PrL}_3 \cdot 8\text{H}_2\text{O}$	801.53	805.99	17.98	18.43	536	17.58	17.48	25.57	25.58	21.23	16.97*
$\text{NdL}_3 \cdot 8\text{H}_2\text{O}$	804.86	814.37	17.90	18.86	524	17.92	17.71	25.88	23.78	20.90	18.84*
$\text{SmL}_3 \cdot 8\text{H}_2\text{O}$	810.99	816.19	17.77	18.29	431	18.55	18.43	26.43	25.16	21.46	21.33
$\text{EuL}_3 \cdot 8\text{H}_2\text{O}$	812.59	816.51	17.73	18.14	420	18.71	18.06	26.58	23.39	21.66	21.55
$\text{GdL}_3 \cdot 8\text{H}_2\text{O}$	817.88	810.34	17.61	16.85	412	19.26	19.41	27.06	25.44	22.16	22.37

M.M. molar mass

* Incomplete decomposition up to 1573 K

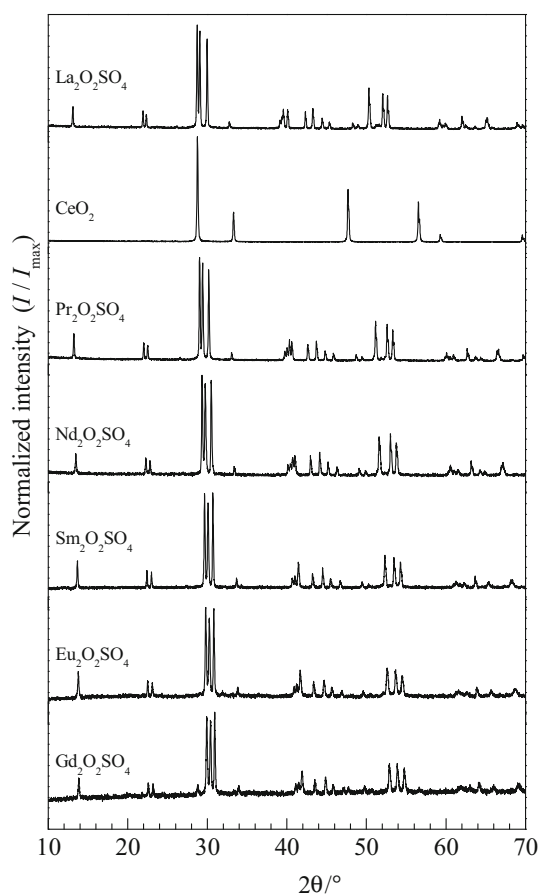


Fig. 5 X-ray diffraction pattern of the samples after heating at 1273 K for 2 h in a muffle furnace

this step, the first one at 714 K and another at 817 K. There was no observed stable intermediate for this compound.

Pr(NH₂C₆H₄SO₃)₃·8H₂O

The TG–DTA curves are shown in Fig. 3c. The dehydration process occurs in the range of 313–447 K with mass loss of 18.4%, attributed to dehydration (≈ 8 H₂O) associated with an endothermic peak in DTA curve at 390 K. In the DSC analysis, the enthalpy was evaluated around 536 kJ mol⁻¹ (Fig. 4). The anhydrous compound is stable up to 517 K and after this temperature, the thermal decomposition of the sulfanilate ligand takes place between 517 and 991 K, producing a stable intermediate Pr₂O₂SO₄ (Fig. 5), associated with exothermic peaks at 721 and 846 K in both DTA and DSC curves. The last event is the partial thermal decomposition of Pr₂O₂SO₄ to Pr₆O₁₁ above 1553 K. At 1573 K, the final residue is a mixture of Pr₂O₂SO₄ and Pr₆O₁₁.

Nd(NH₂C₆H₄SO₃)₃·8H₂O

The TG–DTA curves are shown in Fig. 3d. As can be noted, the initial mass loss of 18.6% is in agreement with the release of eight water molecules and this event was associated with an endothermic peak in DTA and DSC curves (397 K). The dehydration enthalpy found for this compound was 524 kJ mol⁻¹ (Fig. 4) in the DSC analysis. The anhydrous compound is stable up to 529 K and the thermal decomposition of organic material takes place between 529 and 1033 K, with exothermic peaks in DTA and DSC curves at 723 and 843 K, respectively. The Nd₂O₂SO₄ (Fig. 5) was obtained as a stable intermediate between 1033 and 1473 K, and after this temperature, its decomposition takes place producing a mixture of Nd₂O₂SO₄ and Nd₂O₃ as final residue at 1573 K.

Sm(NH₂C₆H₄SO₃)₃·8H₂O

The TG–DTA curves are shown in Fig. 3e. The initial mass loss of 18.3% (8 H₂O) is characterized by an endothermic peak ($T_{\text{peak}} = 391$ K) in the DTA curve and an enthalpy of 431 kJ mol⁻¹ in the DSC curve (Fig. 4). The anhydrous compound is stable between 440 and 515 K, and the thermal decomposition of organic contents occurs in the range of 515 and 991 K, where Sm₂O₂SO₄ is produced (Fig. 5). In this last step, two exothermic peaks at 721 and 849 K are observed. The stable intermediate starts its decomposition only in higher temperature than 1553 K producing the samarium oxide as a final residue.

Eu(NH₂C₆H₄SO₃)₃·8H₂O

The TG–DTA curves are shown in Fig. 3f. The initial mass loss of 18.1% (8 H₂O) is characterized by an endothermic peak at 387 K, and the dehydration enthalpy of 420 kJ mol⁻¹ was evaluated by means of DSC analysis (Fig. 4). The anhydrous compound is stable up to 573 K where the second event of mass loss takes place until 1111 K with two exothermic peaks at 716 and 814 K, producing the Eu₂O₂SO₄ (Fig. 5) as a stable intermediate. The Eu₂O₂SO₄ is stable until 1314 K, and after this temperature the europium oxide is obtained as a final residue from 1453 K.

Gd(NH₂C₆H₄SO₃)₃·8H₂O

The TG–DTA curves are shown in Fig. 3g. For this sample, the dehydration process occurs with an initial mass loss of 16.9% corresponding to eight water molecules released and an endothermic peak at 383 K in DTA curve. The dehydration enthalpy was evaluated in 412 kJ mol⁻¹ in the DSC analysis (Fig. 4). The anhydrous compound is

stable up to 526 K, and above this temperature the decomposition of organic material occurs up to 1037 K, showing two exothermic peaks associated with this event at 728 and 821 K in DTA curve. The decomposition of organic material produces the $\text{Gd}_2\text{O}_2\text{SO}_4$ (Fig. 5) that is stable until 1311 K where the gadolinium oxide is formed as a final residue at 1423 K.

These results indicate that the thermal stability of the compound decreases for the lanthanide ions with lower ionic radius.

From the TG–DTA data, it was possible to establish a general formula to the compound as $\text{LnL}_3 \cdot n\text{H}_2\text{O}$, where Ln represents trivalent lanthanide ions (La, Ce, Pr, Nd, Sm, Eu and Gd), L is 4-amino-benzenesulfonate anion ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$) and $n = 7$ (Ce) and 8 (La, Pr, Nd, Sm, Eu and Gd). The DTA curves show that organic material decomposition ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$) occurred in consecutive steps with, at least, two or three exothermic peaks, related to release of CO_2 , H_2O and SO_3 gases.

When heated at 1273 K for 2 h in a muffle furnace, the compounds formed the respective dioxysulfates ($\text{Ln}_2\text{O}_2\text{SO}_4$). The formation of a stable intermediate, $\text{Ln}_2\text{O}_2\text{SO}_4$, during the thermal decomposition of these compounds based on the TG–DTA curves was confirmed by comparison with the diffraction pattern for $\text{La}_2\text{O}_2\text{SO}_4$ (JCPDF No. 01-085-1534), as can be seen in Fig. 5. All dioxysulfates obtained are isomorphic. For cerium, the formation of CeO_2 was also confirmed.

Conclusions

The infrared spectroscopic data indicate that the trivalent coordination of lanthanide ions occurs through the sulfonic group and the bands observed were associated with the stretches (ν O–H, ν N–H and ν SO_3) and deformations (δ H–S–H and δ H–C–H). The X-ray powder diffraction suggests that the compounds are crystalline and the formation of an isomorphic series. TG–DTA analysis provided previously unreported information concerning the thermal behavior and thermal decomposition of these compounds, and based on the TG curves, a general formula could be established for the synthesized compounds: $\text{LnL}_3 \cdot n\text{H}_2\text{O}$, where Ln = (La, Ce, Pr, Nd, Sm, Eu and Gd); L = ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$) and $n = 7$ for Ce^{3+} and 8 for (La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} and Gd^{3+}). The dehydration process occurs in a single step up to 453 K and the enthalpy of dehydration decreases from La^{3+} to Gd^{3+} as a consequence of the decrease in the ionic radius of the lanthanide ion. The thermal decomposition of all compounds, except cerium, presented in its thermal pathway a

stable intermediate $\text{Ln}_2\text{O}_2\text{SO}_4$, which subsequently decompose to their respective oxides. For the La^{3+} , Pr^{3+} and Nd^{3+} sulfanilates, the formation of residual oxide occurs above 1573 K and in the present work it was obtained as a mixture. The formation of $\text{Ln}_2\text{O}_2\text{SO}_4$ was verified by X-ray diffraction after heating at 1273 K for 2 h.

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