

Thermal degradation study of gadolinium and lutetium methanesulfonates

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Abstract

The synthesis, characterization and thermal degradation study of gadolinium and lutetium methanesulfonates is reported. The prepared salts were characterized by elemental analysis and infrared spectroscopy. The thermal degradation study was performed by using thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). By using thermogravimetric data, a kinetic study of the dehydration of Gd and Lu methanesulfonates is performed employing the Coats–Redfern and Zsakó methods. It is verified that under heating, the gadolinium and lutetium methanesulfonates suffer three main processes: dehydration, thermal degradation and oxide formation. The thermal degradation products were characterized by infrared spectroscopy and X-diffractometry. Furthermore, depending on the atmosphere nature, i.e. inert or oxidant, the thermal degradation process could be endothermic (N₂) or exothermic (air).

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1. Introduction

The first work dealing with the methanesulfonate anion (CH₃SO₃[−]) was developed by Dawson et al. [1]. Caesium and sodium methanesulfonates have been previously investigated from a spectroscopic point of view [2]. With respect to lanthanides, a di-hydrated lanthanum methanesulfonate have been studied, from both, structural and thermogravimetric point of view [3]. Furthermore, Aricó et al. [4,5] have investigated the methanesulfonates of La(III), Nd(III), Er(III), Yb(III), Ce(III), Sm(III) and Tb(III), providing very important information about the structures, chemical and physical properties of such class of compounds.

The aim of this article is to report the synthesis, characterization and thermal degradation study of gadolinium and lutetium methanesulfonates. The prepared salts were characterized by elemental analysis and infrared spectroscopy. The thermal degradation study was performed by using thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

The present study is compared with those previously performed [6–8] since the temperature range now considered (298–623 K) is larger than that previously studied (298–173 K). Furthermore, a complete characterization of the residues after thermal degradation is now performed, as well a kinetic study of the thermal dehydration process for Gd and Lu methanesulfonates.

2. Experimental

All reagents were of analytical grade and were employed without further purification.

The Gd(III) and Lu(III) methanesulfonates were prepared from the respective hydroxycarbonates. The hydroxycarbonates were prepared as follows: 10.0 g of Gd₂O₃ or Lu₂O₃ was suspended in 10.0 cm³ of deionized water, and then was added, under heating, dropwise, a 10% HCl solution until the complete dissolution of the oxides. The obtained solution was evaporated and then diluted to deionized water until a 50 cm³ volume, followed by filtration. Then, more deionized water was added until a 800 cm³ volume was reached. The pH of the solution was in the 3–4 range, and it was

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then heated to boiling. To this last solution was added a 1.0 mol dm^{-3} urea solution until the complete precipitation of the hydroxycarbonates. The obtained hydroxycarbonates were then exhaustively washed with deionized water and dried at room temperature for 12 h, and then dried at 350 K for another 24 h.

The Gd(III) and Lu(III) methanesulfonates were synthesized as follows: 2.0 g of the respective hydroxycarbonate was suspended in 20.0 cm^3 of deionized water. Then, to the boiling suspension was added, dropwise, methanesulfonic acid. The solution obtained was filtered off. The residue was composed of unreacted hydroxycarbonates, and the solution was then evaporated in a water bath. The solids obtained were then dried at room temperature and stored under vacuum in a desiccator.

The CHN elemental analysis results were performed in an elemental analyzer, model 2400 from Perkin-Elmer.

The infrared spectra were obtained in KBr discs on a 1750 Perkin-Elmer spectrophotometer. The metal contents were obtained by EDTA titration, and for sulfur determination the volumetric method of Schöniger was employed [9].

The thermogravimetric curves were obtained in a TGA-50 apparatus from Shimadzu, under nitrogen and air atmosphere at a heating rate of 10 K min^{-1} . To obtain a “large” mass of the final residues from the thermal degradation of the studied methanesulfonates (for X-ray analysis), a TGA-51 apparatus from Shimadzu was used, and the TG curves were obtained under nitrogen atmosphere at a heating rate of 20 K min^{-1} .

The TG–DTA curves were obtained with a SDT1500 equipment from TA Instruments. The DSC curves were obtained by using a Shimadzu DSC-50 apparatus. Both, TG–DTA and DSC curves were obtained under nitrogen

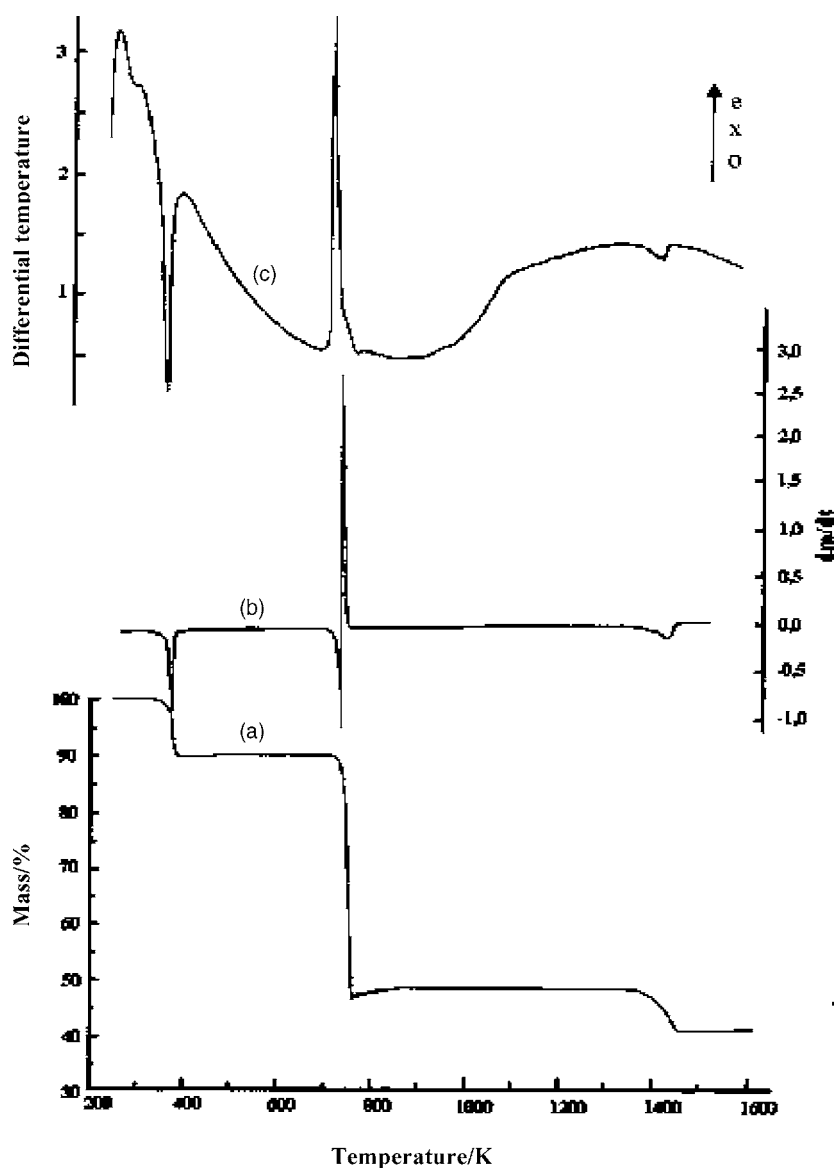


Fig. 1. TG (a), DTG (b) and DTA (c) curves for $\text{Gd}(\text{MS})_3 \cdot 3\text{H}_2\text{O}$ obtained under air atmosphere.

atmosphere at a heating rate of 10 K min^{-1} . The TG–DTA curves were also obtained under air atmosphere.

The X-ray diffraction patterns were obtained using a Phillips PW 1710 diffractometer (Cu $K\alpha$ radiation).

By using thermogravimetric data, a kinetic study of the dehydration of Gd and Lu methanesulfonates is performed employing the Coats–Redfern [10] and Zsakó [11] methods.

3. Results and discussion

The obtained elemental analysis results, and the respective proposed formulas are summarized in Table 1. It was verified that the synthesized methanesulfonates are very hygroscopic. The main infrared bands for the synthesized compounds are summarized in Table 2. All infrared bands obtained are in good agreement with the previously reported results [2,6–8] and confirm the identity of the synthesized methanesulfonates.

Table 1
Elemental analysis results for Gd and Lu methanesulfonates

Proposed formula	Gd(MS) ₃ ·3H ₂ O	Lu(MS) ₃ ·4H ₂ O
Metal	30.8 (31.7)	32.6 (32.9)
Carbon	7.2 (7.3)	6.5 (6.8)
Hydrogen	3.0 (3.0)	3.2 (3.2)
Sulfur	18.1 (19.4)	17.7 (18.1)
H ₂ O	10.9 (10.9)	13.5 (13.5)

Calculated values are in parenthesis. MS: methanesulfonate.

The TG, DTG and DTA curves for the studied methanesulfonates obtained in air and nitrogen atmospheres are shown in Figs. 1–4. The mass loss processes and their respective enthalpy variations are summarized in Table 3. Under heating, the studied methanesulfonates suffers three main processes: dehydration, thermal degradation and oxide formation. In Table 3, T_1 is related with the salt dehydration, T_2 with the salt thermal degradation and T_3 with the respective oxide formation. As can be observed in DTA

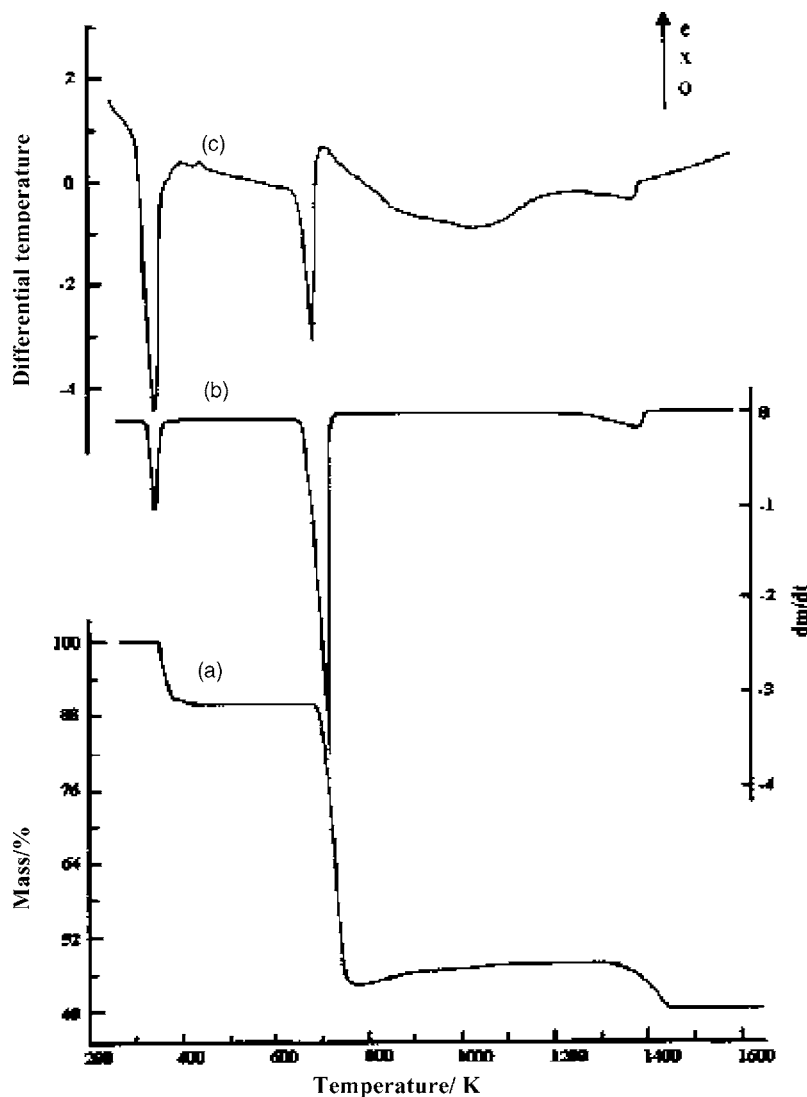


Fig. 2. TG (a), DTG (b) and DTA (c) curves for Gd(MS)₃·3H₂O obtained under nitrogen atmosphere.

Table 2
Main infrared band for the synthesized methanesulfonates

Bands ^a (cm ⁻¹)	Gd(MS) ₃ ·3H ₂ O	Lu(MS) ₃ ·4H ₂ O
$\nu_s(\text{OH})$ (s)	3397	3413
$\nu_{\text{as}}(\text{CH})$ (w)	3027	3019
$\nu_s(\text{CH})$ (w)	2939	2935
$\delta_s(\text{HOH})$ (s)	1644	1650
$\delta_{\text{as}}(\text{CH}_3)$ (w)	1412	1421
$\delta_s(\text{CH}_3)$ (w)	1335	1334
$\nu_{\text{as}}(\text{SO})$ (s)	1211	1207
$\nu_s(\text{SO})$ (m)	1078	1049
$\varpi(\text{CH}_3)$ (m)	967	963
$\nu(\text{CS})$ (m)	786	785

^a (s): strong; (m): medium; (w): weak; s: symmetric; as: asymmetric.

curves and Table 3 data, depending on the atmosphere nature, i.e. inert or oxidant, the thermal degradation process could be endothermic (N₂) or exothermic (air). So, is verified that under an oxidant atmosphere, the rupture of the

metal–ligand bonds (an endothermic process) is followed by the combustion of the organic moiety (an very exothermic process). As can be observed form TG and DTG curves, the gadolinium methanesulfonate suffers dehydration (loss of three water molecules per mole) at one single mass loss step, whereas the lutetium compound exhibits two distinct mass loss steps due to the release of water molecules.

For the thermal degradation process, only the mass loss variations is not enough to make a safe attribution to the identity of the compound formed around 700 K. However, it could be supposed that it is a mixture of sulfate, sulfite and dioxide. To clarify this question, the solid residues after thermal degradation of the methanesulfonates under nitrogen atmosphere were collected at 673, 873, 1073, 1273 and 1623 K, and were analyzed by infrared spectroscopy and X-ray diffractometry.

The infrared spectra for the thermal degradation residues isolated at the previously considered temperatures are shown

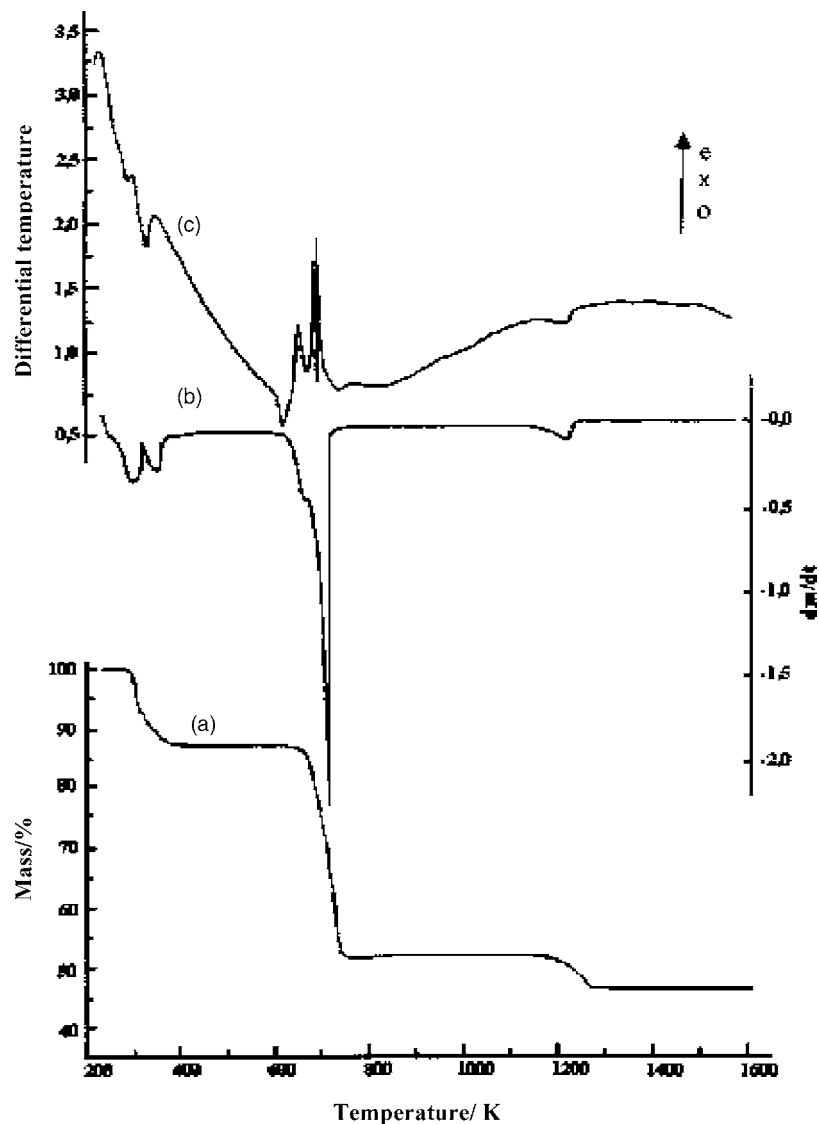


Fig. 3. TG (a), DTG (b) and DTA (c) curves for Lu(MS)₃·4H₂O obtained under air atmosphere.

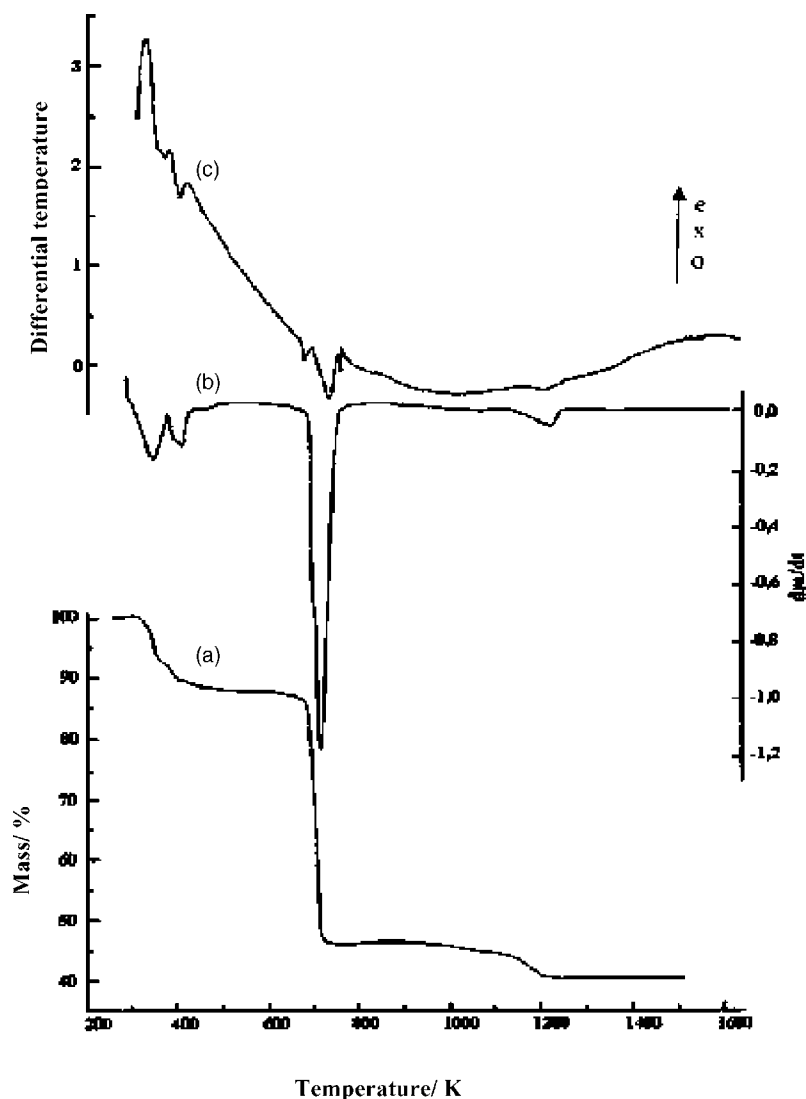


Fig. 4. TG (a), DTG (b) and DTA (c) curves for $\text{Lu}(\text{MS})_3 \cdot 4\text{H}_2\text{O}$ obtained under nitrogen atmosphere.

in Figs. 5 and 6. The main infrared bands for such compounds are summarized in Table 4. These bands are characteristics of the sulfate group in the oxo-sulfates, and are named ν_1 , ν_3 and ν_4 , respectively [12,13].

The X-ray diffraction patterns for the residues after thermal degradation of Gd and Lu methanesulfonates at 673, 873, 1033, 1273 and 1623 K under nitrogen atmosphere are shown in Figs. 7 and 8, respectively. Based on these X-ray

Table 3
Summary for TG and DTA process for Gd and Lu methanesulfonates thermal degradation

	TG						DTA		
	T_1	Δm	T_2	Δm	T_3	Δm	T_1	T_2	T_3
Gd									
N ₂	398	-10.0	753	-45.3	1419	-8.0	384 (-)	701 (-), 707 (+)	1420 (-)
Air	396	-10.3	763	-44.0	1458	-8.0	398 (-)	756, 764 (+)	1458 (-)
Lu									
N ₂	335, 386	-13.5	730	-42.6	1215	-6.0	351, 386 (-)	665, 721, 746 (-)	1215 (-)
Air	352, 389	-13.0	707, 743	-38.9	1272	-6.3	350, 387 (-)	661 (-), 701, 738, 746 (+)	1274 (-)

T are the "onset" temperatures on DTG and DTA curves. Δm is the percentage mass loss. (+) is for an exothermic process and (-) is for an endothermic one. T_1 is related with the salt dehydration, T_2 with the salt thermal degradation and T_3 with the respective oxide formation.

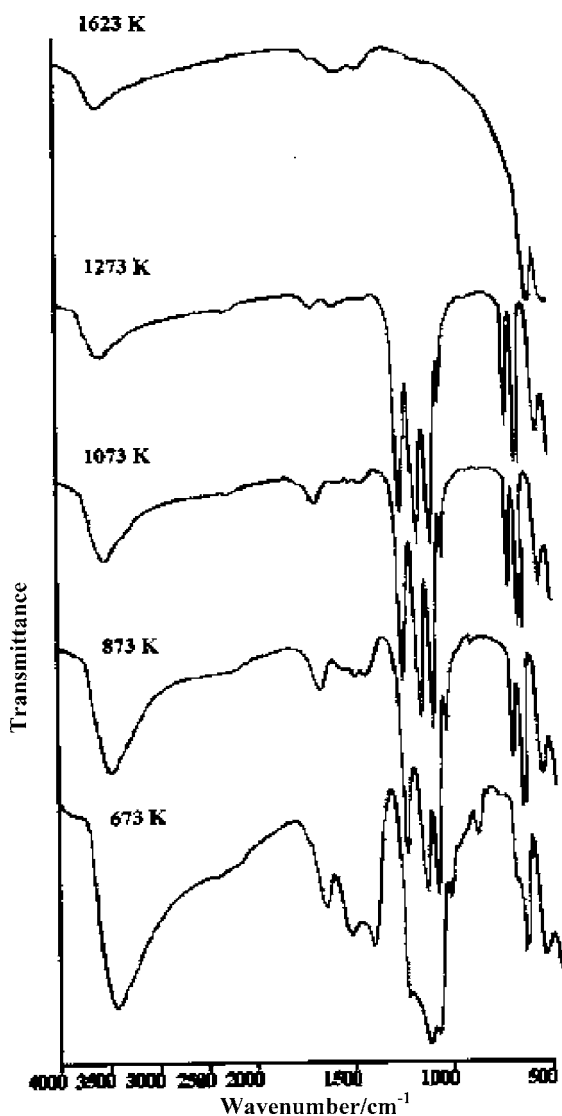


Fig. 5. Infrared spectra for residues after thermal degradation of $\text{Gd}(\text{MS})_3 \cdot 3\text{H}_2\text{O}$ at different temperatures.

data, and by comparison with standard X-ray profiles [14] can be concluded that after thermal degradation under nitrogen atmosphere, the main species are Ln_2S_3 (673 K), $\text{Ln}_2\text{O}_2\text{SO}_4$ (873–1273 K) and Ln_2O_3 (at 1623 K and above),

Table 4

Infrared bands for the residues after thermal degradation of Gd and Lu methanesulfonates at different temperatures under nitrogen atmosphere

	T (K)	ν_3			ν_1			ν_4
Gd	673	1221	1115	1066	1002	667	620	603
	873	1218	1116	1060	1000	667	620	602
	1073	1215	1120	1059	1000	665	620	604
	1273	1214	1125	1057	999	665	619	605
Lu	673	1210	1126	1064	1003	662	612	–
	873	–	1134	1067	1008	670	617	–
	1073	1241	1133	1061	1006	673	618	–
	1273	1240	1134	1060	106	673	616	–

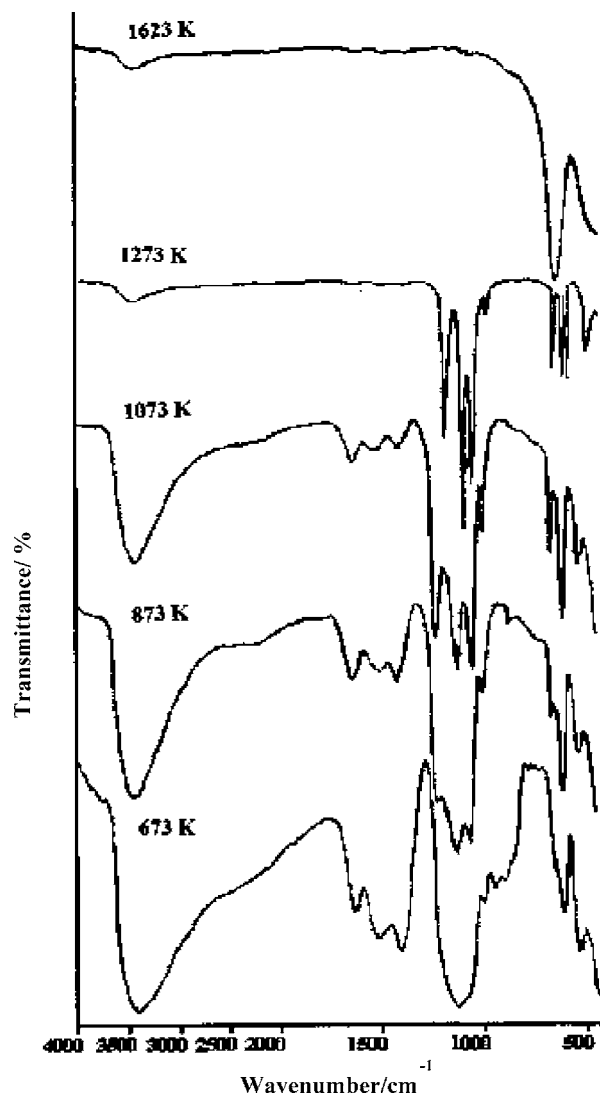


Fig. 6. Infrared spectra for residues after thermal degradation of $\text{Lu}(\text{MS})_3 \cdot 4\text{H}_2\text{O}$ at different temperatures.

$\text{Ln} = \text{Gd}$ or Lu . This conclusion is also reinforced by infrared data. Furthermore, the residue isolated at 673 K is yellow, whereas those isolated at higher temperatures are white. It is also verified that residues isolated at higher temperatures exhibit a higher crystallinity, and larger grain sizes.

The dehydration and thermal decomposition enthalpies for the studied methanesulfonates, as obtained by DSC curves are presented in Table 5. As can be verified, the gadolinium methanesulfonate exhibits a larger dehydration

Table 5

Dehydration and thermal decomposition enthalpies for Gd and Lu methanesulfonates as obtained by DSC curves under nitrogen atmosphere

Compound	Dehydration		Degradation	
	T (K)	ΔH (kJ mol^{-1})	T (K)	ΔH (kJ mol^{-1})
$\text{Gd}(\text{MS})_3 \cdot 3\text{H}_2\text{O}$	385	153.3	765	–254.6
$\text{Lu}(\text{MS})_3 \cdot 4\text{H}_2\text{O}$	345, 372	28.2, 39.2	703	181.3

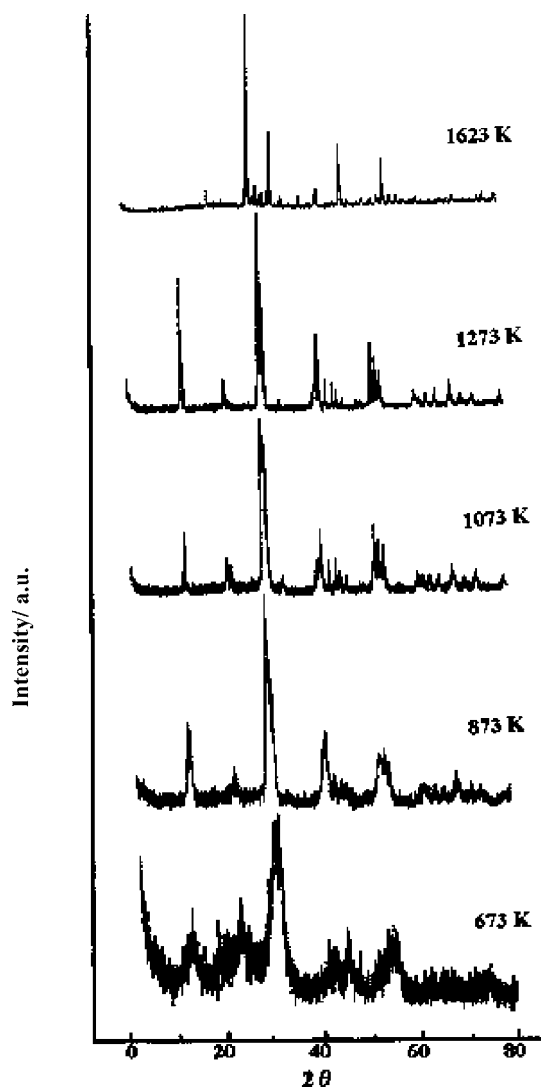


Fig. 7. X-ray diffraction patterns for residues after thermal degradation of $\text{Gd}(\text{MS})_3 \cdot 3\text{H}_2\text{O}$ at different temperatures.

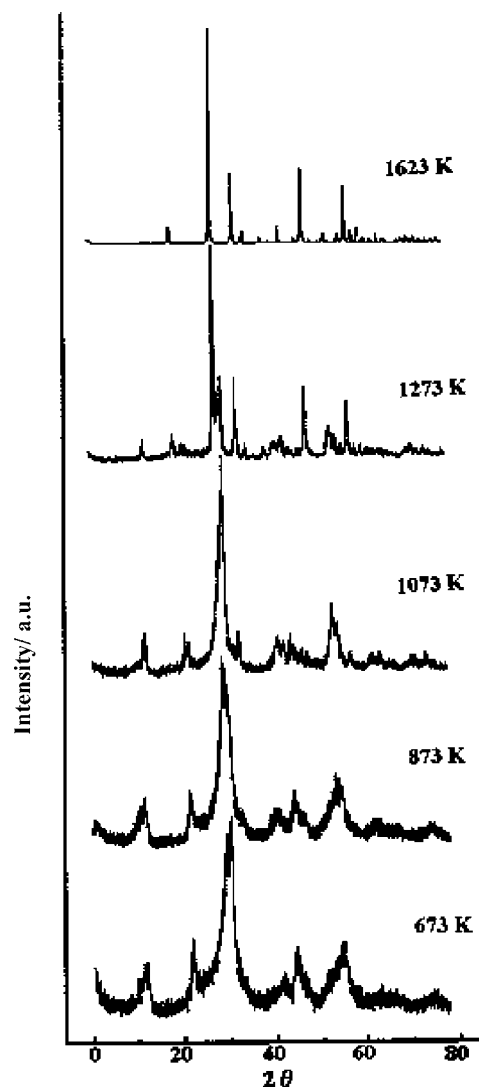


Fig. 8. X-ray diffraction patterns for residues after thermal degradation of $\text{Lu}(\text{MS})_3 \cdot 4\text{H}_2\text{O}$ at different temperatures.

and enthalpy. Such fact suggests a correlation with the atomic and ionic radius, since gadolinium is the largest cation. The DSC curves are shown in Fig. 9. In DSC curve (b) are observed the two endothermic peaks due to dehydration in two distinct steps. As can be verified in Table 5 data, the second water mass loss is more endothermic than the first.

The calculated kinetic parameters for the dehydration processes are summarized in Table 6. These parameters were calculated only for the gadolinium compound, since its TG curve was most “well behaved”, which makes the calculation process most easy. As can be verified, both employed calculations methods provide similar results. Furthermore, the activation energy values are a function of the heating rate, and higher heating rates are associated with lower activation energies. Such differences could be attributed to the increase in the intra and intermolecular vibrations with the increase in the temperature values. That is, the thermal degradation

Table 6
Kinetic parameters for the dehydration of Gd methanesulfonate ($\text{Gd}(\text{MS})_3 \cdot 3\text{H}_2\text{O}$)

Method	β	r	E_a	K_0	n
CR	2.5	0.988	134	3.7×10^{18}	1
	5	0.998	106	2.6×10^{14}	1
	10	0.998	103	7.0×10^{13}	1
	20	0.991	109	1.5×10^{14}	1
Z	2.5	0.990	134	4.5×10^{18}	1
	5	0.998	106	2.3×10^{14}	1
	10	0.998	103	8.3×10^{13}	1
	20	0.992	108	1.8×10^{14}	1

CR: Coats–Redfern method; Z: Zsakó method; β : heating rate (K s^{-1}); r : coefficient of correlation; E_a : activation energy (kJ mol^{-1}); K_0 : frequency or pre-exponential factor (s^{-1}); n : order of reaction.

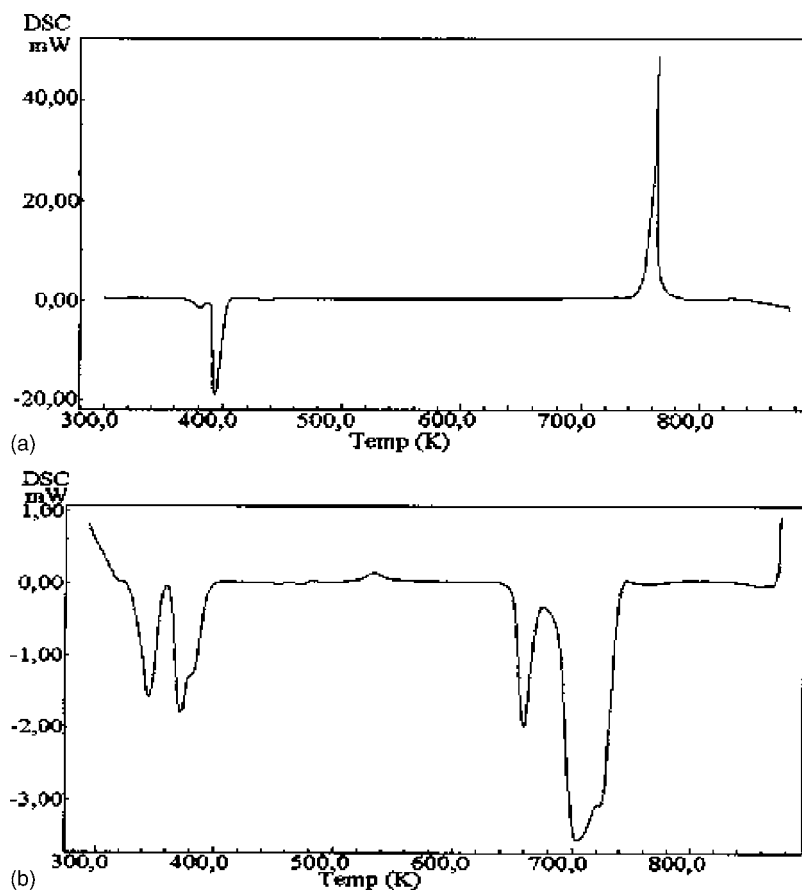


Fig. 9. DSC curves for Gd(MS)₃·3H₂O (a) and Lu(MS)₃·4H₂O (b).

process is, for higher temperatures (higher vibrations) more favorable, requiring lower activation energies.

4. Conclusion

Based on the obtained experimental results can be concluded that:

1. Under heating, the gadolinium and lutetium methanesulfonates suffers three main processes: dehydration, thermal degradation and oxide formation.
2. Depending on the atmosphere nature (inert, N₂, or oxidant, air), the thermal degradation process could be endothermic (N₂) or exothermic (air).
3. After thermal degradation under nitrogen atmosphere, the main species are Ln₂S₃ (673 K), Ln₂O₂SO₄ (873–1273 K) and Ln₂O₃ (at 1623 K and above), Ln = Gd or Lu.

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