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Synthesis and characterization of La methanesulfonate coordination compounds with pyridine-*N*-oxide and 2-, 3-, and 4-picoline-*N*-oxide

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Abstract

Synthesis, characterization and thermal (TG, DSC, GC–MS) study of the coordination compounds $La(MS)_3{\cdot}(pyNO)_2$, $La(MS)_3{\cdot}(2\text{-}picNO)_2$, $La(MS)_3{\cdot}(3\text{-}picNO)_2$ and $La(MS)_3{\cdot}(4\text{-}picNO)_{1.5}{\cdot}H_2O$ are reported. The observed thermal stability trend is 2-picNO $<$ pyNO $<$ 3-picNO $<$ 4-picNO. Under heating, the rupture of the La–*N*-oxide bond is promoted, together with fragmentation of the *N*-oxide molecule.

Keywords: Lanthanum; Coordination compounds; Thermogravimetry; DSC

1. Introduction

Thermal techniques have a prominent role in the study and understanding of the physical–chemical behavior and properties of coordination compounds [1]. Coordination compounds of lanthanide methanesulfonates and picoline-*N*-oxides are of interest because of their spectroscopic properties (luminescence) [2–4] but thermal study of such compounds is lacking. The aim of this publication is to report the synthesis, characterization and thermal (TG, DSC, GC–MS) study of the coordination compounds $La(MS)_3{\cdot}(pyNO)_2$, $La(MS)_3{\cdot}(2\text{-}picNO)_2$, $La(MS)_3{\cdot}(3\text{-}picNO)_2$ and $La(MS)_3{\cdot}(4\text{-}picNO)_{1.5}{\cdot}H_2O$. pyNO = pyridine-*N*-oxide, and 2-picNO, 3-picNO and 4-picNO are 2-, 3-, and 4-picoline-*N*-oxides, respectively.

2. Experimental

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

Lanthanum methanesulfonate was prepared from the hydroxycarbonate. The hydroxycarbonate was prepared as follows: 10.0 g of La_2O_3 was suspended in 10.0 cm^3 of deionized water, and then a 10% HCl solution was added dropwise, under heating, until complete dissolution of the oxide. The solution obtained was evaporated to dryness and then diluted with deionized water to 50 cm^3, followed by filtration. Then, more deionized water was added until an 800 cm^3 volume was reached. The solution with pH 3–4 was then heated to boiling and a 1.0 mol dm^{-3} urea solution added until the complete precipitation of the hydroxycarbonate. The hydroxycarbonate was exhaustively washed with deionized water, dried at room temperature for 12 h, and then dried at 350 K for another 24 h.

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

The lanthanum methanesulfonate coordination compounds were prepared as follows: solutions of pyridine-*N*-oxide, 2-picoline-*N*-oxide, 3-picoline-*N*-oxide or 4-picoline-*N*-oxide were mixed with lanthanum methanesulfonate dissolved in methanol. In a first synthetic attempt, the

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lanthanum methanesulfonate and the respective aromatic aminoxides were mixed in a 1:3 (mol:mol) stoichiometric ratio, with the aminoxides previously dissolved in acetone. By using this synthetic approach, the compounds with pyridine-*N*-oxide, 2-picoline-*N*-oxide and 3-picoline-*N*-oxide were prepared. The synthesis of the 4-picoline-*N*-oxide was achieved by using triethyl orthoformate as solvent for the aminoxide. The obtained compounds were then filtered off, washed with acetone or triethyl orthoformate. The obtained solids (all of them white) were then dried at room temperature and stored under vacuum.

The CHN elemental analysis results were performed in a model 2400 Perkin-Elmer elemental analyzer. Infrared spectra were obtained in KBr discs on a 1750 Perkin-Elmer spectrophotometer. Metal contents were obtained by EDTA titration, and sulfur determinations were done by the volumetric method of Schöniger [5].

Thermogravimetric curves were obtained in a TGA-50 apparatus from Shimadzu, under nitrogen atmosphere at four heating rates: 2.5, 5, 10 and 20 K min^{-1}. DSC curves were obtained with a Shimadzu DSC-50 apparatus, under nitrogen atmosphere and a heating rate of 10 K min^{-1}.

Analysis of the gaseous products released in thermal degradation of the compounds was done with a DTG–GC/MS Shimadzu apparatus, which is equivalent to the TG/DTA (DTG-50H) linked to a GCMS-QP 5000 system.

3. Results and discussion

Elemental analyses of the synthesized compounds are summarized in Table 1. The results are in good agreement with the proposed formulas. Infrared data (not shown) are also in agreement with those previously obtained for similar compounds [2–4] and confirm the identity of the synthesized adducts. The methanesulfonate ions, $H_3CSO_3^-$ are coordinated to La through oxygen. The picoline-*N*-oxide molecules are also coordinated through oxygen.

The thermogravimetric and derivative curves for the synthesized compounds obtained with a heating rate of 2.5 K min^{-1} are shown in Figs. 1–4. The mass loss steps observed for the studied compounds at all four heating rates, i.e. 2.5, 5, 10 and 20 K min^{-1}, are summarized in Table 2. As can be observed from Table 2 data, lower heating rates provide experimental mass loss steps in better agreement with the calculated values.

The pyridine-*N*-oxide and the 3-picoline-*N*-oxide compounds exhibit a single mass loss step associated with the release of *N*-oxide molecules, whereas the other two compounds exhibit more than one mass loss step. This suggests that for pyridine-*N*-oxide and the 3-picoline-*N*-oxide the two ligand molecules are located at energetically equivalent coordination sites whereas for the other two compounds, energetically nonequivalent coordination sites are used by the

Table 1
Elemental analysis of lanthanum methanesulfonate coordination compounds with pyNO, and 2-, 3- and 4-picNO[a]

Compound	M (%)	C (%)	H (%)	S (%)	N (%)
$La(MS)_3{\cdot}(pyNO)_2$	22.9 (22.6)	24.5 (25.4)	3.2 (3.1)	14.9 (15.6)	4.3 (4.6)
$La(MS)_3{\cdot}(2\text{-}picNO)_2$	21.1 (21.6)	28.6 (28.0)	3.3 (3.6)	13.9 (14.4)	4.5 (4.4)
$La(MS)_3{\cdot}(3\text{-}picNO)_2$	21.5 (21.6)	28.1 (28.0)	3.7 (3.6)	14.5 (14.4)	4.3 (4.4)
$La(MS)_3{\cdot}(4\text{-}picNO)_{1.5}{\cdot}H_2O$	22.2 (22.9)	24.1 (23.8)	3.6 (3.6)	12.2 (15.9)	3.5 (3.5)

[a] Calculated values are in parenthesis.

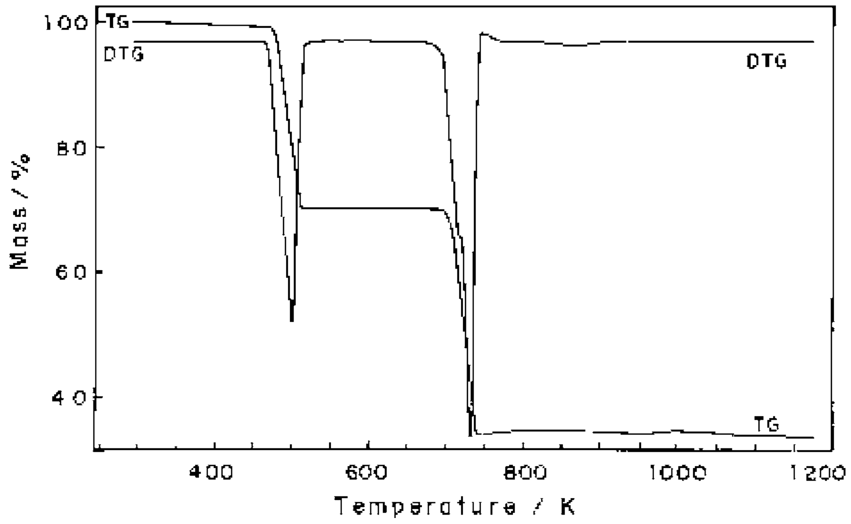

Fig. 1. Thermogravimetric and derivative curves for the compound $La(MS)_3{\cdot}(pyNO)_2$.

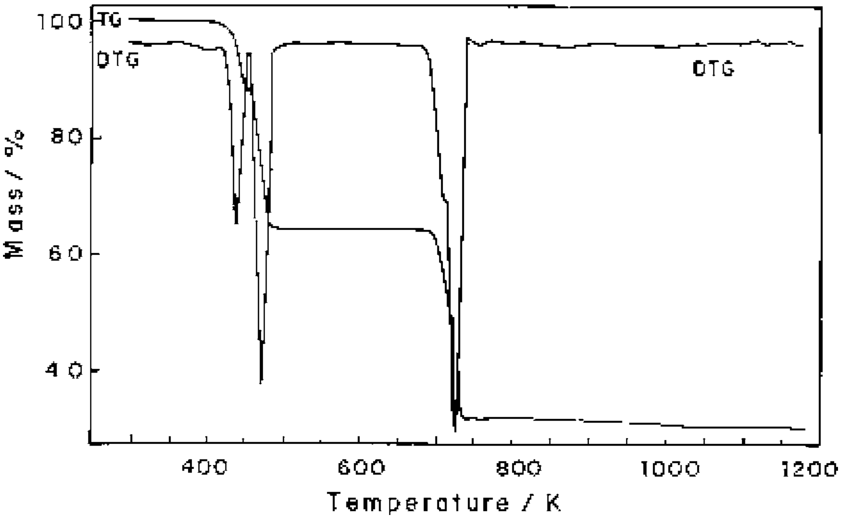

Fig. 2. Thermogravimetric and derivative curves for the compound $La(MS)_3 \cdot (2\text{-}picNO)_2$.

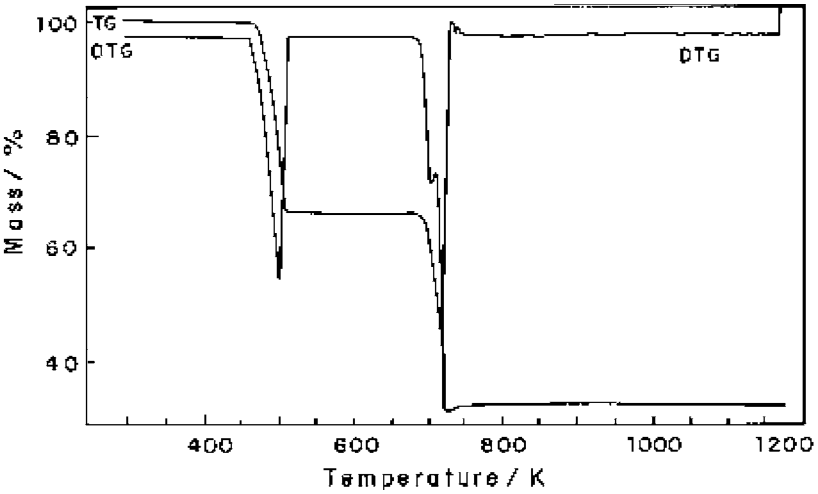

Fig. 3. Thermogravimetric and derivative curves for the compound $La(MS)_3 \cdot (3\text{-}picNO)_2$.

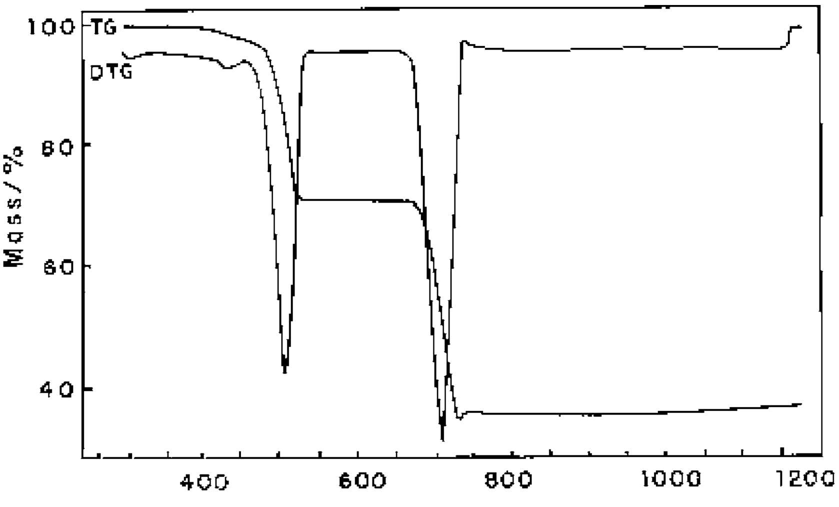

Fig. 4. Thermogravimetric and derivative curves for the compound $La(MS)_3 \cdot (4\text{-}picNO)_{1.5} \cdot H_2O$.

Table 2
Thermogravimetric results for the compounds studied[a]

Compound	β (K min^{-1})	ΔT (K)	Δm (%)	Δm_t (%)
$La(MS)_3 \cdot (pyNO)_2$	2.5	481–511	29.3	29.3
	5	489–523	20.2	29.3
	10	493–528	28.9	29.3
	20	503–529	29.0	29.3
$La(MS)_3 \cdot (2\text{-}picNO)_2$	2.5	386–402	0.6	
		429–447	11.3	
		460–481	23.7	35.6
	5	390–206	1.1	
		432–453	9.5	
		468–482	23.6	35.6
	10	399–410	0.6	
		435–451	8.8	
		475–507	24.1	35.6
	20	409–422	0.8	
		440–466	9.3	
		521–483	24.7	35.6
$La(MS)_3 \cdot (3\text{-}picNO)_2$	2.5	481–509	34.1	35.6
	5	489–521	34.1	35.6
	10	501–552	34.0	35.6
	20	511–550	34.0	35.6
$La(MS)_3 \cdot (4\text{-}picNO)_{1.5} \cdot H_2O$	2.5	418–487	2.1	
		446–519	27.1	29.2
	5	408–454	2.4	
		492–526	26.7	29.2
	10	411–461	2.0	
		506–557	27.5	29.2
	20	429–466	1.8	
		507–569	26.9	29.2

[a] β is the heating rate, ΔT the temperature range for the mass loss step, Δm the percentage mass loss associated with the temperature range and Δm_t the calculated mass loss for total release of the ligands.

Table 3
DSC results for the compounds studied[a]

Compound	ΔT (K)	ΔH (kJ mol^{-1})
$La(MS)_3 \cdot (pyNO)_2$	389–429	4.7
	472–550	243.8
$La(MS)_3 \cdot (2\text{-}picNO)_2$	407–423	23.5
	444–453	55.2
	495–512	177.7
$La(MS)_3 \cdot (3\text{-}picNO)_2$	473–528	264.6
$La(MS)_3 \cdot (4\text{-}picNO)_{1.5} \cdot H_2O$	390–459	67.3
	465–555	161.7

[a] ΔT is the temperature range for the enthalpy change and ΔH the enthalpy change.

N-oxide molecules. The observed thermal stability trend is: 2-picNO < pyNO < 3-picNO < 4-picNO. The lower thermal stability of the 2-picNO compound is probably due to the higher steric hindrance of the methyl group in the *ortho* position of the aromatic ring, i.e. for this ligand, the metal–ligand bond is probably longer and weaker. In the TG–DTG curves for the compound with 4-picNO, a first and minor mass loss step associated with the release of water molecules is observed, confirming the correctness of the proposed formula.

The DSC curves obtained are shown in Figs. 5–8. The main information extracted from the DSC curves are summarized in Table 3. There is a good correlation with the TG–DTG curves, i.e. a single endothermic peak is associated with release of *N*-oxide molecules in the pyNO and 3-picNO compounds. In the former compound, a minor endothermic peak is observed below the temperature range associated with ligand loss. This peak is probably associated with melting of the compound. Furthermore, with the exception of the 4-picNO compound, the adducts studied exhibit very similar enthalpy changes for the release of *N*-oxide molecules, in the order pyNO < 2-picNo < 3-picNO.

The gaseous products released in thermal degradation were characterized for the compounds $La(MS)_3 \cdot (pyNO)_2$ and $La(MS)_3 \cdot (3\text{-}picNO)_2$. Only these compounds were studied because both exhibit a single mass loss step due to the

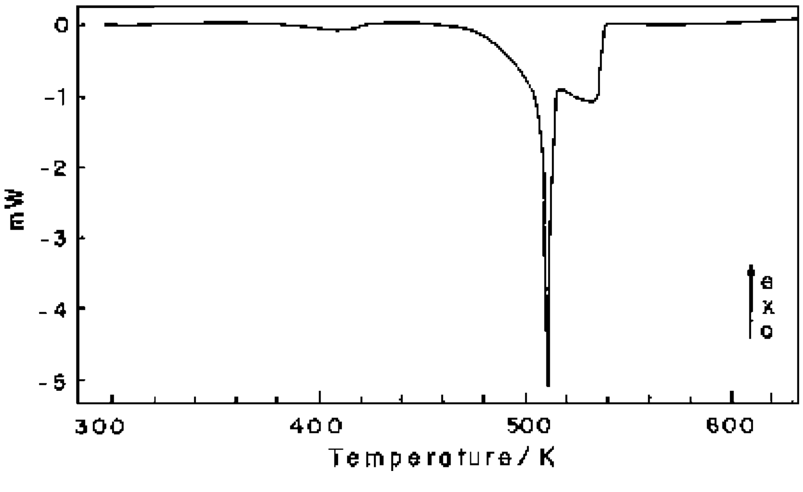

Fig. 5. DSC curve for the compound $La(MS)_3 \cdot (pyNO)_2$.

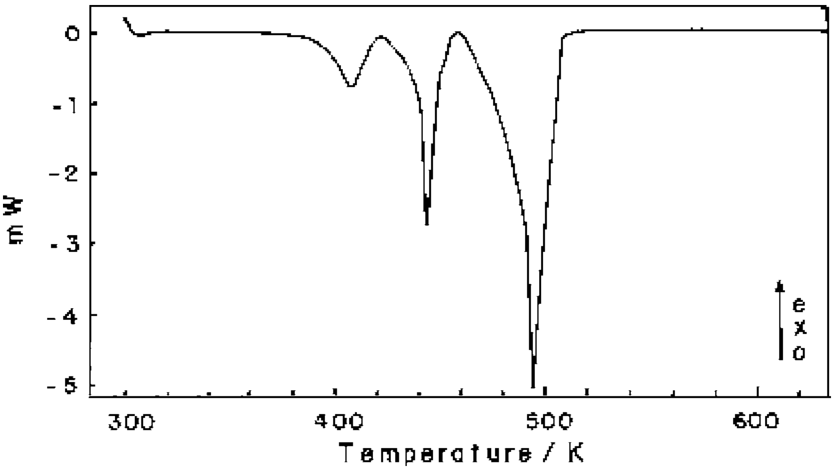

Fig. 6. DSC curve for the compound La(MS)$_3$·(2-picNO)$_2$.

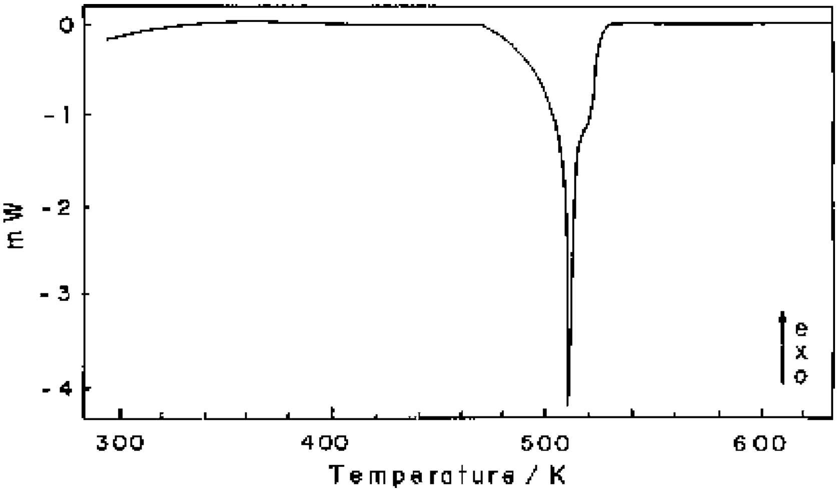

Fig. 7. DSC curve for the compound La(MS)$_3$·(3-picNO)$_2$.

release of ligand molecules, making the comparative study most straightforward.

The GC results, very intense peaks with mass/charge (*m*/*c*) ratio of 79 (py) and 93 (3-mpy), respectively, for pyNO and for 3-picNO compounds, confirm that the main gaseous products are pyridine and 3-methyl pyridine. The absence of pyNO and 3-picNO in the gaseous products could be attributed to the chemical instability of the NO

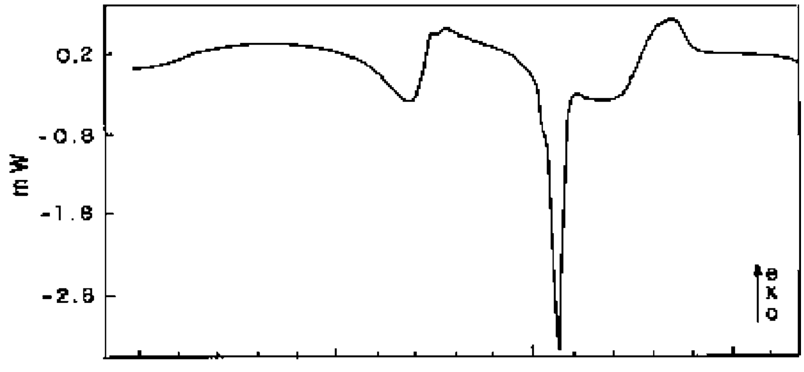

Fig. 8. DSC curve for the compound La(MS)$_3$·(4-picNO)$_{1.5}$·H$_2$O.

group towards reducing agents. Such reduction may have occurred in the fragmentation chamber of the mass spectrometer. For the $La(MS)_3 \cdot (pyNO)_2$ compound, a prominent peak at *m*/*c* ratio 52 is also observed, as well as less intense peaks at *m*/*c* 25 and 54. Thus, not only the rupture of the La–picoline-*N*-oxide bond is promoted under heating, but also fragmentation of the *N*-oxide molecule. This is also true for $La(MS)_3 \cdot (3\text{-}picNO)_2$ for which intense peaks at *m*/*c* 39 and 66 are observed, as well as less intense peaks at *m*/*c* 51 and 78 ($C_5H_4N^-$).

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