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THERMAL DECOMPOSITION AND INDIRECT STRUCTURAL DETERMINATION OF RARE EARTH ELEMENT PICRATES WITH THE *DTSO* LIGAND

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Abstract

The complexes [Ln(pic)$_3$(DTSO)$_3$] (*Ln*=La, Lu and Y; *pic*=picrate; DTSO=1,3-dithiane-1-oxide) were synthesized and characterized. Indirect structural determination by far infrared spectroscopy is presented. Results from thermal decomposition of these complexes by TG/DTG and DSC techniques are reported.

Keywords: DSC, far infrared spectroscopy, lanthanide, TG/DTG

Introduction

The chemistry of the lanthanides and their complexes is a research area that has arisen much interest, motivated by a wide range of applications of these compounds as solid-state lasers, luminescent probes, catalytic processes and other uses [1–3]. The use of sulfoxides as neutral ligands in lanthanide picrates complexes has been an object of investigation at our laboratories [4–9]. Their preparation and thermal behavior of hydrated lanthanide picrates have already been reported [10–15]. In this work, studies on indirect structural determination and thermal behavior of complexes [Ln(pic)$_3$(DTSO)$_3$] are described.

Experimental

Hydrated lanthanide picrates, Ln(pic)$_3$·xH$_2$O, were prepared by reaction of hydrated lanthanide hydroxycarbonates and picric acid in aqueous solution [15]. The ligand 1,3-dithiane-1-oxide (DTSO) was prepared by oxidation of 1,3-dithiane with sodium metaperiodate [4, 16]. The complexes were obtained by reaction in absolute ethanol

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of $Ln(pic)_3 \cdot xH_2O$ and DTSO at 1:3 molar ratio. The yellow crystals formed were washed with ethanol and dried under vacuum over anhydrous calcium chloride.

Lanthanide ions were determined by complexometric titration with EDTA using xylenol-orange as indicator. Microanalysis of carbon, hydrogen and nitrogen were performed using a Perkin Elmer mod. 240 elemental analyzer. IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets.

The indirect structural determination of the complexes by far infrared spectroscopy (600–150 cm^{-1}) was made using a spectrometer Nicolet Nexus 670 in polyethylene matrix.

TG/DTG experiments were performed in a TGA-50 Shimadzu instrument under dynamic air atmosphere (50 mL min^{-1}) at a heating rate of 10°C min^{-1}. DSC measurements were performed in a dynamic nitrogen atmosphere (50 mL min^{-1}) at heating rate of 10°C min^{-1}, using a differential calorimeter DSC-50 Shimadzu. A small amount of material (1.5–2.0 mg) was used for the TG/DTG and DSC analysis.

Results and discussion

The lanthanide contents of *Ln* (*Ln*=La, Lu and Y), C, H and N found in the complexes are in agreement with the proposed stoichiometry: $[Ln(pic)_3(DTSO)_3]$. According to the infrared spectra, νSO (1049 cm^{-1}) shifts in the free ligand to lower frequencies in the complexes (~985 cm^{-1}) indicate coordination of DTSO through the oxygen. The bands due to picrate, ν_{as} NO_2 and νs NO_2, suggest coordination through the phenolic group and one oxygen atom from an ortho-nitro group.

Single crystal X-ray analysis on the Gd complex [4] showed that the Ln(III) ion is 9-coordinated to three monodentate DTSO ligands and three bidentate picrate ions in a monoclinic crystal system ($P2_1/c$) and coordination polyhedron as a distorted monocapped square antiprism.

Absorption spectra at the far infrared region (600–150 cm^{-1}), which corresponds to the spectral region where the vibrations of the structure of the compound take place, provide indirect structural information. Analysis on the spectra (Figs 1 and 2) led to conclude that the compounds constitute an only isomorphous series. The spectra showed several bands, from which the most intense, observed in the spectra of all the compounds from the series, are at about 540, 530, 430, 370, 300, 270 and 210 cm^{-1}. The large number of bands in the far infrared spectra of these compounds, as showed in Table 1, is in agreement with their low symmetry. The similarity of the spectra indicates that the compounds belong to the same isomorphous series and to the same symmetry of the previously investigated [4] gadolinium picrate DTSO complex.

Figures 3 and 4 show the TG/DTG and DSC curves for Gd and Dy complexes. When analyzing TG and DTG curves, and from stoichiometric calculations, it was possible to suggest that the thermal decomposition, in the temperature range investigated (25–900°C), occurs in two stages. The events are sequential and no plateaus were observed in the TG curves. The first event, corresponding to 52% of mass loss, occurred in the 110–400°C range. The second event, corresponding to 27% of mass

Table 1 Wavenumber and relative intensity of the bands in the far IR spectra of the compounds [Ln(pic)$_3$(DTSO)$_3$]

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
$542_{(s)}$	$542_{(s)}$	$542_{(s)}$	$542_{(s)}$	$541_{(s)}$	$541_{(s)}$	$542_{(s)}$	$541_{(s)}$	$541_{(s)}$	$541_{(m)}$	$541_{(sh)}$	$542_{(sh)}$	$542_{(sh)}$	$542_{(sh)}$	$542_{(sh)}$
$530_{(s)}$	$531_{(s)}$	$532_{(s)}$	$532_{(s)}$	$532_{(s)}$	$532_{(s)}$	$532_{(s)}$	$532_{(s)}$	$535_{(s)}$	$535_{(s)}$	$534_{(s)}$	$534_{(s)}$	$534_{(s)}$	$534_{(s)}$	$534_{(s)}$
		$515_{(sh)}$	$515_{(sh)}$	$515_{(sh)}$	$516_{(sh)}$	$514_{(sh)}$	$515_{(sh)}$	$516_{(sh)}$	$516_{(sh)}$	$515_{(sh)}$	$515_{(sh)}$	$516_{(sh)}$	$516_{(sh)}$	$516_{(sh)}$
$490_{(m)}$	$490_{(m)}$	$489_{(m)}$	$491_{(m)}$	$492_{(m)}$	$492_{(m)}$	$492_{(m)}$	$492_{(m)}$	$492_{(m)}$	$492_{(m)}$	$492_{(m)}$	$493_{(m)}$	$493_{(m)}$	$493_{(m)}$	$492_{(m)}$
$426_{(m)}$	$426_{(m)}$	$427_{(m)}$	$428_{(m)}$	$430_{(m)}$	$429_{(m)}$	$429_{(m)}$	$430_{(m)}$	$431_{(m)}$	$432_{(m)}$	$431_{(m)}$	$432_{(sh)}$	$432_{(sh)}$	$432_{(sh)}$	$431_{(sh)}$
$413_{(s)}$	$414_{(s)}$	$415_{(s)}$	$416_{(s)}$	$417_{(s)}$	$418_{(s)}$	$419_{(s)}$	$420_{(s)}$	$420_{(s)}$	$420_{(s)}$	$423_{(s)}$	$422_{(s)}$	$424_{(s)}$	$424_{(s)}$	$422_{(s)}$
$397_{(w)}$	$396_{(w)}$	$399_{(w)}$	$399_{(w)}$	$399_{(w)}$	$401_{(w)}$	$401_{(w)}$	$400_{(w)}$	$402_{(w)}$	$402_{(w)}$	$404_{(w)}$	$404_{(w)}$	$405_{(w)}$	$405_{(w)}$	$403_{(w)}$
$386_{(s)}$	$385_{(s)}$	$386_{(sh)}$	$385_{(sh)}$	$385_{(sh)}$	$386_{(sh)}$	$385_{(sh)}$	$385_{(sh)}$	$384_{(sh)}$	$386_{(m)}$	$385_{(m)}$	$385_{(m)}$	$386_{(m)}$	$386_{(m)}$	$386_{(m)}$
$376_{(s)}$	$376_{(s)}$	$377_{(s)}$	$376_{(s)}$	$378_{(s)}$	$378_{(s)}$	$378_{(s)}$	$378_{(s)}$	$376_{(sh)}$						
$361_{(s)}$	$361_{(s)}$	$361_{(s)}$	$361_{(s)}$	$362_{(s)}$	$362_{(s)}$	$362_{(m)}$	$362_{(m)}$	$363_{(m)}$	$364_{(m)}$	$364_{(m)}$	$364_{(m)}$	$365_{(m)}$	$364_{(m)}$	$364_{(m)}$
$346_{(w)}$	$346_{(w)}$	$346_{(w)}$	$347_{(w)}$	$347_{(w)}$	$347_{(w)}$									
$332_{(s)}$	$332_{(s)}$	$332_{(s)}$	$333_{(s)}$	$333_{(s)}$	$333_{(m)}$	$334_{(m)}$	$333_{(m)}$	$334_{(m)}$	$333_{(m)}$	$334_{(m)}$	$335_{(m)}$	$336_{(m)}$	$336_{(m)}$	$336_{(m)}$
$299_{(s)}$	$300_{(s)}$	$300_{(s)}$	$301_{(s)}$	$301_{(s)}$	$300_{(s)}$	$300_{(s)}$	$300_{(s)}$	$301_{(s)}$	$303_{(s)}$	$303_{(s)}$	$303_{(s)}$	$304_{(s)}$	$304_{(s)}$	$304_{(s)}$
$285_{(w)}$	$284_{(w)}$	$285_{(w)}$	$285_{(w)}$											
$272_{(m)}$	$272_{(m)}$	$273_{(m)}$	$274_{(m)}$	$273_{(m)}$	$274_{(m)}$	$275_{(m)}$	$275_{(m)}$	$276_{(m)}$	$276_{(m)}$	$277_{(m)}$	$277_{(m)}$	$278_{(m)}$	$277_{(m)}$	$278_{(m)}$
$209_{(s)}$	$212_{(s)}$	$211_{(s)}$	$216_{(s)}$	$217_{(s)}$	$218_{(s)}$	$218_{(s)}$	$219_{(s)}$	$222_{(m)}$	$223_{(m)}$	$224_{(m)}$	$222_{(m)}$	$220_{(m)}$	$222_{(m)}$	$230_{(m)}$
$168_{(s)}$	$168_{(s)}$	$169_{(s)}$	$169_{(s)}$	$169_{(s)}$	$168_{(s)}$	$168_{(s)}$	$167_{(s)}$	$167_{(s)}$	$169_{(s)}$	$167_{(s)}$	$166_{(s)}$	$166_{(s)}$	$166_{(s)}$	$177_{(s)}$

(s)=sharp, (m)=medium, (w)=week, (sh)=shoulder

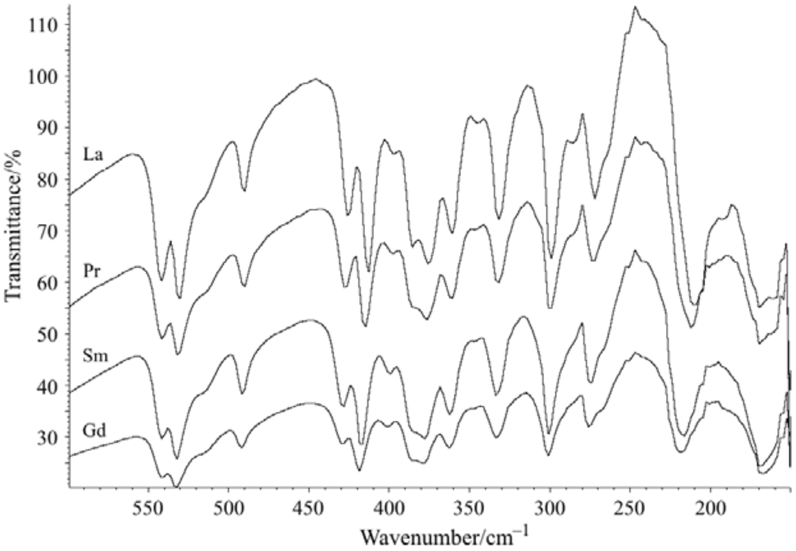

Fig. 1 Far IR spectra of complexes: [Ln(pic)$_3$(DTSO)$_3$], *Ln*=La, Pr, Sm and Gd

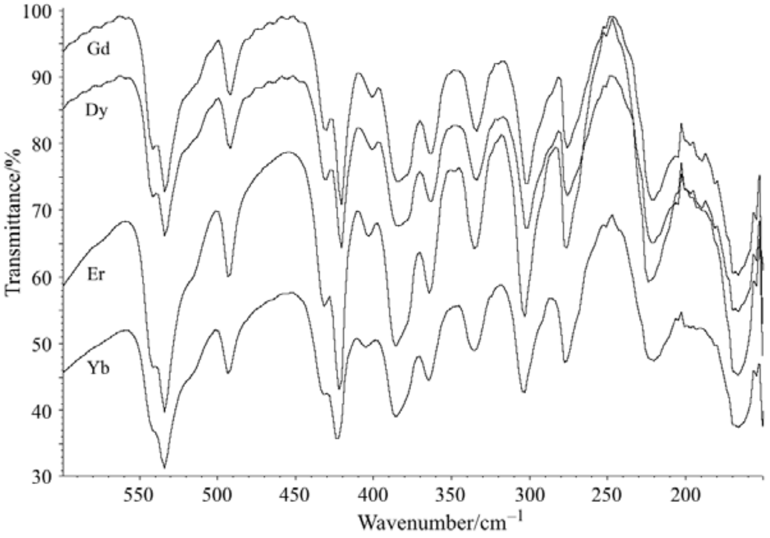

Fig. 2 Far IR spectra of complexes: [Ln(pic)$_3$(DTSO)$_3$], *Ln*=Gd, Dy, Er and Yb

loss, ended at 750°C. The corresponding peaks in DTG curves from these events occurred at about 300 and 550°C, respectively.

In the DSC curves it was observed that the fusion and decomposition events occurs separately, as endothermic events (peaks around 180°C) and exothermic events (310°C), respectively. The exothermic event in the thermal decomposition released ca. 2500 kJ mol^{-1}.

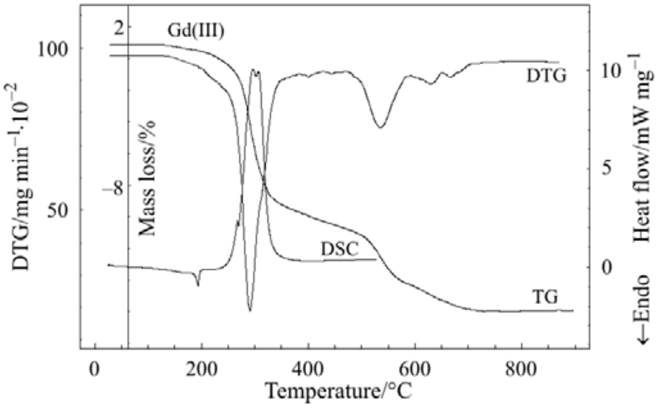

Fig. 3 TG/DTG and DSC curves for [Gd(pic)$_3$(DTSO)$_3$]

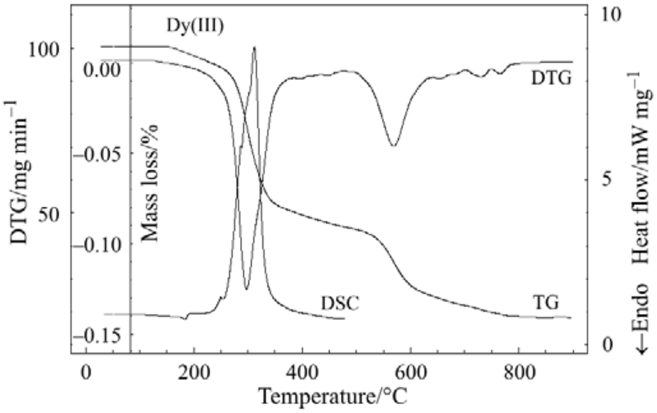

Fig. 4 TG/DTG and DSC curves for [Dy(pic)$_3$(DTSO)$_3$]

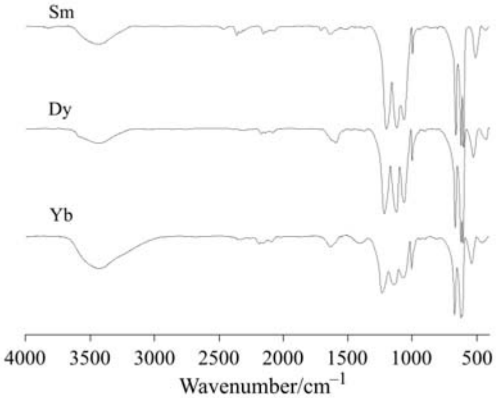

Fig. 5 IR spectra of residues obtained at 900°C

The final product of the thermal decomposition was identified as $Ln_2O_2SO_4$. It was characterized by elementary analysis and infrared spectra. The IR spectra (Fig. 5) from the sample, obtained at 900°C, showed absorption bands characteristic to sulfate ion. The ν_1, ν_3 and ν_4 bands appear nearly in the 1000, 1060–1230 and 600–665 cm^{-1} ranges, respectively. The observed bands are in agreement with previous works [17, 18].

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