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THERMAL DECOMPOSITION AND STRUCTURAL STUDY OF LANTHANIDE COMPLEXES WITH *trans*-1,3-DITHIANE-1,3-DIOXIDE

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Lanthanide picrates with 1,3-dithiane-1,3-dioxide ligand were synthesized and characterized. Thermal decomposition of these compounds by TG/DTG and DSC and structural studies were performed. It was found that the compounds are comprised in a single isomorphous series and their thermal decomposition occurs as exothermic events. The final products were found to be lanthanide dioxysulfates.

Keywords: *lanthanide, thermal decomposition, trans-1,3-dithiane-1,3-dioxide*

Introduction

Coordination chemistry of lanthanides is a promising research area motivated by the wide range of applications for these compounds on fields as different as catalytic processes, electroluminescent devices and solid-state lasers [1–4]. The complexes with *trans*-1,3-dithiane-1,3-dioxide ligand (*trans*-$DTSO_2$) and lanthanide picrates (pic) were synthesized and characterized with the formula $[Ln(pic)_3(trans\text{-}DTSO_2)_2]$ (*Ln*=La–Lu, Y). Thermal decomposition of these compounds was performed by TG/DTG and DSC analysis and their structural study was done by X-ray powder diffraction.

Experimental

Trans-$DTSO_2$ ligand (Fig. 1) was prepared by oxidation of 1,3-dithiane-1-oxide with *m*-chloroperoxybenzoic acid and then separated and purified from the *cis*-isomer by ethanolic treatment [5, 6]. The complexes were prepared by reaction of lanthanide picrates dissolved in absolute ethanol and treated with a ligand solution in the same solvent (molar ratio 1:2). The yellow crystals formed were separated and dried under vacuum over anhydrous calcium chloride. The characterization of the complexes by microanalytical procedures, infrared absorption spectroscopy, emission spectroscopy and crystal structure determination by X-ray was described elsewhere [7].

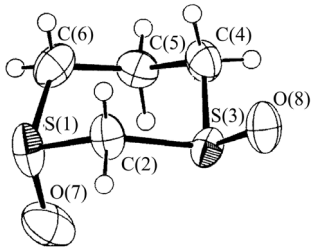

Fig. 1 Molecular structure and the atomic labeling scheme of *trans*-$DTSO_2$ [5]

Structural studies of complexes were done by X-ray powder diffraction. Thermal decomposition studies of complexes were made by TG/DTG and DSC analysis, using a small amount of substance (1–1.5 mg) due to easy explosion of the picrates [8]. TG/DTG experiments have been performed using Shimadzu TGA-50 instrument under dynamic air atmosphere (50 mL min^{-1}) at a heating rate of 10°C min^{-1} up to 900°C. DSC measurements were performed in a dynamic nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10°C min^{-1} up to 600°C, using a Shimadzu DSC-50 cell. The final products of the thermal decomposition were characterized by CHN microanalysis (PerkinElmer 240 instrument) and IR spectra (Nicolet FTIR-8100 spectrometer) using KBr pellets.

Results and discussion

The results of the elemental analysis for C, H, N, S and *Ln* are in a good agreement with the proposed

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stoichiometry: $[Ln(pic)_3(trans\text{-}DTSO_2)_2]$. The coordination of lanthanides through the oxygen of the sulfoxide group was verified by the shifts of the free ligand ν_{SO} (1035 cm^{-1}) to lower frequencies in the IR spectra of complexes (~1020 cm^{-1}). It was observed yet that the picrate anions are coordinated.

For the europium compound, the emission spectrum was interpreted in terms of a C_{2v} symmetry and the X-ray single crystal structure shows that the Eu(III) is octa-coordinated by picrate anions and two *trans*-$DTSO_2$ ligands in a bicapped trigonal prism fashion.

Analysis of the diffractogram (Fig. 2) led to the conclusion that the compounds constitute only an isomorphous series.

Table 1 summarizes the mass loss data taken from the TG curves and the corresponding DTG peak temperatures. Table 2 shows the DSC peak temperatures and the corresponding enthalpies. TG/DTG and DSC curves of Eu(III) and Ho(III) compounds are presented in Figs 3 and 4.

The TG curves of all complexes are similar, showing two sequential steps. There are no plateaus in the decomposition temperature interval in the TG curve, indicating that there is no stable intermediary compound formation. The first step occurs in the range of 200–400°C in two events, except for the initial series La–Nd for which it occurs in one event, resulting about 50% of mass loss. It was observed that the peak temperatures corresponding to DTG curves decreased in the lanthanide series except for the Y(III) compound that appears between those of Dy(III) and Ho(III) compounds. The second step occurs as a single event, which finalized near 800°C with stable final product.

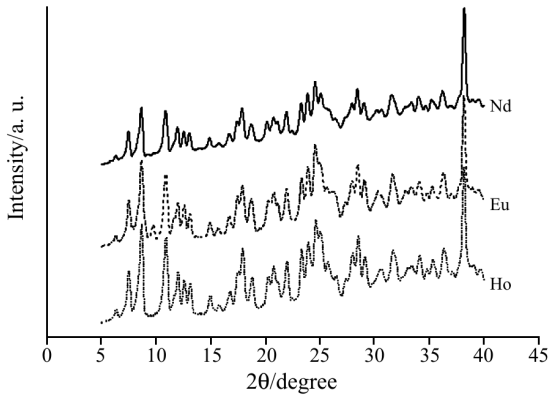

Fig. 2 X-ray diffractogram of Nd(III), Eu(III) and Ho(III) compounds

The compounds undergo simultaneous melting and decomposition. The DSC curve evidences that the thermal decomposition process is highly exothermic (2500–3000 kJ mol^{-1}) with two intense and sharp peaks near to 260 and 300°C.

Table 1 Mass loss values and DTG peak temperatures of the compounds

Ln	1st step			2nd step	
	%	*T*/°C	*T*/°C	%	*T*/°C
La	45.56	299	–	34.03	560
Ce	46.01	283	–	30.33	515
Pr	47.69	279	–	32.97	549
Nd	49.02	279	–	32.52	548
Sm	47.11	286	311	32.88	561
Eu	49.25	261	299	30.38	549
Gd	51.20	283	311	30.11	565
Tb	47.40	265	299	29.11	564
Dy	46.27	277	313	34.84	569
Ho	47.93	275	313	34.55	582
Er	48.99	256	304	32.35	561
Tm	48.36	268	316	34.88	570
Yb	51.66	252	303	29.54	563
Lu	46.91	263	318	32.81	586
Y	54.16	271	314	31.91	580

Table 2 DSC peak temperatures and the corresponding enthalpies of the compounds

Ln	*T*/°C	*T*/°C	ΔH/kJ mol^{-1}
La	273	290	–2588
Ce	286	297	–2928
Pr	282	301	–3039
Nd	279	302	–2829
Sm	280	301	–2236
Eu	263	300	–2434
Gd	276	304	–2200
Tb	266	301	–2851
Dy	267	303	–2381
Ho	265	303	–2509
Er	252	305	–3019
Tm	253	302	–2554
Yb	248	306	–2785
Lu	255	307	–2703
Y	261	304	–2342

By elemental analysis lanthanide dioxysulfates ($Ln_2O_2SO_4$) were identified as final products of the thermal decomposition of the complexes. The characteristic bands in the IR spectra of the compounds were also observed. It was in agreement with the previous works, where complexes of lanthanide picrates with 1,3-dithiane-1-oxide (DTSO) [9] and *cis*-1,3-dithiane-1,3-dioxide (*cis*-$DTSO_2$) [10] ligands were studied.

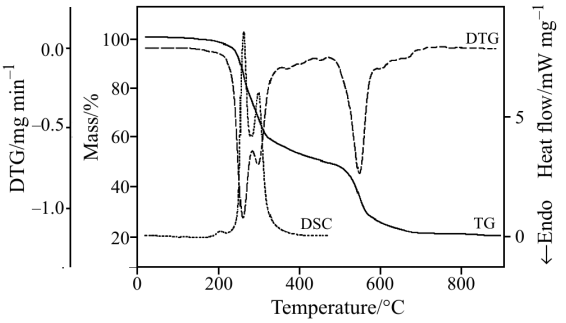

Fig. 3 TG/DTG and DSC curves of Eu(III) compound

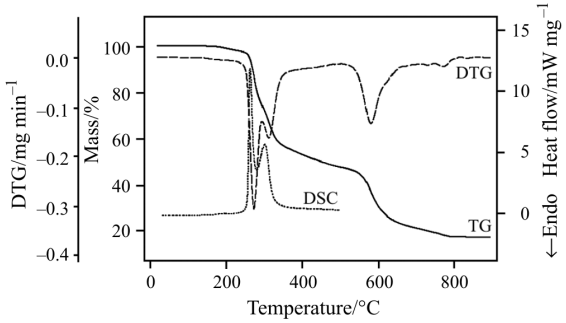

Fig. 4 TG/DTG and DSC curves of Ho(III) compound

Conclusions

The compounds obtained are comprised in a single isomorphous series and their thermal decomposition is exothermic under the applied experimental conditions. The final products were lanthanide dioxysulfates.

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