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THERMAL DECOMPOSITION OF LANTHANIDE COMPLEXES WITH SULFOXID LIGAND AND STUDY OF VOLATILE PRODUCTS LIBERATED

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Thermal behavior studies on complexes $[Ln(cis\text{-}DTSO_2)_4(H_2O)_2](pic)_3$ (*Ln*=Pr–Lu, Y; *cis*-$DTSO_2$=*cis*-1,3-dithiane-1,3-dioxide and *pic*=picrate) were done by TG/DTG and DSC analysis. The volatiles liberated from thermal decomposition were separated by chromatographic packed column (Tenax 60–80 mesh) and detected by mass spectrometry using TG/DTA-GC/MS combined analytical technique. The retention times of volatile products liberated in the chromatographic column were 4.25 min for SO_2 and 21.05 min for methyl-propyl-sulfoxide.

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

Introduction

Studies on supramolecular chemistry of lanthanide complexes are an area of increasing interest due to the wide range of applications for these compounds, as solid-state lasers, luminescent probes, NMR shift reagents, electroluminescent devices, catalytic processes and other uses [1]. Complexes of lanthanide picrates and sulfoxide ligands are under investigation in our laboratories. Studies on the synthesis and characterization, structural determination, spectroscopy and thermal decomposition were previously reported [2–10]. In this paper the thermal behavior of complexes of lanthanide picrates with *cis*-$DTSO_2$ ligand and the volatile products liberated from thermal decomposition using TG/DTG, DSC and TG/DTA-GC/MS techniques are presented.

Experimental

The oxidation of 1,3-dithiane-1-oxide with *m*-chloroperoxybenzoic acid results in the isomers *trans*- and *cis*-1,3-dithiane-1,3-dioxide. The insoluble *cis*-isomer (Fig. 1) was separated and purified from the soluble *trans*-isomer by ethanolic treatment [9]. Hydrated lanthanide picrates were prepared by reaction of lanthanide hydroxycarbonates and picric acid in aqueous solution [6]. The complexes were prepared by reaction of the lanthanide picrates dissolved in absolute ethanol and treatment with a warm ligand solution in the same solvent (molar ratio 1:4). The yellow crystals formed were separated and dried under vacuum over anhydrous calcium chloride.

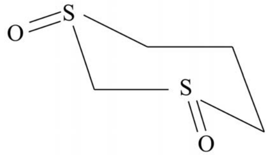

Fig. 1 Structure formula of *cis*-$DTSO_2$ ligand

The characterization of the complexes by microanalytical procedures, infrared absorption spectroscopy, emission and absorption spectroscopy and crystal structure determination by X-ray was described elsewhere [9].

Thermal behavior studies of complexes were made by TG/DTG and DSC analysis. A small amount of material (1–1.5 mg) was used, due to the easy explosion of picrates. TG/DTG experiments have been performed in a TGA-50 Shimadzu instrument under dynamic air atmosphere (50 mL min^{-1}) at a heating rate of 10 K 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 K min^{-1} up to 600°C, using a DSC-50 cell (Shimadzu). The DSC cell was calibrated with indium (*m.p.* 156.6°C; ΔH_{fus}=28.54 J g^{-1}) and zinc (*m.p.* 419.6°C). The final products of the thermal decomposition were characterized by CHN microanalytical (Perkin Elmer 240 instrument) and IR spectra (Nicolet FTIR-8100 spectrometer) using KBr pellets.

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The volatiles liberated from thermal decomposition were evaluated by the TG/DTA-GC/MS simultaneous analytical technique using TG/DTA (model DTG-50H) and GC/MS models GC-14B and QP-5000), Shimadzu instruments. The DTG–GC/MS system was adjusted to operate at the following conditions: (*i*) DTG-50H used simultaneous TG/DTA model operating under dynamic atmosphere of helium (99.999%) with a flow rate of 50 mL $\mathrm{min^{-1}}$ and the heating rate was 20 K $\mathrm{min^{-1}}$ from 30 to 900°C, with sample mass of about 2 mg; (*ii*) the evolved gaseous material was adsorbed in Tenax 60/80 mesh trap cooled at dry ice temperature. After then the trap was heated to 300°C and the gaseous material was desorbed and separated with a gas chromatograph (GC-14B series); and (*iii*) GC/MS-QP5000 system was composed of the chromatograph (GC-14B) with a MS detector operating under helium atmosphere. The injection port was maintained at a constant temperature of 300°C in order to introduce all released material into the column. The packed glass column containing 1.1 m×3.2 mm i.d. and coated with Tenax 60/80 mesh was programmed to heat to 80°C, was held for 5 min, followed by heating at a rate of 20 K $\mathrm{min^{-1}}$ up to 300°C, and held for another 5 min. The Q-MS mass spectrometer was operated in the electron bombardment ionization (70 eV) mode and the *m*/*z* range of 16–300, which enabled the detection of the ions evolved from the sample. Spectral National Institute of Standards (NIST), chemical and structural database was used to assign the mass spectra of unknown evolved compounds.

Results and discussion

The lanthanide (*Ln*=Pr–Lu and Y) C, H and N contents found in the complexes are in agreement with the proposed stoichiometry: $\mathrm{[Ln(cis\text{-}DTSO_2)_4(H_2O)_2](pic)_3}$. According to the IR spectra, shifts of νSO in the free ligand to lower frequencies in the complexes indicate coordination of *cis*-$\mathrm{DTSO_2}$ through the oxygen atom. X-ray powder patterns show only one isomorphous series. X-ray single-crystal data for holmium complex showed that the Ho(III) ion is 8-coordinated by 2 oxygen atoms of one bidentate *cis*-$\mathrm{DTSO_2}$, 4 oxygen atoms of four monodentate *cis*-$\mathrm{DTSO_2}$, one of which acts as a bridge between two neighbour Ho atoms, and two water molecules in a distorted square antiprism fashion. The picrate anions are not bonded to the Ho(III) ion [9].

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. Figure 2 indicates the TG/DTG and DSC curves of $\mathrm{[Sm(cis\text{-}DTSO_2)_4(H_2O)_2](pic)_3}$.

TG curves of all complexes are very similar, showing three mass loss events. The mass losses are consecutive and there are no plateaus in the decomposition temperature interval in the TG curves. This indicates that there is no stable intermediate compound formation. The first event occurs between 100–150°C, resulting about 2.4% of mass loss, which corresponds to the loss of two molecules of coordinated water. The second and third steps correspond to the decomposition of the anhydrous complex, beginning above 200 and ending at about 750°C.

Table 1 Mass loss data and DTG peak temperatures of the $\mathrm{[Ln(cis\text{-}DTSO_2)_4(H_2O)_2](pic)_3}$

Ln	Dehydration		Decomposition				
	1st step		2nd step			3rd step	
	%	*T*/°C	%	*T*/°C	*T*/°C	%	*T*/°C
Pr	2.46	78	51.64	207	295	31.21	558
Nd	2.44	110	50.16	208	295	31.28	555
Sm	2.43	119	45.39	206	302	30.07	567
Eu	2.44	111	50.58	197	289	29.80	545
Gd	2.45	120	58.17	207	302	25.80	567
Tb	2.42	116	53.07	200	297	28.19	561
Dy	2.42	122	51.49	214	306	31.61	570
Ho	2.41	125	50.84	209	308	31.42	586
Er	2.46	114	53.07	193	297	28.12	553
Tm	2.40	121	49.72	204	309	31.99	571
Yb	2.48	110	56.81	187	303	23.62	552
Lu	2.40	122	58.14	205	311	23.98	583
Y	2.54	123	54.12	206	307	32.07	577

Table 2 DSC peak temperatures and enthalpy changes of the [Ln(cis-DTSO$_2$)$_4$(H$_2$O)$_2$](pic)$_3$

Ln	Dehydration		Decomposition			
	T/°C	Δ*H*/kJ mol^{-1}	*T*/°C	*T*/°C	*T*/°C	Δ*H*/kJ mol^{-1}
Pr	115	80	196	243	297	–3440
Nd	118	106	197	237	297	–3225
Sm	120	164	191	238	297	–2989
Eu	122	187	193	246	296	–3481
Gd	123	171	193	239	301	–3597
Tb	126	136	191	246	299	–2738
Dy	123	174	190	237	301	–3356
Ho	122	58	191	238	302	–3691
Er	126	134	189	240	302	–3143
Tm	123	125	188	236	305	–3356
Yb	120	149	181	234	307	–3620
Lu	125	159	189	239	305	–3084
Y	124	148	190	236	302	–3191

In the DSC curves the endothermic peak corresponds to the release of the two water molecules which occurs in a single step. The peaks are at around 120°C, and they were also observed in the DTG curves. The obtained temperatures and the measured dehydration enthalpies suggest that the water molecules are coordinated to the central metal ion. This was previously observed in the resolution of the Ho monocrystal structure.

The compounds undergo simultaneous melting and decomposition. The DSC curve evidenced that the thermal decomposition process is highly exothermic (3.500 kJ mol^{-1}) with three intense and sharp peaks near to 190, 240 and 300°C.

The final products from the thermal decomposition of the complexes were identified as lanthanide dioxysulfate (Ln$_2$O$_2$SO$_4$), characterized by elementary analysis and IR spectroscopy. The IR spectra showed characteristic absorption bands of the sulfate ion ν_1, ν_3 and ν_4, nearly in the 1000, 1060–1230 and 600–665 cm^{-1} ranges, respectively [11].

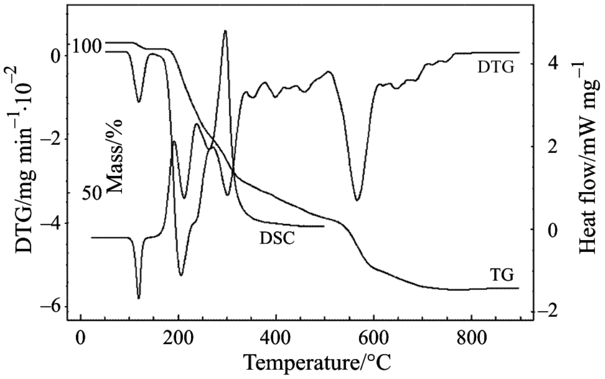

Fig. 2 TG/DTG and DSC curves of Sm complex

Figure 3 shows the chromatogram of the volatiles released during the thermal decomposition and Fig. 4 indicates their mass spectra.

The volatile products liberated upon the thermal decomposition were identified as sulfur dioxide and methyl-propyl-sulfoxide. The retention times in the chromatographic column, for each product, were 4.25 min for SO$_2$ and 21.05 min for methyl-propyl-sulfoxide.

From the results obtained for the thermal decomposition process, it can be concluded that the metal-ligand binding force does not influence the process of fragmentation, since it was observed that lanthanide complexes with *cis*-1,3-dithiane-1,3-dioxide ligand undergo a fragmentation with the release of just SO$_2$ and methyl-propyl-sulfoxide.

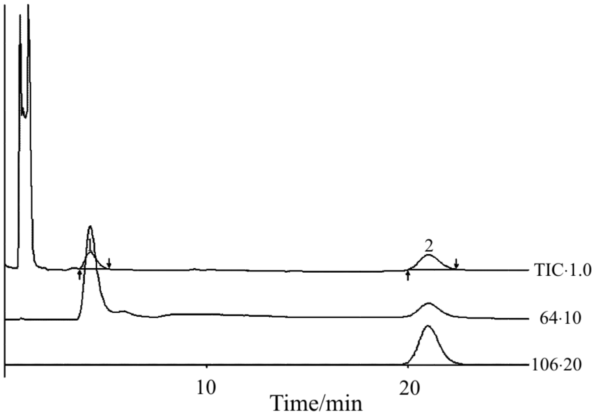

Fig. 3 Total and ion chromatograms of the volatile products liberated from the thermal decomposition process of Sm complex

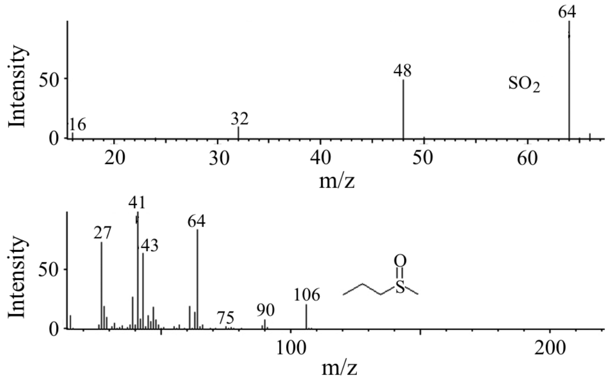

Fig. 4 Mass spectra of the volatile products corresponding to the peaks 1 (top) and 2 (bottom) of total ion chromatogram

Conclusions

The thermal behavior of the studied complexes is similar, as they belong to a single isomorphous series. The dehydration of these compounds indicates the presence of 2 coordinated water molecules. X-ray single-crystal diffraction measurements support this result. The volatile products liberated upon the thermal decomposition were sulfur dioxide and methyl-propyl-sulfoxide, identified by GC/MS and the final products were the corresponding lanthanide dioxy sulfates.

Acknowledgments

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