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THE THERMAL DECOMPOSITION OF OCTAKIS(DI-*p*-METHYLPHENYL SULPHOXIDE) LANTHANIDE(III) PERCHLORATES. FORMATION OF LANTHANIDE OXYSULPHATES

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ABSTRACT

A study was made of the thermal decomposition in air of the complexes $Ln(p\text{-}TSO)_8(ClO_4)_3$ (where Ln = La, Pr, Nd, Sm, Eu, Gd and *p*-TSO = di-*p*-methylphenyl sulphoxide) in a temperature range between 25 and 950 ° C. All the products formed at each stage were characterized by IR spectroscopy, mass spectrometry and X-ray diffraction. A scheme is proposed for the decomposition which implies the persistence, in the residues, of the sulphur atoms from the ligands.

INTRODUCTION

The analysis of the thermal stability of metallic complexes which have sulphoxides as ligands shows the existence of labile intermediate complexes which decompose at temperatures close to the boiling point of the ligand. When these boil the residues found correspond to those expected for a complex-forming anhydrous metallic salt [1].

In a previous work [2], we found that in the thermal decomposition, in air, of the complexes which form the perchlorates of the lanthanides with dipropyl sulphoxide, lanthanide oxysulphates are generated. This suggests that the explosive decomposition of the complexes, due to the presence of an oxygen-containing anion, stabilizes the sulphur, preventing the total loss of the ligand. This study has now been extended to that of other complexes with sulphoxide ligands with a view to establishing a reaction scheme which will allow us to define the conditions of formation of the lanthanide oxysulphates.

EXPERIMENTAL

The complexes of the lanthanide perchlorates (La, Pr, Nd, Sm, Eu and Gd) with di-*p*-methylphenyl sulphoxide (*p*-TSO) were prepared by the same

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methods described previously [3]. Their chemical analysis and IR spectra show, respectively, a stoichiometry of $Ln(p\text{-}TSO)_8(ClO_4)_3$ and a metal–ligand interaction through the transfer of electronic density of the oxygen atom of the sulphoxide group.

Thermal analysis

Thermoanalytical investigation was performed with a Perkin–Elmer thermogravimetric system, model TGS-2, and a Perkin–Elmer differential thermal analyser, model DTA 1700, connected to a Perkin–Elmer model 3600 data station.

The amounts of sample employed ranged from 6 to 8 mg and were diluted with corundum powder to carry out the differential thermal analysis.

The heating rate was set at 20 °C min^{-1} and the synthetic air flow (dehydrated and decarbonated) was 50 cm^3 min^{-1}.

Thermal decomposition

Thermal decompositions were carried out in an atmosphere of air in a Heraeus vertical electric oven (temperature control ±5 °C).

The samples were placed in a small platinum capsule inside a pyrex glass chamber equipped with a gas outlet leading to an external collecting flask. They were then heated from room temperature to maximum temperatures of 350–360, 500–520 and 650–660 °C, where each of them was kept for 2 h. After each heating stage the oven was cooled to room temperature, after which analysis was made of the residual solid product, of the gases condensed during cooling and during heating in the cold parts of the glass system, and of the gaseous products at room temperature present in the collector.

The constituents of each phase were identified using the techniques described below.

IR spectroscopy

The IR spectra of the solid, residual and condensed products were performed in the form of KBr discs at a proportion of 1/300 mg using a Beckman model Acculab 10 spectrophotometer in the 4000–400 cm^{-1} region.

X-ray diffraction

The powder diagrams of the different solid, intermediate or end products of decomposition were performed on a Siemens model Kristalloflex 810 apparatus with Cu K_α radiation ($\lambda = 154.050$ pm) and a nickel filter.

Mass spectrometry

The gases collected in the collecting flask were injected into a chromatograph on an empty column of a Hewlett-Packard model 5930-A apparatus using helium as the carrier with a flow rate of 60 cm^3 min^{-1}. The temperature of the ion source was 170 ° C and the ionization energy was 60 eV.

RESULTS AND DISCUSSION

Table 1 shows the weight losses during the different stages of thermal decomposition together with the final product found and the energy effects accompanying the decomposition for each of the complexes studied. It may be deduced that, except for slight variations, the thermograms of all the complexes are very similar. As an example, Fig. 1 shows the curves corresponding to the complex $Nd(p\text{-}TSO)_8(ClO_4)_3$.

Identification of the thermogravimetric residues was performed by IR spectroscopy and X-ray diffraction. The IR spectra show three very strong bands at 1195 ± 5, 1122 ± 7 and 1072 ± 2 cm^{-1}, which can be assigned to the antisymmetric stretching vibration, ν_3, of an ion of T_d symmetry cleaved

TABLE 1

Thermal data on octakis(di-*p*-methylphenyl sulphoxide) lanthanide(III) perchlorates

Complex	Decomposition temperature (° C)		Weight loss (%)	Final residue weight $Ln_2O_2SO_4$ (%)		DTA onset temperature (° C) (exo.)
	Initial	Final		Experimental	Theoretical	
$La(p\text{-}TSO)_8(ClO_4)_3$	205	360	63.6			335
	410	520	6.9			520
	560	670	20.2	9.2	8.9	
$Pr(p\text{-}TSO)_8(ClO_4)_3$	210	350	67.6			325
	400	520	6.4			512
	550	660	16.6	9.2	9.0	
$Nd(p\text{-}TSO)_8(ClO_4)_3$	200	360	68.1			335
	410	510	6.3			525
	560	670	16.2	9.2	9.1	
$Sm(p\text{-}TSO)_8(ClO_4)_3$	210	360	65.9			332
	420	500	6.7			505
	550	660	17.8	9.4	9.4	
$Eu(p\text{-}TSO)_8(ClO_4)_3$	215	360	67.6			330
	400	510	6.0			515
	550	670	16.6	9.6	9.4	
$Gd(p\text{-}TSO)_8(ClO_4)_3$	210	360	67.5			338
	420	500	6.6			510
	560	670	16.9	9.8	9.6	

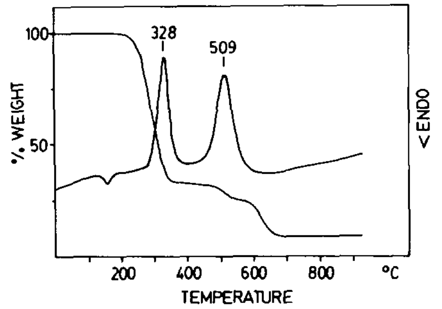

Fig. 1. TG–DTA curves of $|Nd(p\text{-}TSO)_8|(ClO_4)_3$.

in an environment of C_{2v} symmetry. Similarly, it is possible to observe the bands corresponding to the ν_1 vibration, symmetric stretching (995 ± 5 cm^{-1}), ν_4 vibration, antisymmetric bending cleaved in three bands of strong intensity (651 ± 1, 620 ± 1 and 601 ± 3 cm^{-1}), and the ν_2 vibration, symmetric bending (493 ± 8 cm^{-1}). The frequencies of these absorption maxima are in good agreement with those of the sulfate ion in lanthanide oxysulphates [4].

Regarding the interplanar spacings, the X-ray diffraction diagrams provide analogous values to those reported for lanthanide oxysulphates [2] and which better fit the values calculated, from the reticular values published for such oxysulphates, taking into account a body-centered, orthorhombic structure [5].

Table 1 includes the percentages calculated for a residue composition of pure $Ln_2O_2SO_4$ and good concordance can be seen between these values and those found experimentally. This presence of sulphate ions in the residue suggests that, in the thermal decomposition of the complexes under study, oxidation takes place of the sulphur present in the ligand forming the compound.

In order to determine the products formed during decomposition, and hence to confirm the presence of lanthanide oxysulphate in the residue, stepwise pyrolysis was performed using amounts of compounds ranging from 50 to 100 mg, heating the samples in an oven to the maximum temperatures of each of the intervals mentioned above.

Figure 2 shows the mass spectra of the gases given off during heating up to 360 ° C of the neodimium and gadolinium compounds as representative of all those studied. The most significant peaks observed in all of them are attributed to carbon dioxide with a mass/charge (m/z) ratio of 44, to sulphur dioxide ($m/z = 64$) and its ionization product SO^+ ($m/z = 48$) and to methylbenzene and its ionization fragments with m/z ratios of 79, 91 and 92 [6]. The peaks with values of 35, 36 and 38 for the m/z ratio are attributed to the presence of chloride in the gaseous mixture.

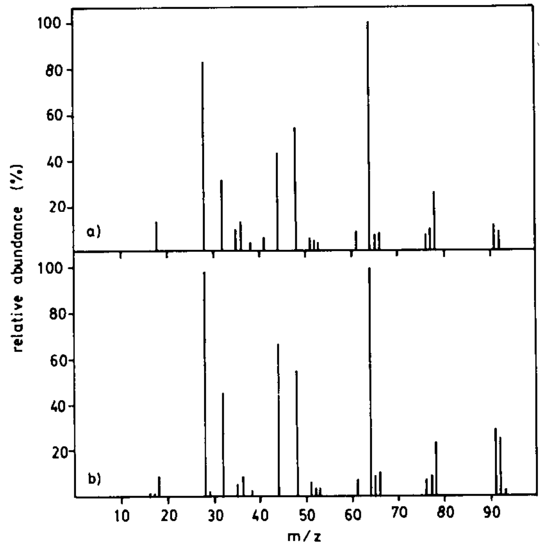

Fig. 2. Mass spectra of the gases given off during heating to 360 ° C of the compounds: (a) $|Nd(p\text{-}TSO)_8|(ClO_4)_3$; (b) $|Gd(p\text{-}TSO)_8|(ClO_4)_3$.

Figure 3 shows the IR spectrum of the condensation products arising from cooling to room temperature of the gases given off during heating to 360 ° C of one of the compounds obtained. In the figure it is possible to see the bands due to the presence of free *p*-TSO [3], together with three strong bands at 1320, 1150 and 550 cm^{-1}, which can be assigned to the antisymmetric stretching vibration, to that of symmetric stretching and scissoring modes active in IR of aromatic sulphones, and a band of medium intensity at 1700 cm^{-1}, which is attributed to a combination of the bands at 1150 and 550 cm^{-1} [7]. In turn, these condensation products are characterized by being insoluble in water and soluble in dry methanol.

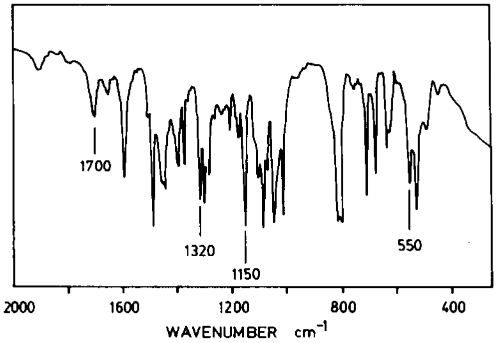

Fig. 3. IR spectra of the gases condensed at room temperature produced in calcination of the complex $|Sm(p\text{-}TSO)_8|(ClO_4)_3$ to 360 ° C.

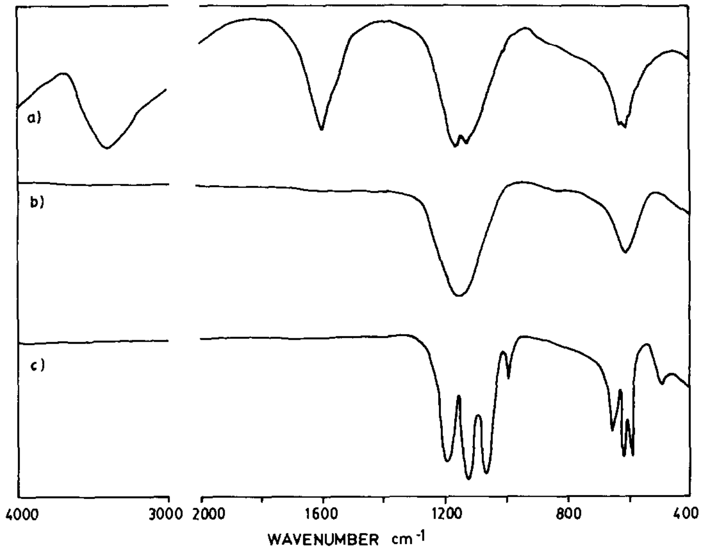

Fig. 4. Representative IR spectra of the residues of calcination of the complexes studied up to temperatures of (a) 360 ° C, (b) 500 ° C and (c) 650 ° C.

The solid residues at 360 ° C are partially soluble in water and are black; Fig. 4 shows a generalized spectrum for all of them. In the figure it is possible to observe the absorptions assigned to the ν_{O-H} stretching vibration (3400 cm^{-1}) and δ_{HOH} bending vibration (1600 cm^{-1}) of the water, together with those assigned to the active absorptions in the IR of a C_{3v} point group generated by a decrease in the T_d symmetry of the sulphate ion as a result of the crystallization water [8].

The same figure also shows the IR spectrum of the residues after calcination of the compounds up to 500–520 ° C; they maintain their black colour and are partially soluble in water, and their bands correspond to the vibrational modes active in IR of a T_d point group, such as that corresponding to the symmetry of the undistorted sulphate ion.

The spectra do not reveal the presence of organic compounds, though the residue contains approximately 11% of carbon, which accounts for the black colour of the compounds, as has been reported previously [9].

Unlike the solid residues at 360 ° C, whose X-ray diffraction diagrams do not show lines, possibly due to both the presence of amorphous carbon and to the low crystallinity of the hydrated sulphates of undefined stoichiometry, in the residues at 500–520 ° C the X-ray diagrams show some reflections which are coincident with those published for anhydrous sulphates of lanthanum and gadolinium [10].

Table 1 shows that the weight loss in the temperature range between 360 and 500–520 ° C is of 6–7% and is attributed to the loss of the water present in the residues, which leads to the formation of stable anhydrous lanthanide sulphates at the maximum heating temperature of this stage.

Figure 4 similarly shows the IR spectrum of the residues obtained at 650–660 °C, white in colour, whose absorption maxima are identical to those found for the residues obtained from the thermogravimetries at 950 °C and which correspond, as has been pointed out above, to lanthanide oxysulphates.

As a result of this, the following simple scheme may be put forward for the thermal decomposition in an atmosphere of air of the complexes $\mathrm{Ln}(p\text{-TSO})_8(\mathrm{ClO_4})_3$:

$$2\,|\mathrm{Ln}(p\text{-TSO})_8|(\mathrm{ClO_4})_3$$

$$+\mathrm{O_2}\ \left\downarrow \begin{array}{l} -p\text{-TSO}\\ -\mathrm{CO_2}\\ -\mathrm{SO_2}\\ -\mathrm{H_2O}\\ -\mathrm{HCl} \end{array}\right.$$

$$\mathrm{Ln_2(SO_4)_3}\cdot x\mathrm{H_2O} + y\mathrm{C} \quad (x \simeq 21,\ y \simeq 42)$$

$$+\mathrm{O_2}\quad -\mathrm{H_2O}$$

$$\mathrm{Ln_2(SO_4)_3} + y\mathrm{C}$$

$$+\mathrm{O_2}\ \left\downarrow \begin{array}{l} -\mathrm{CO_2}\\ -\mathrm{SO_2} \end{array}\right.$$

$$\mathrm{Ln_2O_2SO_4}$$

The scheme shows the stabilization in the residues of the sulphur of the sulphoxide group as a sulphate at an amount necessary to equilibrate the lanthanide ions present, together with the important fact that the thermal decomposition of the complexes studied does not produce the residues which would be expected for the decomposition in air of the simple salts.

Also, the decomposition of the carbon at a temperature greater than 560 °C catalyses the transformation of the sulphate to oxysulphate, which would explain why this takes place at temperatures notably lower than those of the decomposition in air of the anhydrous lanthanide sulphates (ref. 11 and references therein).

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