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A thermal study of lanthanoid trifluoromethanesulfonate complexes with diphenylphosphinamide (DPPA)

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Abstract

Complexes of composition $Ln(F_3C\text{–}SO_3)_3 \cdot 5DPPA$ (where Ln is La, Ce, Nd–Lu, Y) were investigated by TG analysis, IR spectroscopy and visible emission spectroscopy of one of the decomposition products. When heated in dynamic air atmosphere the compounds initially lose some of the DPPA molecules and then the products decompose giving a mixture of carbon, lanthanoid phosphate and lanthanide-oxo-trifluoromethanesulfonate.

INTRODUCTION

The complexes formed between lanthanide salts and diphenylphosphinamide and some of their properties have already been described [1–7].

In this article, we report the thermal behavior of complexes with composition $Ln(F_3C\text{–}SO_3)_3 \cdot 5DPPA$ (where Ln is La, Ce, Nd–Lu, Y). They form an isomorphous series and behave as 1:1 electrolytes in nitromethane and as 1:2 electrolytes in acetonitrile. The complexes display a C_{3v} symmetry and a distorted trigonal anti-prism geometry, consistent with an $Eu(O)_6$ chromophore, with one oxygen from a monodentate trifluoromethanesulfonate group and five oxygens from phosphoryl groups [6].

EXPERIMENTAL

The compounds were prepared and characterized according to the procedures described in ref. 6.

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TG analyses were performed on a Mettler 4000 system at a heating rate of 5 K min^{-1}, using dynamic air atmosphere and 2–3 mg of sample.

IR spectra of the compounds and of the residues obtained from the TG analyses were performed on a Bomem FTIR MB-102 spectrophotometer using Nujol mulls between KBr plates.

The emission spectra were recorded on a Hitachi, Perkin–Elmer MPF-4 spectrofluorimeter using 394 nm excitation radiation.

RESULTS AND DISCUSSION

Three different types of TG curves were obtained: (a) in the lanthanum complex, decomposition occurs with elimination of two DPPA molecules between 495 and 590 K; then another molecule of DPPA is lost between 590 and 655 K; (b) the decomposition of the cerium compound occurs with evolution of three DPPA molecules between 455 and 575 K, and one more DPPA between 575 and 655 K; (c) for the remainder of the compounds, elimination of four DPPA molecules occurs between ≈475 and 675 K.

In all cases, after ≈675 K, decomposition takes place with partial carbonization and formation of lanthanide phosphate, probably lanthanide-oxo-trifluoromethanesulfonate and carbon.

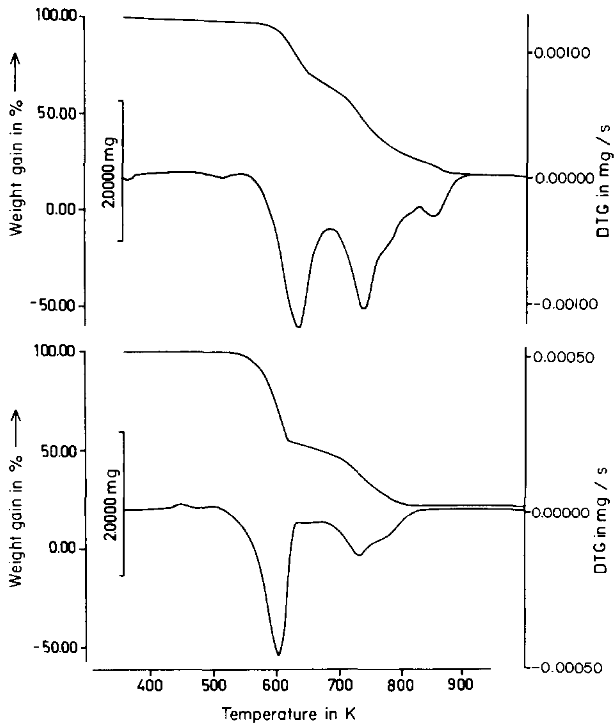

Fig. 1. TG and DTG curves of the compounds of lanthanum (top) and cerium (bottom).

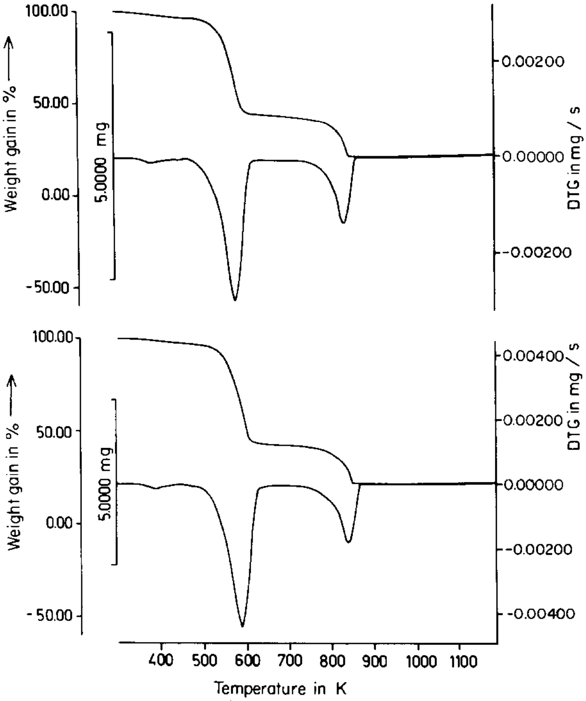

Fig. 2. TG and DTG curves of the compounds of gadolinium (top) and holmium (bottom).

Figure 1 shows the TG curves obtained for lanthanum and cerium and Fig. 2 gives two representative TG curves for the series from neodymium to lutetium and yttrium. Table 1 contains data from the curves.

In almost all cases, very small amounts of hygroscopicity were detected in the curves.

The decomposition steps were followed by IR spectroscopy. Figure 3 shows the IR spectra of a complex and of the residues obtained at 625 and 825 K. The spectrum of the residue obtained at 625 K still displays peaks attributed to the trifluoromethanesulfonate ion and to DPPA. The residue spectrum obtained at 825 K contains peaks due to trifluoromethanesulfonate and it is also possible to see peaks at 1010 cm^{-1} (ν_3) and at 570 cm^{-1} (ν_4) attributed to phosphate ions. The existence of this anion was confirmed by the formation of a yellow precipitate with ammonium phosphomolybdate in the presence of nitric acid. The absence of fluoride was also verified in the residue by reaction with concentrated sulfuric acid in a lead crucible covered with a glass; no corrosion was observed in all cases. The residues contain small amounts of carbon that slowly burn in the dynamic air atmosphere at $\approx$1240 K. According to the data reported in a previous article [6], one trifluoromethanesulfonate is bonded directly to the central ion in the complex species and it remains attached in the residues. TG data

TABLE 1

Thermal data for the decomposition of the complexes $Ln(F_3C–SO_3)_3 \cdot 5DPPA$

Ln	Temperature range in K	Weight loss or residue in %		Attribution
		Theor.	Exp.	
La	495–590	25.98	26.0	−2DPPA
	590–655	12.98	16.4	−1DPPA
	856–950	–	20.4	Residue
Ce	455–575	38.94	41.0	−3DPPA
	575–655	12.98	13.0	−1DPPA
	785–950	–	23.7	Residue
Nd	450–575	51.79	52.5	−4DPPA
	783–950	–	21.0	Residue
Sm	475–675	51.60	51.8	−4DPPA
	893–1095	–	21.2	Residue
Eu	475–635	51.60	52.0	−4DPPA
	875–950	–	22.5	Residue
Gd	475–675	51.40	53.0	−4DPPA
	873–1175	–	22.4	Residue
Tb	495–675	51.34	52.0	−4DPPA
	893–1175	–	23.9	Residue
Dy	475–675	51.23	51.0	−4DPPA
	875–1175	–	23.0	Residue
Ho	475–675	51.17	53.0	−4DPPA
	875–1175	–	21.8	Residue
Er	475–675	51.10	52.0	−4DPPA
	885–1175	–	22.4	Residue
Tm	475–635	51.05	52.0	−4DPPA
	865–950	–	22.2	Residue
Yb	475–655	50.92	51.0	−4DPPA
	875–950	–	23.5	Residue
Lu	455–605	50.86	51.5	−4DPPA
	795–950	–	20.4	Residue
Y	475–655	53.56	54.0	−4DPPA
	865–950	–	19.3	Residue

show that one DPPA is more strongly bonded and that this ligand is partially carbonized and the phosphorous oxidized to phosphate at temperatures higher than 625 K.

The emission spectrum of the europium residue obtained at 625 K is presented in Fig. 4. The presence of the band attributed to the $^5D_0 \rightarrow ^7F_0$ transition is indicative of the existence of C_n, C_{nv} or C_s symmetry [8]. The bands due to the $^5D_0 \rightarrow ^7F_2$ transition with two E species (four strong bands) and one A_1 species (medium) may indicate a C_{3v} symmetry for the residue formed [9].

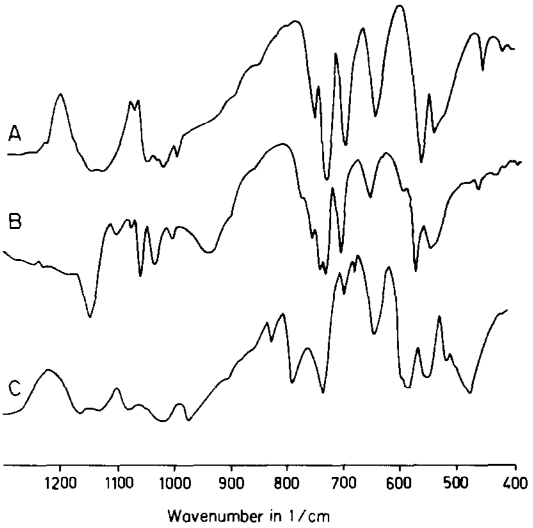

Fig. 3. IR spectra: curve A, complex at room temperature; curve B, residue obtained at 625 K; curve C, residue obtained at 825 K.

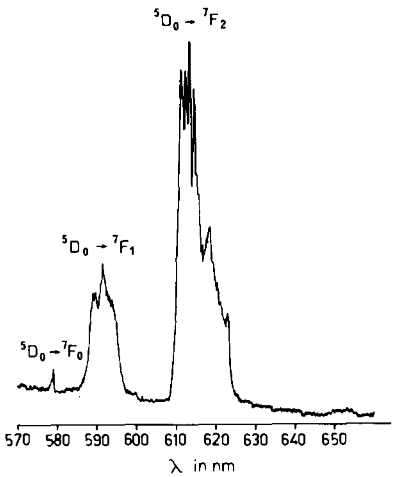

Fig. 4. Emission spectrum of the residue obtained at 625 K.

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