Thermochimica Acta, 143 (1989) 351–353
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMOGRAVIMETRIC STUDY OF δ-VALEROLACTAM LANTHANOID TRIFLUOROMETHANESULPHONATE COMPLEXES

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(Received 12 July 1988)

Thermoanalytical investigations on lanthanoid trifluoromethanesulphonate complexes containing several ligands such as dimethylsulphoxide [1], thioxane-oxide [2], *trans*-1,4-dithiane-1,4-dioxide [3], 4-picoline-*N*-oxide [4,5] and dimethylformamide [6] have been performed in our laboratories. Recently, δ-valerolactam complexes with composition $Ln(CF_3SO_3)_3 \cdot 8L$ where L = δ-valerolactam and Ln = La–Lu, Y have been reported [7]. In this note we describe the thermogravimetric study of such complexes.

EXPERIMENTAL

The hydrated trifluoromethanesulphonates [8] were heated at 200 °C, cooled and then treated with the ligand in triethylorthoformate. The crystals were formed slowly. They were filtered, washed with the solvent and dried in vacuo over anhydrous calcium chloride [7].

The compounds were characterized by microanalytical procedures, conductance measurements, IR spectra, visible electronic absorption spectra (Nd^{3+}) and fluorescence spectrum (Eu^{3+}) [7].

TG studies were performed under nitrogen atmosphere in a Perkin–Elmer TGS-1 system, using samples varying in weight from 0.695 to 0.975 mg and a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The complexes behave as 1 : 2 electrolytes in acetonitrile and 1 : 1 in nitromethane. The ligand is coordinated through the oxygen. The coordina-

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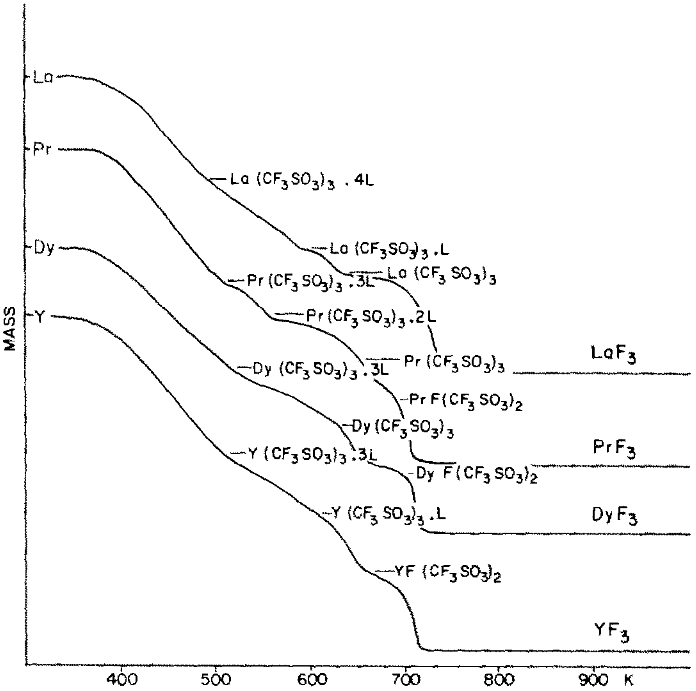

Fig. 1. Thermogravimetric curves for some representative complexes in nitrogen atmosphere. Mass: La, 0.782 mg; Pr, 0.848 mg; Dy, 0.783 mg; Y, 0.842 mg.

tion of the anion is unclear and X-ray single crystal studies are necessary in order to clarify this. D_{4d} symmetry is suggested for the complex species, based on the emission spectrum [7].

Only the compounds from lanthanum to erbium, ytterbium and yttrium were investigated thermogravimetrically. All complexes, except those of ytterbium and yttrium, present an apparent melting range [7], but simultaneously decomposition starts. The evolution of the ligand does not occur in sharply defined steps. The anhydrous salts have a short temperature range of existence, the decomposition, with evolution of COF_2 and SO_2 [9], also occurs stepwise. An intermediary $LnF(CF_3SO_3)_2$ lanthanoid fluoridefluoromethanesulphonate species is observed in most cases. The final residues are in all cases the lanthanoid fluorides, as observed in the decomposition of other trifluoromethanesulphonate complexes [1–6]. Figure 1 contains four typical thermogravimetric curves. The cerium behaviour is similar to that of lanthanum. Praseodymium presents a slightly different curve. The remainder of the compounds shows very similar behaviour and is represented in Fig. 1 by the curves of dysprosium and yttrium.

An analysis of the TG data reveals that, under the experimental conditions used, three different decomposition schemes exist. The first one contains the equations for the decomposition of lanthanum and cerium complexes; the second that for praseodymium, and the third that for neodymium to erbium, ytterbium and yttrium.

$$\left.\begin{array}{l} Ln(CF_3SO_3)_3\cdot 8L \rightarrow Ln(CF_3SO_3)_3\cdot 4L + 4L \\ Ln(CF_3SO_3)_3\cdot 4L \rightarrow Ln(CF_3SO_3)_3\cdot L + 3L \\ Ln(CF_3SO_3)_3\cdot L \rightarrow Ln(CF_3SO_3)_3 + L \\ Ln(CF_3SO_3)_3 \rightarrow LnF_3 + 3COF_2 + 3SO_2 \end{array}\right. \qquad (1)$$

$$\left.\begin{array}{l} Ln(CF_3SO_3)_3\cdot 8L \rightarrow Ln(CF_3SO_3)_3\cdot 3L + 5L \\ Ln(CF_3SO_3)_3\cdot 3L \rightarrow Ln(CF_3SO_3)_3\cdot 2L + L \\ Ln(CF_3SO_3)_3\cdot 2L \rightarrow Ln(CF_3SO_3)_3 + 2L \\ Ln(CF_3SO_3)_3 \rightarrow LnF(CF_3SO_3)_2 + COF_2 + SO_2 \\ LnF(CF_3SO_3)_2 \rightarrow LnF_3 + 2COF_2 + 2SO_2 \end{array}\right. \qquad (2)$$

$$\left.\begin{array}{l} Ln(CF_3SO_3)_3\cdot 8L \rightarrow Ln(CF_3SO_3)_3\cdot 3L + 5L \\ Ln(CF_3SO_3)_3\cdot 3L \rightarrow Ln(CF_3SO_3)_3 + 3L \\ Ln(CF_3SO_3)_3 \rightarrow LnF(CF_3SO_3)_2 + SO_2 + COF_2 \\ LnF(CF_3SO_3)_2 \rightarrow LnF_3 + 2COF_2 + 2SO_2 \end{array}\right. \qquad (3)$$

ACKNOWLEDGEMENTS

The authors wish to thank the following for financial support: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Financiadora de Estudos e Projetos (FINEP) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

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