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THERMAL STUDIES ON SOME LANTHANIDE COMPLEXES

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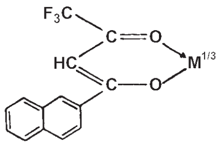
Abstract

Thermal behaviour of a few lanthanide complexes of the type ML_3(I) [*M*=Eu, Gd; *HL*=4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione and EuL_3·0.5dmm dmm=2,6-dimethylmorpholine(II)], has been investigated. From thermogravimetric (TG) curves, the decomposition pattern of the compounds has been analysed on the basis of mass loss data. The order and activation energy of the thermal decomposition reactions have been elucidated. From differential thermal analysis (DTA) studies, the heat of reaction and rate of thermal decomposition reaction have been enumerated.

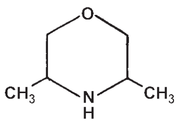
Keywords: complexes, kinetics, TG-DTA

Introduction

In earlier communications [1–3], we reported the synthesis and characterisation of some lanthanide complexes. In this paper we report the thermal behaviour of europium and gadolinium compounds. This follows from our interest in the thermal studies of rare earth chelates [4].



M = Eu, Gd



Experimental

The chelates were prepared by adding a solution of hexahydrated chloride of europium or gadolinium (2.7 mM) in ethanol (30 ml) to a solution of 4,4,4-trifluoro-

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1-(2-napthyl)-1,3-butadione (*L*, 8.1 mM) in ethanol (30 ml). The contents were stirred vigorously for 1 h. The pH of the reaction mixture was raised by dropwise adding ammonia solution. At pH 6, chelates of the composition ML_3 (*M*=Eu, Gd) separated out. These were filtered and dried. The products were recrystallised from benzene solution.

The EuL_3·0.5dmm complex was prepared by reacting europium(III) chloride hexahydrate (2.7 mM), 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (8.1 mM) and 2,6-dimethylmorpholine (8.1 mM) and following the above procedure.

Thermal studies were carried out by means of a derivatograph containing platinum, platinum-rhodium thermocouples. The measurements were made in a static air atmosphere at a heating rate of 10^{o} min^{-1} and a chart speed of 20 cm h^{-1}. For DTA studies, α-alumina (Aldrich) was used as a reference.

Results

EuL₃

The TG of this complex revealed mass loss in the temperature range 473–813 K. Within this temperature range the europium complex decomposed into the carbonate, $Eu_2(CO_3)_3$. At 943 K, the carbonate began to decompose into europium(III) oxide, Eu_2O_3. The decomposition continued up to 1063 K.

The DTA profile showed an endothermic thermal effect with T_{max} 483 K corresponding to the formation of the carbonate. The exothermic peak with T_{max} 1003 K corresponded to the decomposition of the carbonate to the oxide.

GdL₃

From the TG curve it was observed that the mass change began at 493 K and continued upto 883 K. The mass loss corresponded to the formation of gadolinium carbonate, $Gd_2(CO_3)_3$. Above 943 K, the carbonate began to decompose into gadolinium(III) oxide, Gd_2O_3. The decomposition ceased at 1053 K.

The DTA curve showed an endothermic peak with T_{max} 503 K, corresponding to the decomposition of the complex to the carbonate. This was followed by an exothermic thermal effect with T_{max} 1013 K, corresponding to the decomposition of the carbonate to the oxide.

EuL₃·0.5dmm

The TG curve of this compound indicated a mass change in the temperature range 453–573 K. The mass change corresponded to the loss of 2,6-dimethylmorpholine ligand. The second mass loss initiated at 613 K and continued upto 723 K. During this step, the complex EuL_3 decomposed into europium(III) oxide, Eu_2O_3.

The DTA profile showed two endothermic thermal effects. The one with T_{max} 563 K corresponded to the evaporation of 2,6-dimethylmorpholine, while the other with T_{max} 683 K corresponded to the decomposition of the complex to oxide.

Table 1 TG and DTA data

Complex	Step	TG				DTA			
		Temp. range/ K	Mass loss obs. (calc.)/ %	n	E_a/ Kcal mol^{-1}	Thermal effect	T_{max}/ K	ΔH/ cal g^{-1}	K (T) % Conv. min^{-1}
EuL_3	I	473–813	50(49)	1	13.7	endothermic	483	0.7	5.55(443)
	II	943–1063	28(27.2)	1	45.8	exothermic	1003	12.5	2.66(933)
GdL_3	I	493–883	44(48)	1	14.6	endothermic	503	0.7	5.55(473)
	II	943–1053	23.3(26)	1	61.0	exothermic	1013	4.9	3.33(963)
$EuL_3 \cdot 0.5dmm$	I	453–573	5(5.2)	1	10.0	endothermic	563	2.5	5.55(553)
	II	613–723	81(81.2)	1	38.1	endothermic	683	5.8	2.77(633)

Discussion

The thermal data are presented in Table 1. The TG and DTA curves are shown in Figs 1 and 2, respectively. The linearisation curves for the first step decomposition of EuL_3 and GdL_3 complexes are shown in Fig. 1. The corresponding curves for the sec-

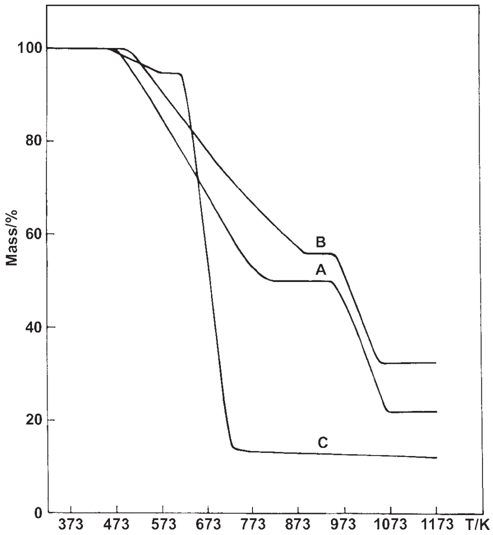

Fig. 1 TG curves of: A –EuL_3; B – GdL_3; C – $EuL_3$0.5dmm

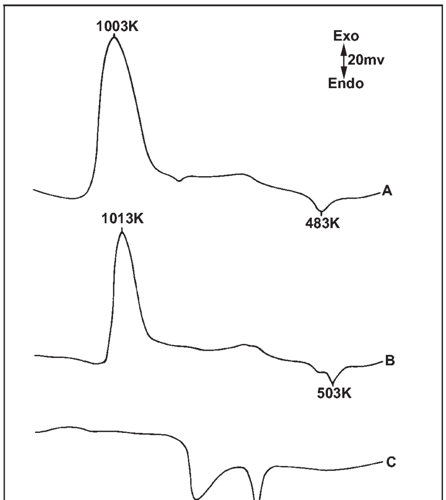

Fig. 2 DTA curves of: A – EuL_3; B – GdL_3; C – $EuL_3$0.5dmm

ond step decomposition of these complexes are shown in Fig. 2. From the TG curves, the order of reaction (n) and activation energy (E_a) were evaluated by the method of Coats and Redfern [5]. The order of reaction in each case was unity.

From the DTA studies, the heat of reaction (ΔH) was calculated from each thermal effect [6]. The temperature dependent calibration coefficient was obtained from

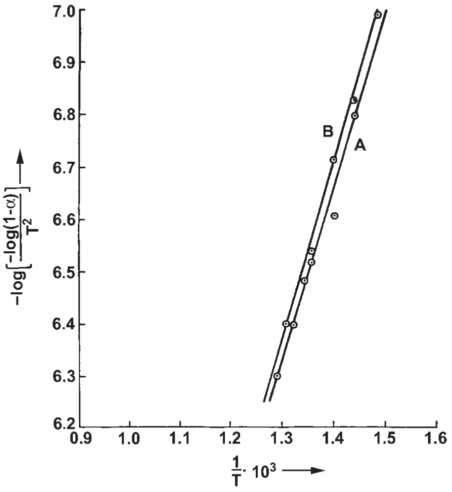

Fig. 3 Linearisation curves for first step decomposition of: A – EuL_3; B – GdL_3

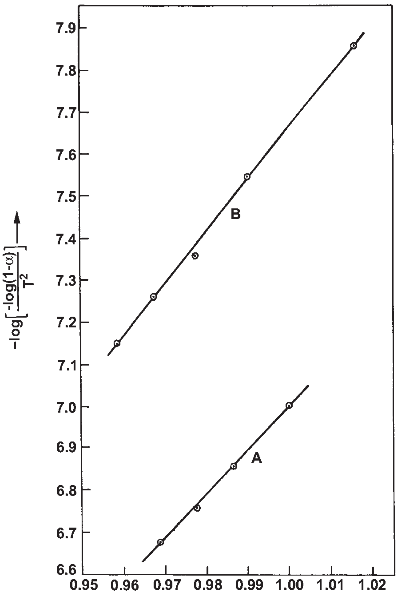

Fig. 4 Linearisation curve for second step decomposition of: A – EuL_3; B – GdL_3

the Currell equation [7]. The rate of thermal decomposition reaction for each step was enumerated by the literature method [8].

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