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Kinetic study of the thermal decomposition of Eu^{3+} with β -diketone ligands and 1,10-phenanthroline or 2,2-dipyridine

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Abstract

The complexes of general formula: $Eu(\beta-dik)_{3}L$ (where $\beta-dik=4,4,4$ -trifluoro-1-phenyl-1,3-butanedione (btfa), 4,4,4-trifluoro-butyryl-(+)camphor (hfc) or 2,2-dimethyl-6,6,7,7,8,8-heptafluoro-3,5-octadione (fod) and L=1,10-phenanthroline or 2,2-bipyridine) were synthesized by reacting the corresponding metal salt of chloride with the β -diketone and the other ligands. The thermal decomposition was studied by non-isothermal thermogravimetry. The kinetic models that better described the thermal decomposition reaction for the $Eu(\beta-dik)_{3}L$, were F1, R1 and R2.

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1. Introduction

There has been a large body of research on coordination of compounds with organic ligands such as complex of lanthanide ions with β -diketone, which can act as excellent light conversion molecular device (LCMD) [1–6]. There have also been discussions on the synthesis, luminescence, quantum yields, spectroscopic characteristics, structure, among others properties of these complexes, including the possibility of production of thin films [7–9].

Concerning the kinetic and the thermochemical of the β -diketone complexes and metallic β -diketone, the literature shows that extensive studies have been carried out, but only with metals of first transition succession, which is why very little is known about thermochemical and kinetic of these ligands with lanthanide ions [10,11].

The present work seeks to evaluate thermal stability, and determine the kinetic parameters and mechanism of thermal decomposition of the complexes $Ln(btfa)_3L$.

2. Experimental

2.1. Sample

The starting materials to synthesize the complex were high purity Eu_2O_3 (99%), btfa (99%), hfc (99%), fod (99%), phen (99%) and bipy (99%) supplied by Aldrich. Here, btfa stands for 4,4,4-trifluoro-1-phenyl-1,3-butanedione, hfc stands for 4,4,4-trifluoro-butyryl-(+)camphor, fod stands for 2,2-dimethyl-6,6,7,7,8,8-heptafluoro-3,5-octadione, phen stands for 1,10-phenanthroline and bipy stands for 2,2-bipyridine. The complexes of $Eu(\beta-dik)_3L$ were synthesized by reacting the corresponding metal salt of chloride with β -diketone and other ligands [8].

2.2. Thermal measurements

The DSC curves were obtained with Shimadzu differential scanning calorimeter (model DSC-50) in a temperature range of 25-500 °C using an aluminum crucible, with a heating rate of 10 °C min⁻¹, under nitrogen atmosphere with a flow of 50 ml min⁻¹. Thermogravimetric curves were obtained using a Shimadzu thermobalance (model TGA-50) using an alumina crucible, with a heating rate of

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Fig. 1. TG/DTG/DSC plots of the Eu(btfa)₃phen.

 10 °C min^{-1} in a temperature range of 25–900 °C, under nitrogen atmosphere with a flow of 50 ml min⁻¹. The sample mass was 2.0 ± 0.5 mg. The TG and DSC curves were analyzed with the aid of the TASYS software from Shimadzu.

2.3. Other measurements

The kinetic parameters, activation energy, reaction order and frequency factor were obtained across thermogravimetric data by the integral methods proposed by Coats– Redfern (CR) [12] and Madhusudanan (MD) [13], and the approximation methods proposed by Horowitz–Metzger (HM) [14] and Van Krevelen (VK) [15].

3. Results and discussion

3.1. Thermal decomposition

The TG/DTG/DSC curves of the $Eu(btfa)_3$ phen show that the complexes decompose before the coalition (Fig. 1a,b), as also occurs with $Eu(btfa)_3$ bipy.

Generally, we can observe that the profiles of these TG curves are sufficiently similar, with weight loss in some steps corresponding to thermal decomposition reaction of the complexes. The profiles of the thermal decomposition of the Eu(btfa)₃phen, Eu(btfa)₃bipy, Eu(hfc)₃L and Eu(fod)₃L were four, three, two and one decomposition stages, respectively (Fig. 2a,b). The characteristic tempera-



Fig. 2. TG curves of (a) $Eu(btfa)_3L$, (b) $Eu(hfc)_3L$ and $Eu(fod)_3L$.

Table 1 Thermal decomposition data for Eu(β -dik)L complexes at 10 °C min⁻¹

Complexes	Steps of decomposition	Temperature range (°C)	Weight loss (%)
Eu(fod) ₃ phen	1	132-338	99.98
Eu(fod), bipy	1	152-326	97.92
Eu(hfc) ₃ bipy	1	32-163	8.82
	2	163-373	79.14
Eu(btfa) ₃ bipy	1	158-358	39.79
	2	358-583	24.43
	3	697-941	27.52
Eu(btfa) ₃ phen	1	25-88	9.00
	2	216-460	53.27
	3	460-684	4.05
	4	715-899	9.07

tures of these reactions, weight loss, as well as the causes for the weight loss, are listed in Table 1. In order to analyses these effects, we will consider all the steps, which possibly refer to the loss output of the β -diketone ligands. According to the results presented, we can suggest the following order of thermal stability (Fig. 3): Eu(fod)₃phen>Eu(fod)₃bipy>Eu(btfa)₃bipy> Eu(hfc)₃bipy>Eu(btfa)₃phen.



Fig. 3. TG curve of $Eu(\beta-dik)_3L$.

3.2. Kinetic studies of non-isothermal decomposition

The thermal decomposition kinetic study of the reactions of complexes was realized using the best experimental conditions according to the relation between the thermo-

Table 2

Kinetic parameters of lanthanide complexes calculated from the dynamic thermogravimetric data at heating rates of 10 °C min⁻¹

Complex	Parameter	Methods ^a			
		CR	MD	HM	VK
Eu(btfa) ₃ bipy					
1 stage	$E_{a} (kJ mol^{-1})$ A (s ⁻¹)	62.25 12.24×10^{2}	61.71 11.89×10^{2}	87.07 31.61×10^{4}	73.20 50.17×10^8
2 stage	$n = E_{a} (kJ mol^{-1}) A (s^{-1}) n$	0.40 112.02 16.38×10 ⁴ 0.54	0.36 112.39 19.10×10 ⁴ 0.54	$0.69 \\ 142.21 \\ 32.02 \times 10^{6} \\ 0.77$	$0.52 \\ 126.02 \\ 10.20 \times 10^{11} \\ 0.64$
Eu(btfa), phen					
1 stage	$E (kJ mol^{-1})$ A (s ⁻¹)	128.64 10.24×10^{8} 1.93	124.23 41.64×10^{7} 1.83	156.49 32.20×10^{10} 2.30	139.95 39.72×10^{14} 2.04
2 stage	$ E_{a} (kJ mol^{-1}) A (s^{-1}) $	120.93 11.11×10^{4}	120.07 10.51×10^{4}	159.54 36.37×10^{6}	137.79 10.69×10^{11} 1.00
Eu(hfc) hipy	n	0.00	0.82	1.10	1.00
1 stage	$E_{a} (kJ mol^{-1})$ A (s ⁻¹) n	88.80 59.24×10 ⁴ 0.63	88.77 63.75×10^4 0.62	109.59 86.76×10 ⁶ 0.84	99.47 21.36 \times 10 ¹¹ 0.73
Eu(fod) ₃ phen					
1 stage	$E_{a} (kJ mol^{-1})$ A (s ⁻¹) n	83.91 20.07×10 ⁴ 0.00	84.15 23.19×10 ⁴ 0.00	100.59 12.90×10^{6} 0.00	91.63 36.17×10 ¹⁰ 0.00
Eu(fod)3bipy					
1 stage	$E_{a} (kJ mol^{-1})$ A (s ⁻¹) n	96.85 74.47 \times 10 ⁵ 0.47	100.61 20.12×10 ⁶ 0.58	$119.56 \\ 17.91 \times 10^8 \\ 0.70$	$ 109.44 \\ 44.31 \times 10^{12} \\ 0.72 $

^a Integral methods proposed by Coats-Redfern (CR) [12] and Madhusudanan (MD) [13], and the approximation methods proposed by Horowitz-Metzger (HM) [14] and Van Krevelen (VK) [15].

Table 3

Kinetic parameters derived from application of the function $g(\alpha)$ in the Coats–Redfern equation for $\phi = 10$ °C min⁻¹

Complex	Parameter	Value	Model
Eu(btfa) ₃ bipy	$E_{a} (kJ mol^{-1})$ A (s ⁻¹)	64.69 1.10×10 ³	R2
Eu(btfa) ₃ phen	r E_a (kJ mol ⁻¹) A (s ⁻¹)	0.999 93.92 4.47×10^5	F1
Eu(hfc) ₃ bipy	r $E_{\rm a}$ (kJ mol ⁻¹) A (s ⁻¹)	0.981 80.05 6.32×10^{4}	R1
Eu(fod) ₃ phen	r $E_{a} (kJ mol^{-1})$ $A_{a} (s^{-1})$	0.32×10^{-10} 0.999 83.88 1.99 × 10 ⁵	R1
Eu(fod) ₃ bipy	r $E_{a} (kJ mol^{-1})$	0.998 92.56	R1
	A (S) r	0.999	

gravimetric profile and the heating rate, using decomposed fraction (α) from 0.10 to 0.90.

The evaluation of the kinetic parameters regarding reaction order (n), apparent activation energy (E_a) and frequency factor (A) for the first and second steps were more significant in each complex (Table 2). The apparent activation energy for the methods of Horowitz–Metzger and Van Krevelen are larger than those for the integral methods of Coats–Redfern and Madhusudanan.

In this way, the matching of these values of activation energy suggests the following decreasing order of thermal stability for the first steps, which we consider most significant, for the splitting of almost all of the β -diketones: Eu(btfa)₃phen>Eu(fod)₃bipy>Eu(hfc)₃bipy> Eu(fod)₃phen>Eu(btfa)₃bipy.

The kinetic models that better described the thermal decomposition reaction for the Eu(β -dik)₃L, were F1, R1 and R2 (Table 3). The model F1 indicating that the mechanism is controlled by a reaction order and is defined by the function $g(\alpha) = -\ln(1 - \alpha)$, indicating a first order reaction. The model R1 indicating that the mechanism is controlled by a one-dimensional phase-boundary (zero order) and is defined by the function $g(\alpha) = 1 - (1 - \alpha)$. The final model R2 indicating that the mechanism is controlled by a phase-boundary reaction (cylindrical sym-

metry) and is defined by the function $g(\alpha) = 2[1 - (1 - \alpha)^{1/2}]$, indicating a mean reaction order [16].

4. Conclusion

The values of the kinetic parameters obtained by the different integral and approach methods were in agreement with the respective mathematical models. The apparent activation energy values obtained by these different methods were similar, but the thermal stability order of the various compounds were not.

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