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THERMAL DECOMPOSITION OF LANTHANIDE(III) COMPLEXES WITH 4,4,4-TRIFLUORO-1-PHENYL-1,3-BUTANEDIONE

Photoluminescent properties and kinetic study

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The complexes of general formula Ln(btfa)$_3$L, where *Ln*=Eu or Tb, *btfa*=4,4,4-trifluoro-1-phenyl-1,3-butanedione, *L*=1,10-phenanthroline (*phen*) or 2,2-bipyridine (*bipy*), were synthesized by reacting the corresponding metal chloride with the proper β-diketone and the other ligand. The complexes were obtained in the powder form and were characterized by photoluminescence and TG. Their thermal decomposition was studied by non-isothermal thermogravimetric techniques. The Eu(btfa)$_3$bipy complex presented the highest thermal stability and it melts before being decomposed. The complex Eu(btfa)$_3$phen presented the largest activation energy for a heating rate of 5°C min^{-1}.

Keywords: *lanthanide, photoluminescence, thermal decomposition kinetics*

Introduction

There has been a large research activity on coordination compounds of the lanthanide ions with organic ligands including β-diketones, which can act as excellent light conversion molecular device (LCMD) [1–5]. However, several aspects are to be considered [6–8], in order to obtain a highly luminescent complex: (*i*) molar absorbance of the ligands, (*ii*) energy transfer from the ligands to the metal, (*iii*) photoluminescence of the metal ion and (*iv*) non-radioactive decay processes due to OH and CH oscillators.

The use of these compounds ranges from radiation sensors to a variety of photonic and integrated optoelectronic devices [4], as well as probes in bioinorganic systems [5, 9, 10] and luminescent labels in fluoroimmunoassays [5, 9]. In addition, these materials may also be applied in the development of ultraviolet dosimetry technology. An ultraviolet dosimeter, highly sensitive and selective to UV cumulative measurements, was developed from thin films of these complexes [11]. These thin films were prepared by a thermoevaporation process, in which the powder complex was heated under high vacuum, volatilized and deposited on a substrate.

Nevertheless, in order to obtain high quality thin films for such application, these compounds must be submitted to such thermoevaporation process without any significant thermodecomposition. Therefore, a kinetic and thermodynamic study is necessary in order to predict whether the complex is stable enough to be successfully heated and thermoevaporated.

Several properties of these complexes have been studied, such as synthesis, luminescence, quantum yields, spectroscopic characteristics and structure, including also the production of thin films, but not much is known about their thermal decomposition kinetics [6, 9, 10].

In the present work, it is proposed to study the photoluminescent properties and the thermal decomposition kinetics, using non-isothermal heating methods [7, 8, 11] of Ln(btfa)$_3$L, in which Ln stands for Eu^{3+} or Tb^{3+}, *btfa* stands for 4,4,4-trifluoro-1-phenyl-1,3-butanedione and *L* stands for *phen* and *bipy*.

Experimental

Starting materials

The starting materials used to synthesize the complexes were high purity Eu$_2$O$_3$ (99%) and Tb$_2$O$_3$ (99%), *btfa* (99%), *phen* (99%) and *bipy* (99%) supplied by Aldrich Chemical Co. Here, *btfa* stands for 4,4,4-trifluoro-1-phenyl-1,3-butanedione, *phen*

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stands for 1,10-phenanthroline and *bipy* stands for 2,2-bipyridine. The complexes $Eu(btfa)_3L$ and $Tb(btfa)_3L$ were synthesized by reacting the corresponding metal chlorides with the β-diketone and the other ligands as reported [6].

The complexes were synthesized in the form of powder and were placed inside an alumina crucible, placed inside the deposition chamber. The thin films were later deposited over a boron silicate glass target, previously cleaned and degreased to assure proper film adhesion, by thermo-evaporation. For the mixed complex thin film presented in Fig. 1, the two compounds ($Tb(btfa)_3phen$ and $Eu(btfa)_3bipy$) were vigorously blended in order to obtain homogeneity, and they were later thermally co-evaporated.

The films were photolitographically defined to form a rectangular structure of about 1 cm^2. The depositions were monitored in real time by a 6 MHz quartz crystal thickness-meter model STM-100/MF from Sycon Instruments, which measures the film thickness by the shift of frequency of the quartz oscillator. Ellipsometric measurements, with a model Rudolph Research AutoEL-IV ellipsometer, were also performed at several wavelengths to assure film high quality and uniformity.

Methods

Thermal measurements

The thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance with an alumina crucible, and with heating rates of 5, 10, 15 and 20°C min^{-1} at a temperature range of 25–900°C and under a nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The sample mass was 2.0±0.5 mg. TG curves were analyzed with the aid of the TASYS software from Shimadzu.

Photoluminescence

The photoluminescence spectra were obtained at room temperature using a double Jobin-Yvon Ramanor U-1000 monochromator, coupled to a RCAC31034-RF photomultiplier tube. The excitation source was a 150 W Xe–Hg lamp emitting at 315 nm with a Corning 7-54 filter. The photoluminescence spectra were obtained with the aid of a Spectralink interface connected to a microcomputer.

Other measurements

The kinetic parameters, activation energy, reaction order and frequency factor were obtained from the 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].

The kinetic parameters in the dynamic heating method were determined according to the Coats–Redfern [12] equation, using the thermal decomposition model that better fits the data obtained in the isothermal experiments.

Results and discussion

Luminescence results

Figure 1 illustrates the emission spectrum of a 600 Å thick-mixed 5:95 $Eu(btfa)_3bipy/Tb(btfa)_3phen$ thin film under 315 nm excitation. This spectrum presents sharp and narrow lines and also the overlapping of the transitions corresponding to the emissions associated to the Eu(III) and Tb(III) ions mixed in the film. The two main transitions $^5D_0 \rightarrow {}^7F_2$ for Eu(III) and $^5D_4 \rightarrow {}^7F_5$ for Tb(III) are highlighted in the figure. As can be noticed, these are two very sharp and high intensity peaks, allowing promising applications in optical devices.

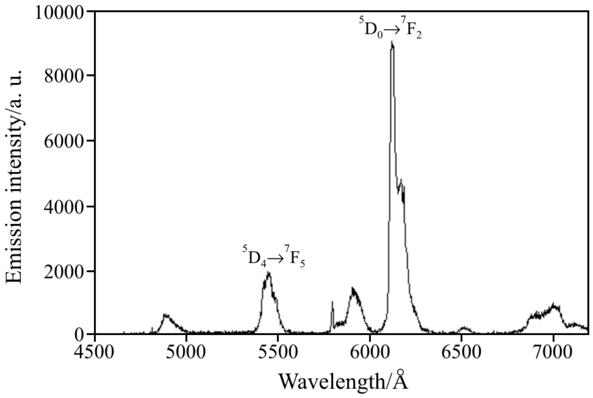

Fig. 1 Emission spectrum of a 600 Å thick-mixed 5:95 $Eu(btfa)_3bipy/Tb(btfa)_3phen$ 60 nm thick thin film under 315 nm excitation

Thermal behavior

Figures 2a and b show the overlapping of the thermogravimetric curves for the complexes $Eu(btfa)_3bipy$ and $Tb(btfa)_3phen$, at different heating rates. The profile of these TG curves indicates that the different decomposition steps correspond to thermal decomposition reactions of the complexes. The thermal decomposition curves of the complexes $Eu(btfa)_3bipy$, $Eu(btfa)_3phen$, $Tb(btfa)_3bipy$ and $Tb(btfa)_3phen$ displayed three, four, five and six decomposition steps, respectively (Fig. 3).

The characteristic temperatures and mass losses of these reactions are listed in Table 1. In order to

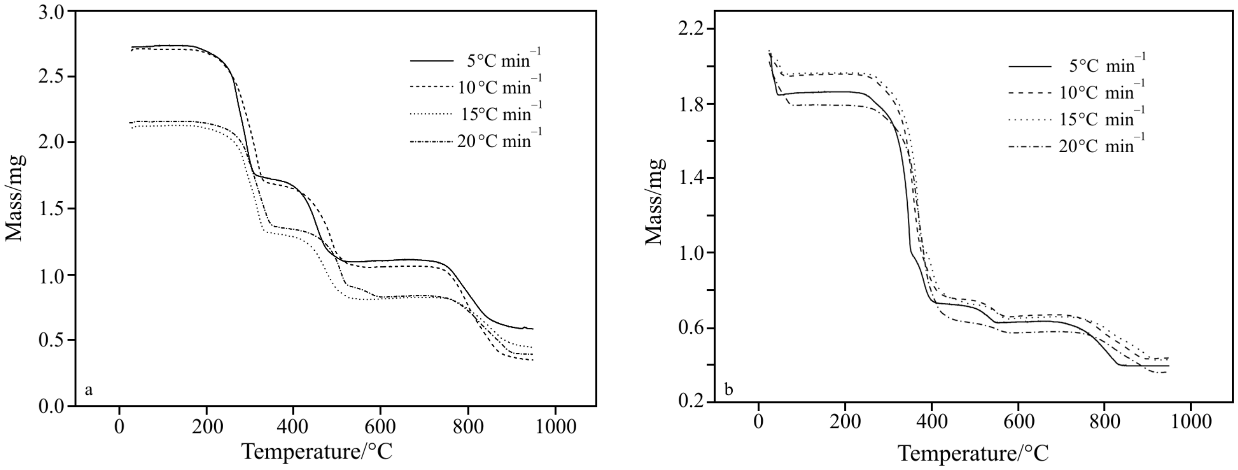

Fig. 2 TG curves of the complexes, at different heating rates; a – Eu(btfa)$_3$bipy and b – Tb(btfa)$_3$phen

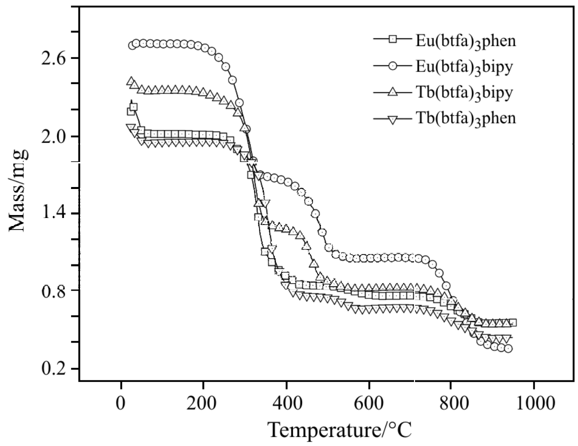

Fig. 3 TG curve of the Ln(btfa)$_3$L complexes obtained using a heating rate of 10°C min^{-1}

analyze these effects, one should consider all thermal decomposition steps, which possibly refer to the loss of the β-diketone ligands. According to the results presented, the following order of thermal stabilities can be suggested:

$$\mathrm{Eu(btfa)_3bipy>Tb(btfa)_3bipy>}$$
$$\mathrm{Eu(btfa)_3phen>Tb(btfa)_3phen}$$

Kinetic studies of the non-isothermal decompositions

A kinetic study was undertaken for the thermal decomposition reactions of complexes. This study correlates the thermogravimetric profiles and the heating rate, taking into account only the values of the decomposed fraction (α) from 0.10 to 0.90.

The kinetic parameters in the dynamic heating method were determined according to the Coats–Red-

Table 1 Thermal decomposition data for the Ln(btfa)$_3$L complexes heated at 10°C min^{-1}

Complex	Decomposition step	Temperature range/°C	Mass loss/%		Lost species
			experimental	theoretical	
Tb(btfa)$_3$phen	first	24–74	5.5	5.5	1/3 phen
	second	210–384	48.0	48.5	2/3 phen+1 4/7 btfa
	third	384–457	9.5	10.5	3/7 btfa
	fourth	497–577	4.0	4.0	1/5 btfa
	fifth	718–823	6.0	6.0	1/5 btfa+1/10 btfa
	sixth	823–910	5.0	6.5	1/5 btfa
Tb(btfa)$_3$bipy	first	27–70	2.5	2.5	1/6 bipy
	second	169–383	43.5	44.5	5/6 bipy+1 1/3 btfa
	third	383–503	17.5	17.0	2/3 btfa+1/8 btfa
	fourth	503–578	2.5	2.5	1/8 btfa
	fifth	657–904	11.5	12.0	4/8 btfa
Eu(btfa)$_3$phen	first	25–88	9.0	9.0	1/2 phen
	second	216–460	53.5	53.0	1/2 phen+2 btfa
	third	460–684	4.0	4.0	2/10 btfa
	fourth	715–899	9.0	9.0	4/10 btfa
Eu(btfa)$_3$bipy	first	158–358	40.0	39.5	1 bipy+1 btfa
	second	358–583	24.5	24.5	1 btfa+1/12 btfa
	third	697–941	27.5	27.5	9/12 btfa

Table 2 Kinetic parameters of the first and second decomposition steps of the lanthanide complexes calculated from the dynamic thermogravimetric data at 10°C min^{-1} heating rate

Decomposition step	Parameter	Methods			
		CR	MD	HM	VK
		Eu(btfa)$_3$bipy			
First	E_a/kJ mol^{-1}	62	62	87	73
	A/s^{-1}	$1.2{\cdot}10^{3}$	$1.2{\cdot}10^{3}$	$3.2{\cdot}10^{5}$	$5.1{\cdot}10^{9}$
	n	0.40	0.36	0.69	0.52
Second	E_a/kJ mol^{-1}	112	112	142	126
	A/s^{-1}	$1.6{\cdot}10^{5}$	$1.9{\cdot}10^{5}$	$3.2{\cdot}10^{7}$	$1.0{\cdot}10^{12}$
	n	0.54	0.54	0.77	0.64
		Eu(btfa)$_3$phen			
First	E_a/kJ mol^{-1}	129	124	156	140
	A/s^{-1}	$1.0{\cdot}10^{9}$	$4.2{\cdot}10^{8}$	$3.2{\cdot}10^{11}$	$4.0{\cdot}10^{15}$
	n	1.93	1.83	2.30	2.04
Second	E_a/kJ mol^{-1}	121	120	160	138
	A/s^{-1}	$1.1{\cdot}10^{5}$	$1.1{\cdot}10^{5}$	$3.7{\cdot}10^{7}$	$1.1{\cdot}10^{12}$
	n	0.86	0.82	1.18	1.00
		Tb(btfa)$_3$bipy			
First	E_a/kJ mol^{-1}	111	111	132	117
	A/s^{-1}	$2.3{\cdot}10^{7}$	$2.9{\cdot}10^{7}$	$3.0{\cdot}10^{9}$	$3.6{\cdot}10^{13}$
	n	0.69	0.70	0.86	0.74
Second	E_a/kJ mol^{-1}	243	241	277	265
	A/s^{-1}	$1.5{\cdot}10^{15}$	$1.1{\cdot}10^{15}$	$4.8{\cdot}10^{17}$	$3.1{\cdot}10^{13}$
	n	1.13	1.11	1.30	1.22
		Tb(btfa)$_3$phen			
First	E_a/kJ mol^{-1}	107	104	127	115
	A/s^{-1}	$2.8{\cdot}10^{6}$	$1.9{\cdot}10^{6}$	$1.9{\cdot}10^{8}$	$6.9{\cdot}10^{12}$
	n	0.57	0.51	0.67	0.63
Second	E_a/kJ mol^{-1}	156	168	189	174
	A/s^{-1}	$3.3{\cdot}10^{7}$	$2.5{\cdot}10^{8}$	$5.7{\cdot}10^{9}$	$3.6{\cdot}10^{14}$
	n	0.26	0.44	0.42	0.35

fern [12] equation, using the thermal decomposition model suggested by the data obtained in the isothermal experiments.

The evaluation of the kinetic parameters: reaction order (n), apparent activation energy (E_a) and frequency factor (A) for the first and second steps, which are considered as the most significant steps, are listed for each complex in Table 2. The apparent activation energy for the Horowitz–Metzger (HM) and Van Krevelen (VK) approximation methods are higher than those for the Coats–Redfern (CR) and Madhusudanan (MD) integral methods.

Therefore, the comparison of these values of activation energy suggests the following decreasing order of thermal stability for the first steps:

$$\mathrm{Eu(btfa)_3phen > Tb(btfa)_3phen > Tb(btfa)_3bipy > Eu(btfa)_3bipy}$$

The kinetic models that best described the thermal decomposition reaction for the Ln(btfa)$_3$L complexes were F1 and R2 (Table 3).

The F1 model indicates that the mechanism is controlled by reaction order and is defined by the function $g(\alpha)=-\ln(1-\alpha)$, indicating a first order reaction. The R1

Table 3 Kinetic parameters determined using dynamic thermogravimetric method of Coats–Redfern's equation for ϕ=10°C min^{-1}

Decomposition step	Parameter	Complex			
		Tb(btfa)$_3$phen	Tb(btfa)$_3$bipy	Eu(btfa)$_3$phen	Eu(btfa)$_3$bipy
First	E_a/kJ mol^{-1}	103	127	98	65
	A/s^{-1}	$7.5{\cdot}10^{6}$	$9.4{\cdot}10^{8}$	$1.2{\cdot}10^{6}$	$1.1{\cdot}10^{3}$
	r	0.999	0.996	0.984	0.999
	model	R2	F1	F1	R2
Second	E_a/kJ mol^{-1}	172	229	131	140
	A/s^{-1}	$2.1{\cdot}10^{9}$	$1.3{\cdot}10^{14}$	$5.4{\cdot}10^{5}$	$2.2{\cdot}10^{7}$
	r	0.999	0.999	0.999	0.998
	model	R2	F1	F1	F1

model points out that the mechanism is controlled by one-dimensional phase-boundary (zero order) and it is defined by the function $g(\alpha)=1-(1-\alpha)$. The R2 model indicates that the mechanism is controlled by a cylindrical symmetry phase-boundary reaction and it is defined by the function $g(\alpha)=2[1-(1-\alpha)^{1/2}]$, corresponding to a one half reaction order [16].

Conclusions

The complexes Tb(Btfa)$_3$phen, Tb(Btfa)$_3$bipy, Eu(Btfa)$_3$phen and Eu(Btfa)$_3$bipy were synthesized and characterized by several techniques.

These complexes present a sharp and high intensity luminescence spectra, what make them very efficient light converters for optical devices applications.

The thermal decomposition of the complexes Ln(btfa)$_3$L, in nitrogen atmosphere, occurs in various stages. According to the thermogravimetric curves, the thermal stability order observed was:

$$\mathrm{Eu(btfa)_3bipy > Tb(btfa)_3bipy > Eu(btfa)_3phen > Tb(btfa)_3phen}$$

Conversely the activation energy indicates the following stability order:

$$\mathrm{Eu(btfa)_3phen > Tb(btfa)_3phen > Tb(btfa)_3bipy > Eu(btfa)_3bipy}$$

Satisfactory kinetic parameters were obtained by the approximation and integral methods and a good correlation was observed between the values obtained from the different methods for the same sample. Generally, the activation energy values obtained using the integral methods are smaller than the values obtained by the approximation methods. The kinetic models that best described the thermal decomposition reactions for the Ln(btfa)$_3$L complexes were F1 and R2.

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