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SYNTHESIS AND NON-ISOTHERMAL KINETIC STUDY OF THE THERMAL DECOMPOSITION OF GADOLINIUM(III) COMPLEXES

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In this work the synthesis and determination of kinetic parameters of thermal decomposition of the complexes Gd(thd)$_3$phen and Gd(thd)$_3$bipy (where *thd*=2,2,6,6-tetramethyl-3,5-heptanodione; *phen*=1,10-phenantroline and *bipy*=2,2-dipyridine) by non-isothermal thermogravimetry is reported. The kinetic parameters of activation energy, reaction order and frequency factor were obtained from the thermogravimetric data by non-isothermal integral methods proposed by Coats–Redfern and Madhusudanan, as well as by approximation methods proposed by Horowitz–Metzger and Van Krevelen. The kinetic model that best described the thermal decomposition reaction for the two complexes was R1 indicating that the mechanism is controlled by one-dimensional phase-boundary (zero order) and is defined by the function $g(\alpha)=1-(1-\alpha)$. Based on the values of activation energy obtained by Coats–Redfern method, the following order in the thermal stability was noticed: Gd(thd)$_3$phen<Gd(thd)$_3$bipy.

Keywords: *Coats–Redfern, β-diketone, lanthanide, non-isothermal kinetic*

Introduction

The interest on β-diketonates of metals has progressively increased over the last decades, not only from the point of view of the structural features which help to elucidate the chemistry of coordination [1, 2] but also concerning the determination of thermodynamic parameters involving these complexes. The coordination compounds formed with such a type of ligand have the cation charge neutralized and depending on the radical bonded to the chelate part of oxygen-bidentate centre, can display a hindering effect [3].

β-Dicarbonyl compounds feature a class of important and extensively employed ligands [4–6]. They are very versatile and, besides the usual bidentate behavior of monoanions, exhibit a great variety of coordination modes [7]. The XC(O)–CH$_2$–C(O)X type β-diketones have attracted great interest by structural chemists, because of possible enol–diketo tautomerism [8, 9]. Here, two oxygen atoms of the chelating ligand serve as the bridging donor atoms. The coordination behavior of β-diketones also significantly influences the relative stabilities of the mixed-ligand complexes [10, 11] as well as their use in biomedicine [6, 12].

The thermodecomposition of solids has been studied widely in the recent years and kinetic parameters of pharmaceuticals and foods it have been determined. Besides several papers related to the adjustment of the equations involved in the determination of these parameters [13–15].

Concerning to the kinetic and the thermochemical parameters of the β-diketone complexes and metal ion, the literature indicates that extensive studies have been carried out, but only with metals of the first transition succession, which is why very little is known about thermochemical and kinetic of these ligands with lanthanide ions [16–19].

Thus, this work seeks for syntheses and determination of kinetic parameters of non-isothermal decomposition of two gadolinium complexes of Gd(thd)$_3$L, where *thd* represents the β-diketone 2,2,6,6-tetramethyl-3,5-heptanodione and *L* is 1,10-phenanthroline (*phen*) or 2,2-bipyridine (*bipy*).

Experimental

Sample

The starting materials to synthesize the complex were high purity Gd$_2$O$_3$ (99%); 2,2,6,6-tetramethyl-3,5-heptanodione; 1,10-phenanthroline and 2,2-dipyridine supplied by Aldrich Chemical Co. The complexes were synthesized by reacting the metal ion salt of chloride with the β-diketone and the other ligands [16].

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Characterization

The melting temperatures of the two compounds were determined by means of a Microquímica model MQAPF-301 apparatus. Microanalysis for carbon, hydrogen and nitrogen were performed with a Thermoquest CE Instruments model EA 1110 CHNS-O. The metal content in the complexes was determined through of complexometric titration using bromopyrogallol red as indicator and EDTA solution [20].

Infrared spectra were recorded in KBr pellets, in the region 4000–400 cm^{-1} using a Bomem, model MB-102 series FTIR Spectrophotometer. The UV-Visible absorption spectra were recorded with a Perkin Elmer UV-Vis Spectrophotometer Lambda 6 Model 2688-002.

Thermoanalytical measurements

The DSC curves were obtained with Shimadzu Differential Scanning Calorimeter, model DSC-50, in a temperature range of 25–400°C using an aluminium crucible, at heating rate of 10 K min^{-1}, under nitrogen atmosphere with rate of 50 mL min^{-1}.

TG curves were recorded using a Shimadzu thermobalance, model TGA-50, using an alumina crucible, applying heating rates of 5, 10 and 15 K min^{-1} in a temperature range of 25–400°C, under nitrogen atmosphere with rate of 50 mL min^{-1}. The sample mass used was about 3.0 mg. The TG and DSC curves were analyzed with the aid of TASYS software from Shimadzu.

Kinetic parameters

The theoretical basis for kinetic calculations using non-isothermal thermogravimetry is based on Eq. (1):

$$g(\alpha) = \frac{A}{\phi}\int_0^T \exp\left(-\frac{E_a}{RT}\right)dT \qquad (1)$$

where A is the pre-exponential factor, T is the temperature, R is the gas constant, ϕ is the heating rate and E_a is the apparent activation energy.

This expression represents the mathematical equation that describes the thermogravimetric curve. The term $g(\alpha)$ represents the reaction mechanism and the second term does not have analytical meaning, being calculated by approximated numerical methods. Several researchers developed methods for the resolution of the part of the equation that doesn't have analytical solution, which have been divided in integral and approximation methods.

In the present work the kinetic parameters, activation energy, reaction order and frequency factor were obtained using the kinetic models by the integral methods proposed by Coats–Redfern (CR) [21] and Madhusudanan (MD) [22], and the approximation methods proposed by Horowitz–Metzger (HM) [23] and Van Krevelen (VK) [24].

Results and discussion

Characterization

The reaction of the samarium chloride with 2,6,6-tetramethyl-3,5-heptanodione (*thd*), 1,10-fenanthroline (*phen*) and 2,2-bipiridine (*bipy*) ligands resulted solid complexes in powder form. They are soluble in organic solvents, e.g. alcohols, chloroform and acetone, but insoluble in water. The CHN elemental analysis of the complexes, $Gd(thd)_3bipy$ and $Gd(thd)_3phen$ are in good agreement with the expected values for compounds, the relative error was about 10% when the theoretical and experimental values were compared as it is, as shown in Table 1. The characteristics of the synthesized complexes in this work are shown in Table 2.

The IR vibrational spectra provided good evidence that the metal ion is coordinated to the ligands via the C=O and C–N groups [16, 25]. The most important IR bands of the complexes are reported in Table 2. In order to evaluate its potential for device applications and to understand better the optical characteristics of the complexes their UV-VIS spectra were recorded. An intense absorption area usually from UV is a basic feature from complexes with intense luminescence on visible area. The complex $Gd(thd)_3bipy$ presented only a maximum absorption band at 281 nm. On the other hand, the $Gd(thd)_3phen$ complex presented two absorption bands; one with less intensity at 231 nm and the second of larger intensity at 266 nm. These values can be associated with the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions.

Figures 1 and 2 show the TG/DSC curves of the two complexes studied at a heating rate of 10 K min^{-1}. According to the TG/DSC data it was verified that the mass loss for the complexes started before their melting temperature. The thermal decomposition of

Table 1 Elemental analysis for $Gd(thd)_3bipy$ and $Gd(thd)_3phen$ complexes

Complex	Theoretical values/%				Experimental values/%			
	Ln	C	H	N	Ln	C	H	N
$Gd(thd)_3bipy$	18.15	59.62	7.91	3.23	18.23	54.00	6.53	2.41
$Gd(thd)_3phen$	17.66	60.71	7.70	3.15	17.65	58.70	6.76	2.67

Table 2 General characteristics of Gd(thd)$_3$bipy and Gd(thd)$_3$phen complexes and some of their infrared and UV-VIS spectroscopic data

Complex	Molecular formula	Molar mass/g mol^{-1}	IR/cm^{-1}		UV-VIS/nm	Melting temperature	
			ν(C=O)	ν(C–N)		*T*/°C	*
Gd(thd)$_3$bipy	Gd($C_{43}H_{28}O_2N_2$)	866.28	1574	1227	281	194.5	*D*/*M*
Gd(thd)$_3$phen	Gd($C_{45}H_{28}O_2N_2$)	890.32	1573	1227	231; 266	222.5	*D*

**D*/*M*→decomposition/melting; *D*→decomposition.

the complex Gd(thd)$_3$bipy started in solid phase at 94°C and then sample melted at 194°C (Table 2), while for the complex Gd(thd)$_3$phen the thermal decomposition took place in solid-state all along in the investigated temperature range (Table 2).

The analyzed complexes showed only one event during the thermal decomposition reaction. For the complex Gd(thd)$_3$bipy it occurred between 156–293°C and the corresponding mass loss is 87.6% (Fig. 1). On the other hand, the Gd(thd)$_3$phen complex decomposed in the range of 203–341°C accompanied by 95.4% of mass loss (Fig. 2). On the base of the obtained data the following thermal stability order can be suggested: Gd(thd)$_3$bipy<Gd(thd)$_3$ phen.

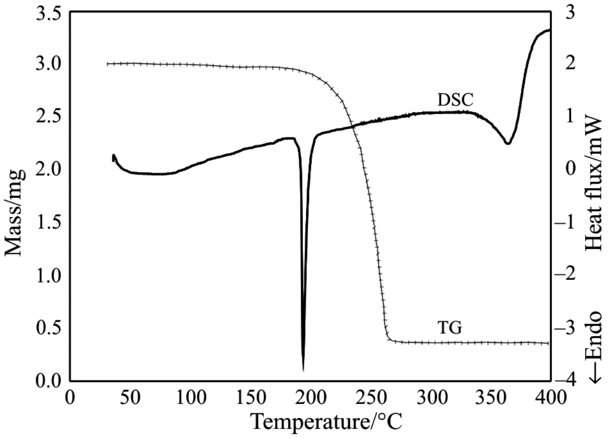

Fig. 1 The TG/DSC curves of Gd(thd)$_3$bipy complex

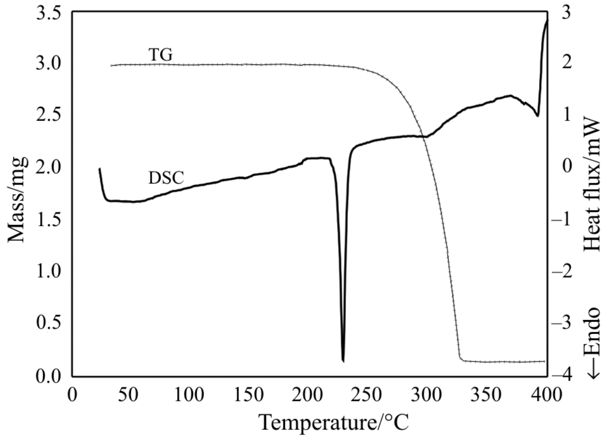

Fig. 2 The TG/DSC curves of Gd(thd)$_3$phen complex

Non-isothermal kinetic analysis

Figures 3 and 4 illustrate the TG curves of the analyzed complexes with various heating rates. The kinetic parameters at various heating rates obtained for the thermal decomposition of Gd(thd)$_3$bipy and Gd(thd)$_3$phen complexes were collected in Table 3.

The kinetic study of the thermal decomposition of the complexes was revealed using decomposed fraction (α) from 0.10 to 0.90. Table 3 shows the kinetics parameters obtained from the previously mentioned methods.

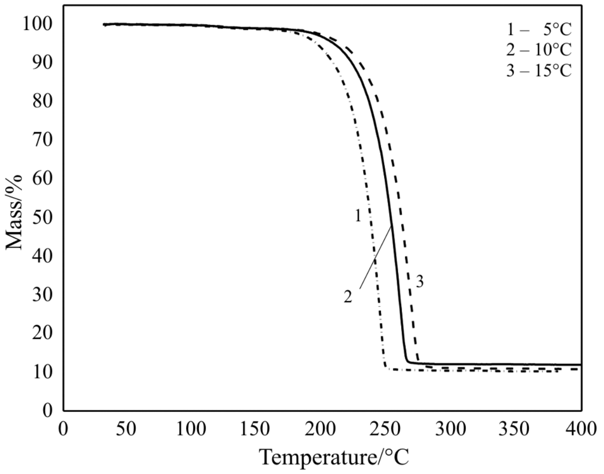

Fig. 3 TG curves of Gd(thd)$_3$bipy at different heating rates

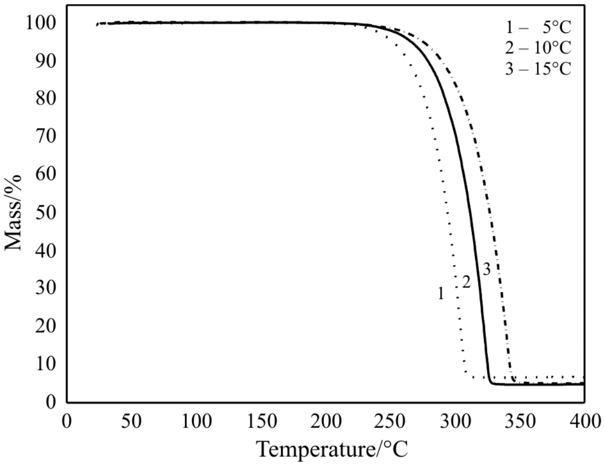

Fig. 4 TG curves of the Gd(thd)$_3$phen at different heating rates

Table 3 Kinetic parameters of the complexes obtained at different heating rates

Complex	Heating rate	Parameter	Model			
			CR	MD	HM	VK
$Gd(thd)_3bipy$	5 K min^{-1}	n	0.10	0.06	0.09	0.13
		E_a/kJ mol^{-1}	117.7956	116.6537	133.3100	123.8980
		A/s^{-1}	$2.996\cdot10^{9}$	$2.383\cdot10^{9}$	$1.658\cdot10^{11}$	$3.465\cdot10^{15}$
		r	1.0004	1.0004	0.9999	0.9899
	10 K min^{-1}	n	0.23	0.14	0.39	0.27
		E_a/kJ mol^{-1}	118.4097	115.4619	140.1860	129.2826
		A/s^{-1}	$3.084\cdot10^{9}$	$1.578\cdot10^{9}$	$6.926\cdot10^{11}$	$1.148\cdot10^{16}$
		r	0.9997	0.9996	0.9999	1.0060
	15 K min^{-1}	n	0.07	0.09	0.26	0.22
		E_a/kJ mol^{-1}	111.1867	112.0515	133.6768	126.9091
		A/s^{-1}	$5.030\cdot10^{8}$	$6.665\cdot10^{8}$	$1.304\cdot10^{11}$	$6.095\cdot10^{15}$
		r	0.9999	0.9999	0.9999	1.0110
$Gd(thd)_3phen$	5 K min^{-1}	n	0.22	0.03	0.25	0.23
		E_a/kJ mol^{-1}	131.6320	124.8330	151.3418	146.5350
		A/s^{-1}	$3.131\cdot10^{9}$	$6.976\cdot10^{8}$	$2.626\cdot10^{11}$	$2.718\cdot10^{16}$
		r	0.9997	0.9994	0.9999	1.0183
	10 K min^{-1}	n	0.20	0.23	0.29	0.26
		E_a/kJ mol^{-1}	128.1496	129.5559	150.4950	142.0590
		A/s^{-1}	$1.199\cdot10^{9}$	$1.753\cdot10^{9}$	$1.571\cdot10^{11}$	$8.239\cdot10^{15}$
		r	1.0000	1.0000	0.9999	1.0090
	15 K min^{-1}	n	0.24	0.08	0.26	0.15
		E_a/kJ mol^{-1}	118.5205	113.3262	138.2161	127.0238
		A/s^{-1}	$1.193\cdot10^{8}$	$4.079\cdot10^{7}$	$8.209\cdot10^{9}$	$2.477\cdot10^{14}$
		r	1.0003	1.0002	0.9999	1.0097

Table 4 Kinetic parameters derived from the application of $g(\alpha)$ function in the Coats–Redfern equation

Complex	Heating rate	Parameter	Mechanism			
			D1	D2	R1	R2
$Gd(thd)_3bipy$	5 K min^{-1}	E_a/kJ mol^{-1}	237.13	258.81	114.41	131.90
		A/s^{-1}	$5.33\cdot10^{21}$	$6.30\cdot10^{23}$	$1.26\cdot10^{9}$	$5.56\cdot10^{10}$
		r	0.9998	0.9993	0.9998	0.9984
		s	0.0225	0.0482	0.0112	0.0396
	10 K min^{-1}	E_a/kJ mol^{-1}	229.73	251.74	110.58	128.43
		A/s^{-1}	$3.53\cdot10^{20}$	$3.92\cdot10^{22}$	$4.38\cdot10^{8}$	$1.88\cdot10^{10}$
		r	0.9993	0.9996	0.9996	0.9992
		s	0.0482	0.0367	0.0242	0.0292
	15 K min^{-1}	E_a/kJ mol^{-1}	226.42	248.02	108.86	126.34
		A/s^{-1}	$1.04\cdot10^{20}$	$9.71\cdot10^{21}$	$2.85\cdot10^{8}$	$1.05\cdot10^{10}$
		r	0.9996	0.9997	0.9997	0.9991
		s	0.0351	0.0340	0.0176	0.0306
$Gd(thd)_3phen$	5 K min^{-1}	E_a/kJ mol^{-1}	256.65	280.47	123.70	142.93
		A/s^{-1}	$9.76\cdot10^{20}$	$1.08\cdot10^{23}$	$5.04\cdot10^{8}$	$2.11\cdot10^{10}$
		r	0.9998	0.9998	0.9998	0.9991
		s	0.0220	0.0271	0.0111	0.0300
	10 K min^{-1}	E_a/kJ mol^{-1}	251.21	274.90	120.83	140.00
		A/s^{-1}	$1.13\cdot10^{20}$	$1.05\cdot10^{22}$	$2.33\cdot10^{8}$	$8.54\cdot10^{9}$
		r	0.9998	0.9998	0.9998	0.9991
		s	0.0245	0.0267	0.0124	0.0304
	15 K min^{-1}	E_a/kJ mol^{-1}	230.51	252.18	110.37	127.87
		A/s^{-1}	$6.30\cdot10^{17}$	$3.43\cdot10^{19}$	$1.98\cdot10^{7}$	$4.70\cdot10^{8}$
		r	0.9998	0.9997	0.9998	0.9990
		s	0.0225	0.0292	0.0114	0.0309

The kinetics parameters obtained by integral and approximation methods show good correlation, however the values obtained from approximation methods were larger than those calculated from integral methods. This is due to the different mathematical treatment of the obtained data.

The selection of the mechanism which best describes the thermal decomposition of the complexes was determined by $g(\alpha)$ function and was calculated using the method proposed by Coats–Redfern [20] according to Eq. (2):

$$\ln\left(\frac{g(\alpha)}{T^2}\right)=\ln\left(\frac{AR}{\phi E_a}\right)-\frac{E_a}{RT} \qquad (2)$$

where T is the absolute temperature, E_a is the apparent activation energy, A is the pre-exponential factor, R is the gas constant, ϕ is the heating rate and $g(\alpha)$ is the kinetic model.

Among the kinetic models with their respective $g(\alpha)$ functions, the selected one was which correlation coefficient is the closest to 1 and has the lowest standard deviation. Table 4 summarizes the kinetic models R1, R2, D1 and D2 which described well the thermal decomposition of the $Gd(thd)_3bipy$ and $Gd(thd)_3phen$. Based on the established criteria in this paper, R1 model which describes best the thermal decomposition reaction of studied complexes. This model indicates that the decomposition mechanism is controlled by one-dimensional phase-plane (first order) and is defined by the function $g(\alpha)=1-(1-\alpha)$.

Conclusions

The formation of the complex occurred through the ligands via the C=O and C–N groups of the ligands. The values of the kinetic parameters obtained by the different integral and approximation methods showed good correlation, but the values obtained by approximation methods were larger compared to those obtained by integral methods.

According to the TG/DSC data it was verified that the thermal decomposition of the complexes started in solid phase. Based on the kinetic data obtained for the activation energy by Coats–Redfern method using non-isothermal thermogravimetric experiments, the following stability order for the complexes was established: $Gd(thd)_3bipy<Gd(thd)_3phen$. R1 is the best kinetic model to describe the thermal decomposition reaction of complexes.

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