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Synthesis and characterization of four new lanthanide complexes coordinate with β-diketone ligands and 1,10-phenanthroline or 2,2-dipyridine

Síntese e caracterização de quarto novos complexos de lantanídeos coordenados com ligantes β-dicetonas e 1,10-fenantrolina ou 2,2-bipiridina

Síntesis y caracterización de cuatro nuevos complejos de lantánidos coordinados con β-dicetonas y ligandos de 1,10-fenantrolina o 2,2-bipiridina

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Abstract

In this work the complexes $Ln(\beta\text{-dik})_3L$ (where Ln= Nd^{+3} e Er^{+3}, β-dik= 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Btfa) and L= 1,10-Phenanthroline (Phen) or 2,2'-Bipyridyl (Bipy)), were synthesized from the direct reaction of $LnCl_3$ with β-diketone and the ligands. The purpose was to create new lanthanide complexes with perspectives of use in markers. After the syntheses, the complexes were characterized by Solubility Test, Scanning Electron Microscopy (SEM) and the thermal properties of compounds were studied using Thermogravimetry Analisys (TGA), Differential Scanning Calorimetry (DSC) and

Determination of Melting/Decomposition Intervals. Based on the verified properties, the solubility test found that the complexes are not soluble in chloroform and water. The microscope images showed an excellent crystallization of the complexes. The complexes are stable up to 120°C, after this temperature they show a peak in the DSC referring to the fusion and the beginning of decomposition. The values of activation energy suggests the following decreasing order of stability: $Er(Btfa)_3Phen>Nd(Btfa)_3Phen>Er(Btfa)_3Bipy>Nd(Btfa)_3Bipy$.

Keywords: Synthesis; Lanthanide; Erbium; Neodymium.

Resumo

Neste trabalho os complexos $Ln(\beta\text{-dic})_3L$ (onde Ln = Nd^{+3} e Er^{+3}, β-dic = 4,4,4-trifluoro-1-fenil-1,3-butanodiona (Btfa) e L = 1,10-Fenantrolina (Phen) ou 2,2'-Bipiridina (Bipi)), foram sintetizados a partir da reação direta de $LnCl_3$ com a β-dicetona e os ligantes. O objetivo foi criar novos complexos de lantanídeos com perspectivas de uso como marcadores Após as sínteses, os complexos foram caracterizados por Teste de Solubilidade, Microscopia Eletrônica de Varredura (MEV) e as propriedades térmicas dos compostos foram estudadas por Análise de Termogravimetria (TGA), Calorimetria Varredura Diferencial (DSC) e Determinação de Intervalos de Fusão/Decomposição. Com base nas propriedades verificadas, o teste de solubilidade constatou que os complexos não são solúveis em clorofórmio e água. As imagens microscópicas mostraram uma excelente cristalização dos complexos. Os complexos são estáveis até 120°C, após esta temperatura os complexos apresentam um pico no DSC referente à fusão e ao início da decomposição. Os valores de energia de ativação sugere a seguinte ordem decrescente de estabilidade: $Er(Btfa)_3Phen>Nd(Btfa)_3Phen>Er(Btfa)_3Bipi>Nd(Btfa)_3Bipi$.

Palavras-chave: Síntese; Lantanídeos; Érbio; Neodímio.

Resumen

En este trabajo los complejos $Ln(\beta\text{-dic})_3L$ (donde Ln = Nd^{+3} y Er^{+3}, β-dic = 4,4,4-trifluoro-1-fenil-1,3-butanodiona (Btfa) y L = la 1,10-fenantrolina (Phen) o la 2,2'-Bipiridina (Bipi)), se sintetizaron a partir de la reacción directa de $LnCl_3$ con β-dicetone y ligandos. El objetivo fue crear nuevos complejos de lantánidos con perspectivas de uso como marcadores. Después de la síntesis, los complejos se caracterizaron mediante Prueba de Solubilidad, Microscopía Electrónica de Barrido (MEB) y las propiedades térmicas de los compuestos se estudiaron mediante Análisis de Termogravimetría (TGA), Calorimetría Diferencial de Barrido (DSC) y Determinación de Intervalos de Fusión/Descomposición. Con base en las propiedades

verificadas, la prueba de solubilidad encontró que los complejos no son solubles en cloroformo y agua. Imágenes microscópicas mostraron una excelente cristalización de los complejos. Los complejos son estables hasta 120°C, después de esta temperatura los complejos muestran una pico en DSC con respecto a la fusión y el inicio descomposición. Los valores de energía de activación sugieren el siguiente orden decreciente de estabilidad: $Er(Btfa)_3Phen>Nd(Btfa)_3Phen>Er(Btfa)_3Bipi>Nd(Btfa)_3Bipi$.

Palabras clave: Síntesis; Lantánidos; Erbio; Neodimio.

1. Introduction

The development of material sciences has made important contributions to technological advancement. The search for new systems with performance and properties optimized for innovative applications and the improvement of existing ones is one of the reasons for the current technological and scientific evolution.

The possibility of designing new lanthanide-based materials as efficient molecular light-converting devices has become an increasingly important topic in research on new materials. It has achieved important technological consequences, receiving the attention of several groups worldwide (Werts et al., 1997).

Photonic systems have aroused growing interest in medical, biological and technological applications, with the use of lasers, sensors, waveguides, optical fibers, light-emitting diodes, among others (Kajihara, 2013; Bouras et al., 2014; Lukowiak et al., 2015; Rai and Fanai, 2016).

The use and applications of lanthanides are concentrated in high-tech areas, with no existing elements that can replace them with the same performance (Assunção et al., 2013). Researchers all around the world are interested in studying the ion metallic complex with β-diketone, the β-diketone forms chelates with nearly all the elements of the periodical table (Lehn, 1990; Boyd et al., 2004).

Coordination compounds with organic ligands, lanthanide ions with β-diketones, can act as excellent molecular light-converting devices (DMCL), absorbing ultraviolet radiation and emittingvisible (Lehn 1990; Sabbatini et al., 1996).However, the luminescent properties of the coordination compounds containing lanthanide ions are affected by coordinated water molecules, which reduces the emission intensity due to the resonance between their vibrational states and metal ion emitters states (Silva et al., 2004). In an attempt to circumvent the situation, preserve and enhance the properties of the complex, we opted for a second

ligand, of heterobiaryl type, Bipy or Phen, since it presents a high coefficient of molar absorptivity, and is efficient in transferring energy to the lanthanide ion (Frey et al., 1994).

Studies indicate that lanthanide complexes are an alternative in the treatment of cancer (Momani et al., 2013) and have recently become an effective strategy to develop highly accurate methods for the rapid identification and isolation of patients infected with SARS-CoV-2 (Ji et al., 2020)

This work aims to study the synthesis and properties of the $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$ lanthanide complexes that were developed with perspectives of use in markers.

2. Methodology

2.1 Reagents and synthesis of the complexes

The materials used for the synthesis of the complexes were: neodymium (III) oxide 99% (Aldrich); erbium (III) oxide 99% (Aldrich); 4,4,4-trifluoro-1-phenyl-1,3-butanodione (Btfa) 99% (Aldrich); 1,10-phenanthroline (Phen) 99% (Aldrich) and 2,2'Bipyridyl (Bipy) 99% (Aldrich).

The complexes $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$ were synthesized by reacting the corresponding metal salt of chloride, prepared from the lanthanide oxides, with the β-diketone and the ligands. The β-diketone was added in an ethanolic solution of $LnCl_3$.The ligands were added by dripping separately at 30 minute intervals under constant magnetic agitation at a temperature of 60°C in stoichiometric ratios of 1:3:1. After that, a solution of NaOH at 0.1M was added to reach pH 6, maintaining the reflux for four hours. The resulting solution was left at room temperature for drying. After evaporation of the solvent, a complex in the form of crystalline powder was obtained. The syntheses of the complexes were carried out based on the method proposed by do Nascimento et al. (2010) and Morais et al. (2007).

2.2 Characterization

In the solubility test the results were obtained using the fixed concentration of 5g of the solid sample of the binders and the synthesized complexes for each litre of solvent (water, methanol, ethanol, acetone and chloroform) ($5g.L^{-1}$). The solution was shaken vigorously in

the test tube for approximately 3 minutes and it was observed if the sample had solubilized.

The Scanning Electron Microscopy images were obtained using a TESCAN microscopy, model VEGA3, with constant acceleration voltage of 15 kV. The magnifications used were 500x and 3000x.

Thermogravimetric curves were obtained in a Shimadzu thermobalance, model DTG-60H – simultaneous TG-DTA, using an alumina crucible, a heating rate of 10ºC.min^{-1} in a dynamic atmosphere of nitrogen, the flux of 50mL.min^{-1} and temperatures ranging from room to 400°C.

DSC curves were obtained using a TA INSTRUMENTS, model DSC 2920 Modulated DSC, a heating rate of 10ºC.min^{-1} in a dynamic atmosphere of nitrogen, the flux of 50mL.min^{-1} and temperatures ranging from room to 380°C, in order to measure the enthalpic transitions of the complexes.

The temperatures referring to the melting/decomposition intervals were obtained using a FISATOM Melting Point device, model 430, with controlled heating rate.

3. Results and Discussion

3.1 Lanthanide Complexes Coordinated with Mixed Organic Binders

The reaction of the lanthanide salts $ErCl_3$ and $NdCl_3$ with the organic ligands Btfa, Bipy and Phen gave solid complexes in powder form with the following general formula: $Ln(Btfa)_3Phen$ and $Ln(Btfa)_3Bipy$. In this formula, Ln represents the Er^{3+} metal ions and Nd^{3+}; Btfa represents the group β-diketones and the ligands 1,10-phenanthroline(Phen) and 2,2'-bipyridine(Bipy) the organic heterobiary ligands. The molecular formulas, molar masses and coloring of Btfa, Phen, Bipy, $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$ $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$ are shown in Table 1.

The equation below represents the generic chemical equation for the reaction.

$$LnCl_3 + Btfa + Bipy/Phen \longrightarrow Ln(Btfa)_3Bipy/Phen$$

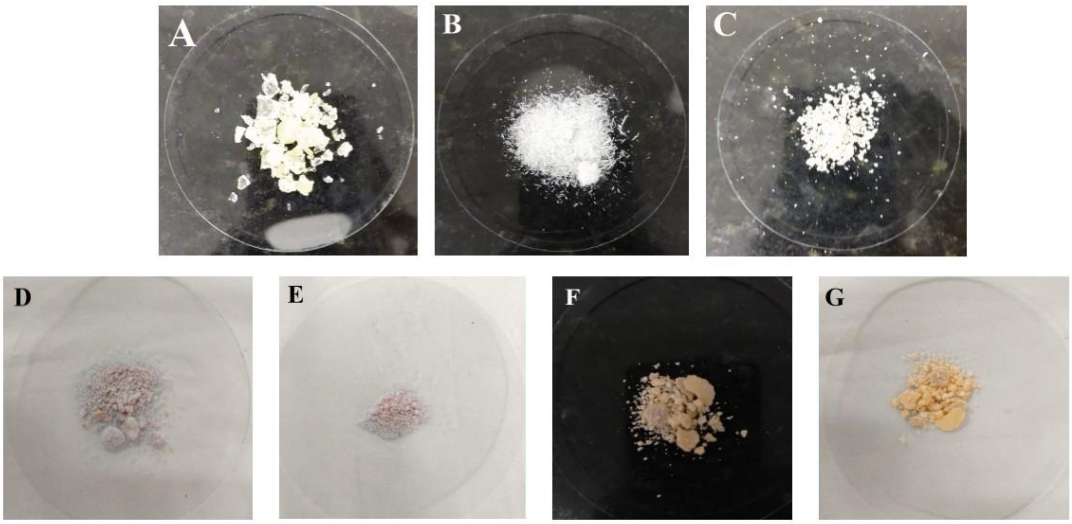
Table 1. Molecular Formula, Molecular Weight and Coloration of synthesized ligands and complexes.

Compounds	Molecular Formula	Molecular Weight	Coloration
Btfa	$C_{10}H_7F_3O_2$	216.16	White
Phen	$C_{12}H_8N_2$	180.21	White
Bipy	C10H8N2	156.18	White
$Nd(Btfa)_3Phen$	$Nd(C_{10}H_7F_3O_2)_3(C_{12}H_8N_2)$	972.89	Blue
$Nd(Btfa)_3Bipy$	$Nd(C_{10}H_7F_3O_2)_3(C_{10}H_8N_2)$	948.87	Blue
$Er(Btfa)_3Phen$	$Eu(C_{10}H_7F_3O_2)_3(C_{12}H_8N_2)$	995.90	Orange
$Er(Btfa)_3Bipy$	$Er(C_{10}H_7F_3O_2)_3(C_{10}H_8N_2)$	971.88	Orange

Source: Research Data.

Figure 1 shows the coloration of the $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$ nanocomplexes. These complexes obtained in the form of powder showed different coloration from the isolated ligands, which suggests the occurrence of coordination between the lanthanide ions and the organic ligands.

Figure 1. Sample Coloration: Btfa (A), Phen (B), Bipy (C), $Nd(Btfa)_3Phen$ (D), $Nd(Btfa)_3Bipy$ (E), $Er(Btfa)_3Phen$ (F) e $Er(Btfa)_3Bipy$ (G).



Source: Research Data.

The occurrence of a chemical phenomenon or chemical reaction occurs with the alteration of the composition of matter, that is, any and all changes undergone by a material in such a way that there is a change in its internal constitution. Thus, some evidence is important

to verify this change, among them, the color change (Shriver and Atkins, 2008).

3.2 Solubility Test

Table 2 shows the solubility tests of the complexes in some solvents.

Table 2. Solubility of ligands (β-diketone and Heterobiaris) and complexes.

Compounds	Solvents				
	Water	Methanol	Ethanol	Acetone	Chloroform
Btfa	Insoluble	Soluble	Soluble	Soluble	Soluble
Phen	Insoluble	Soluble	Soluble	Soluble	Soluble
Bipy	Insoluble	Soluble	Soluble	Soluble	Soluble
$Nd(Btfa)_3Phen$	Insoluble	Soluble	Soluble	Soluble	Insoluble
$Nd(Btfa)_3Bipy$	Insoluble	Soluble	Soluble	Soluble	Insoluble
$Er(Btfa)_3Phen$	Insoluble	Soluble	Soluble	Soluble	Insoluble
$Er(Btfa)_3Bipy$	Insoluble	Soluble	Soluble	Soluble	Insoluble

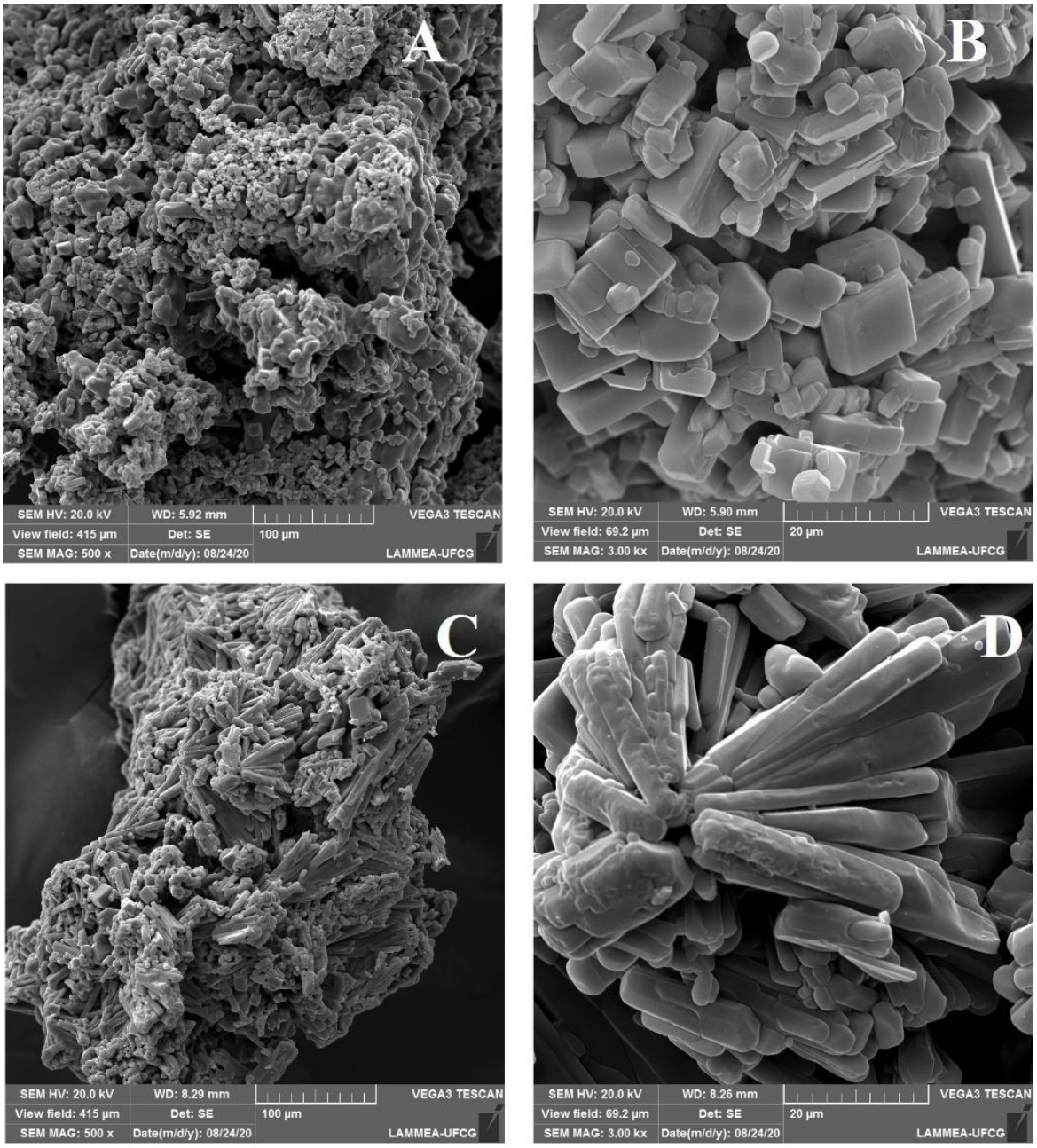
Source: Research Data.

Analyzing the data presented in Table 2, it can be seen that all the complexes synthesized in this work are insoluble in water and chloroform. However, it was found that the complexes were quite soluble in methanol, ethanol and acetone.

3.3 Scanning Electron Microscopy (SEM)

Figure 2a-d shows the images obtained in the scanning electron microscope of the complexes synthesized with the lanthanide Neodymium. In complex $Nd(Btfa)_3Phen$ it was possible to observe the presence of defined crystals with irregular conglomeration in the shape of blocks and varied dimensions. Complex $Nd(Btfa)_3Bipy$ appears in the form of agglomerates with homogeneous surfaces acquiring a more crystalline appearance, marked by the presence of well-defined rod-like crystals, with a smooth and polished aspect, showing the crystallinity of the complexes.

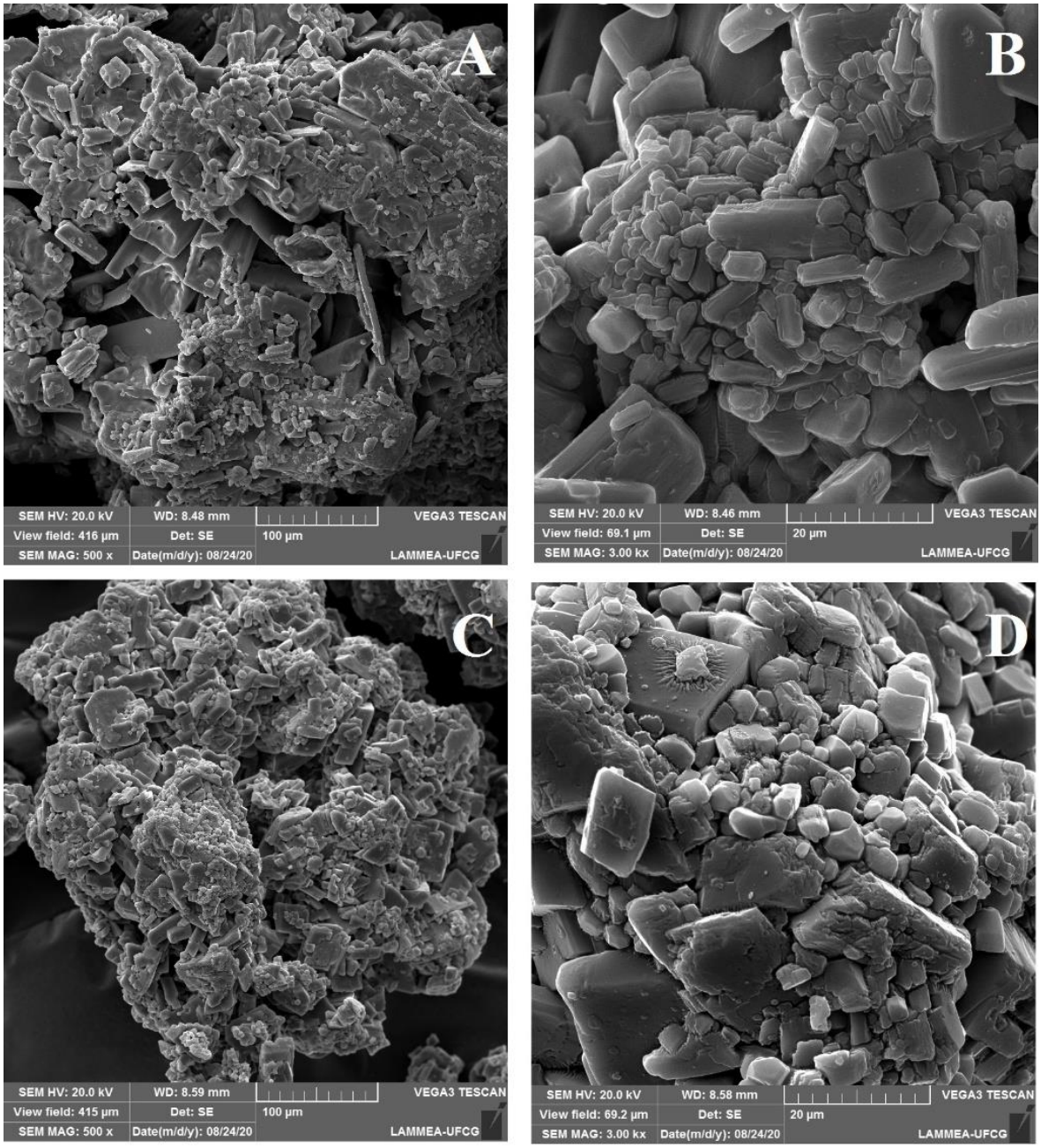
Figure 2. Scanning electron microscopy of lanthanide complexes: $Nb(Btfa)_3Phen$ with magnification of 500x (A), $Nb(Btfa)_3Phen$ with magnification of 3000x (B), $Nb(Btfa)_3Bipy$ with magnification of 500x (A) and $Nb(Btfa)_3Bipy$ with magnification of 3000x (D).



Source: Research Data.

In Figure 3a-d we have the images of the complexes synthesized with the lanthanide Érbio ($Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$). It was possible to observe the presence of defined crystals in the complexes, with irregular conglomeration in the form of blocks and varied dimensions with smooth and polished appearance, showing the crystallinity of the complexes.

Figure 3. Scanning electron microscopy of lanthanide complexes: $Er(Btfa)_3Phen$ with magnification of 500x (A), $Er(Btfa)_3Phen$ with magnification of 3000x (B), $Er(Btfa)_3Bipy$ with magnification of 500x (A) and $Er(Btfa)_3Bipy$ with magnification of 3000x (D).

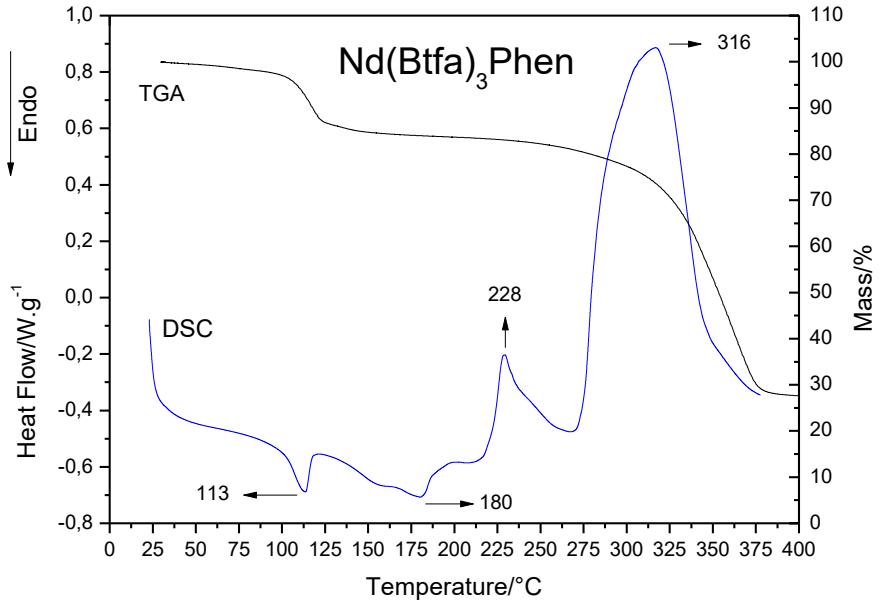


Source: Research Data.

3.4 Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Figure 4 shows the overlap of the thermogravimetric analysis curves and the differential exploratory calorimetry of the $Nd(Btfa)_3Phen$ complex.

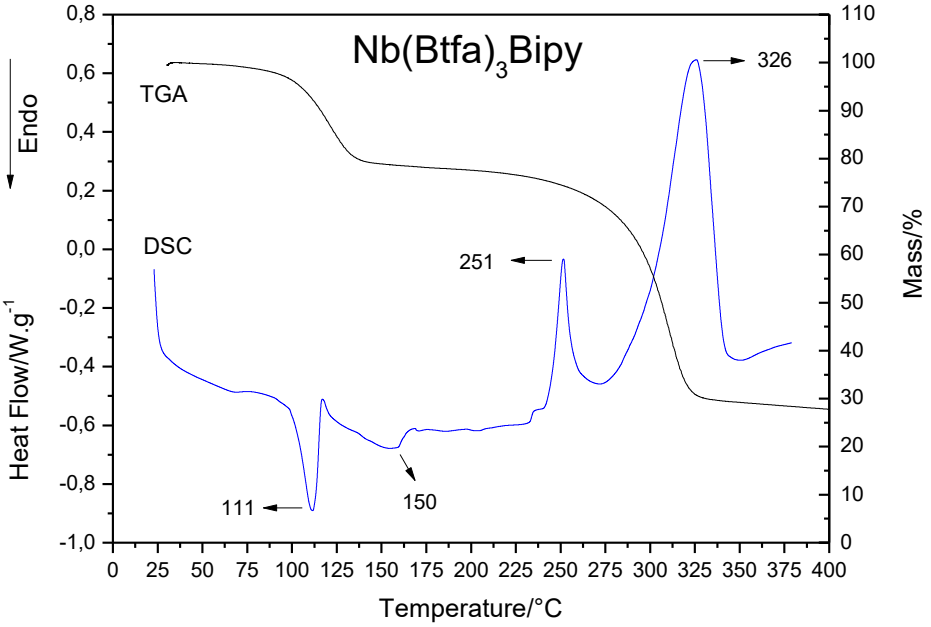
Figure 4. Overlapping TGA/DSC curves of the $Nd(Btfa)_3Phen$ complex at a heating rate of 10°C.min^{-1}, in a controlled atmosphere of Nitrogen.



Source: Research Data.

For the $Nd(Btfa)_3Phen$ complex (Figure 4), an initial endothermic peak at 113°C is observed, which is characteristic of solvent volatilization. The second endothermic peak is visualized at 180°C. It suggests the melting processes followed by decomposition of the complex. All endothermic peaks between 100 and 200°C correspond to the first loss of mass observed in the thermogravimetric curve of this complex. All previous events equate to an energy total of 30.5KJ.mol^{-1}. The exothermic peaks at 228 and 316°C correspond to the greatest loss of mass, and is due to the thermal decomposition process that involves the exit of fragments of the Phen and Btfa molecules. In the last event, the enthalpy of decomposition presented a total value of 379.92KJ.mol^{-1}. Figure 5 shows the differential exploratory calorimetry curve of the $Nd(Btfa)_3Bipy$ complex.

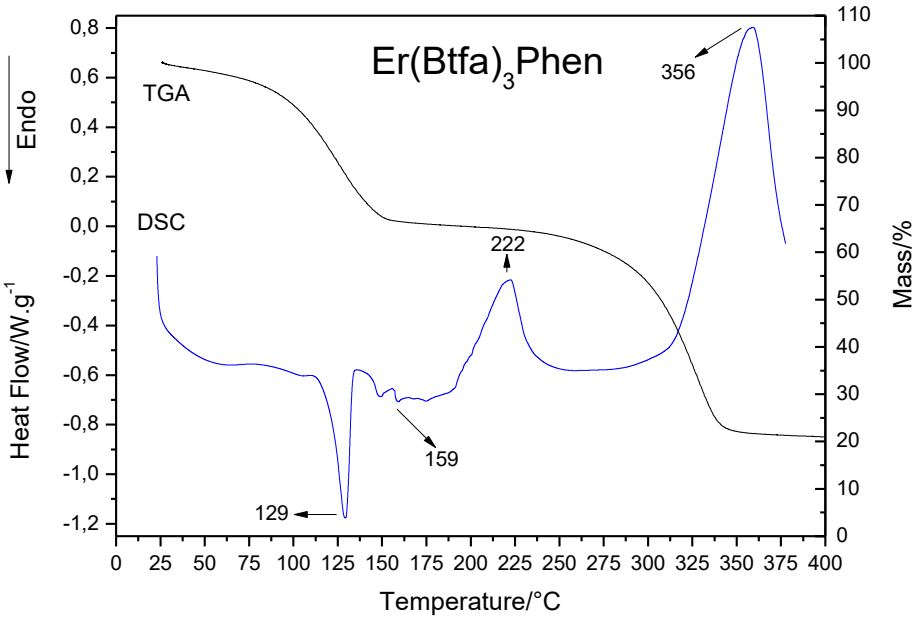
Figure 5. Overlapping TGA/DSC curves of the $Nd(Btfa)_3Bipy$ complex at a heating rate of 10°C.min^{-1}, in a controlled atmosphere of Nitrogen.



Source: Research Data.

The curve obtained from the $Nd(Btfa)_3Bipy$ complex (Figure 5) shows a curve very similar to the $Nd(Btfa)_3Phen$ complex. An initial endothermic peak at 111°C is observed, characteristic of solvent volatilization. The second endothermic peak at 150°C is due to the melting processes followed by decomposition of the complex. All endothermic peaks between 100 and 200°C correspond to the first loss of mass observed in the thermogravimetric curve of this complex. All previous events equate to an energy total of 38.83KJ.mol^{-1}. The exothermic peaks at 251 and 326°C correspond to greater loss of mass, and is due to the thermal decomposition process that involves the leaving of fragments of the Bipy and Btfa molecules. In the last event the decomposition enthalpy showed a total value of 145.66KJ.mol^{-1}. Figure 6 shows the differential exploratory calorimetry curve of the $Nd(Btfa)_3Phen$ complex.

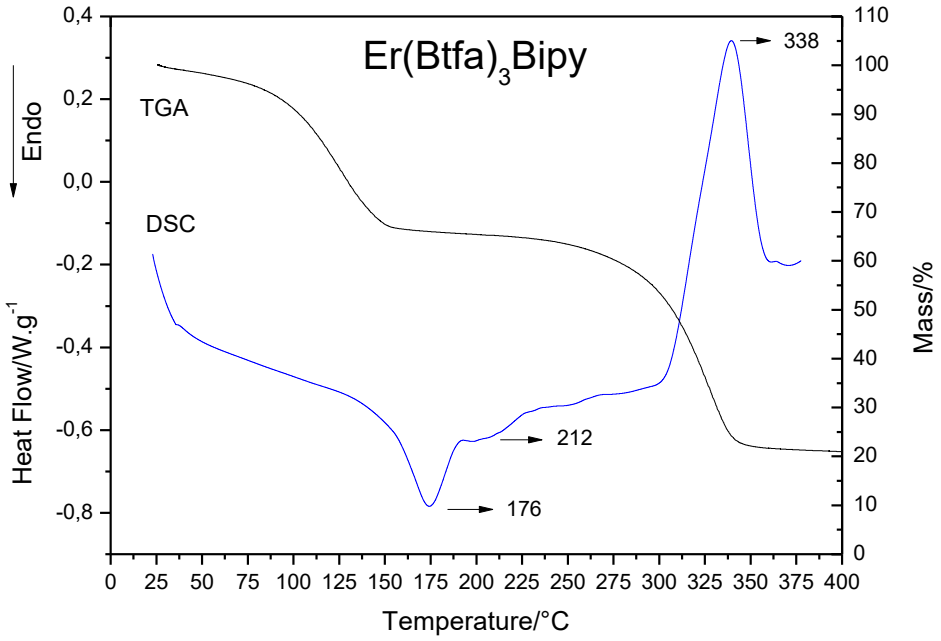
Figure 6.1 Overlapping TGA/DSC curves of the Er(Btfa)$_3$Phen complex at a heating rate of 10°C.min^{-1}, in a controlled atmosphere of Nitrogen.



Source: Research Data.

The complexes with the lanthanide Erbium behave similarly to the complexes with the lanthanide Neodymium. For the Er(Btfa)$_3$Phen complex (Figure 6) an initial endothermic peak is observed at 129°C, characteristic of solvent volatilization, the second endothermic peak at 159°C is due to the melting processes followed by decomposition of the complex, starting at lower temperatures, comparing with the values of the neodymium. All endothermic peaks between 100 and 200°C correspond to the first loss of mass observed in the thermogravimetric curve of this complex. All previous events equate to an energy total of 49.58KJ.mol^{-1}. The exothermic peak at 222°C corresponds to the second loss of mass found in the thermogravimetric curves, and the fourth peak at 356°C, exothermic, corresponds to the greatest loss of mass, both exothermic events are due to the thermal decomposition process that involves the fragmentation of the Phen and Btfa molecules. In the last event, the enthalpy of decomposition showed a total value of 193.8KJ.mol^{-1}. Figure 7 shows the differential exploratory calorimetry curve of the Er(Btfa)$_3$Biy complex.

Figura 7. Overlapping TGA/DSC curves of the $Er(Btfa)_3Bipy$ complex at a heating rate of 10°C.min^{-1}, in a controlled atmosphere of Nitrogen.



Source: Research Data.

For the $Nd(Btfa)_3Bipy$ complex (Figure 7), a different behavior is observed from the other complexes. There are two sequential endothermic curves with peaks at 176 and 212°C The initial endothermic peak is characteristic of solvent volatilization, while the second one results from the melting processes followed by the decomposition of the complexes; corroborating with the values obtained in the test of determination of the melting/decomposition intervals. All endothermic peaks correspond to the first loss of mass observed in the thermogravimetric curve of this complex. All previous events equate to an energy total of 24.78KJ.mol^{-1}. The exothermic peak at 338°C corresponds to the greatest loss of mass, and is due to the thermal decomposition process that involves the departure of fragments of the Bipy and Btfa molecules. In the last event, the enthalpy of decomposition showed a total value of 107.98KJ.mol^{-1}.

All the values observed in the DSC curves of the $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$ complexes, peak temperatures (°C) and enthalpy variations (ΔH), is listed in Table 3.

Table 31. DSC curve data for complexes $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$, at a heating rate of 10°C.min^{-1}, in a controlled atmosphere of Nitrogen.

Complexes	Events	Enthalpy Variation (ΔH)		Peak Temperature (°C)
		KJ.mol^{-1}	J.g^{-1}	
$Nd(Btfa)_3Phen$	1	8.90	9.1	113
	2	21.60	22.2	180
	3	38.82	39.9	228
	4	379.92	390.5	316
$Nd(Btfa)_3Bipy$	1	19.96	21.0	111
	2	18.86	19.9	150
	3	19.48	20.5	251
	4	145.66	153.3	326
$Er(Btfa)_3Phen$	1	31.32	31.3	129
	2	18.45	18.5	159
	3	63.03	63.3	222
	4	193.80	194.6	356
$Er(Btfa)_3Bipy$	1	21.99	22.6	176
	2	2.79	2.9	212
	3	107.98	111.1	338

Source: Research Data.

Table 3 shows that the lowest values of enthalpy variation occur in the first event, which only indicates the release of solvent or free water. The highest values are found at the last peak of each complex, indicating a large mass release, showing similar behavior between the synthesized complexes.

After overlapping the curves, it is possible to verify that the thermogravimetric curves and derivatives of the four complexes synthesized show two mass losses up to a temperature of 400ºC. In the four complexes, the first loss corresponds to solvent and free water output, while the second loss corresponds to the loss of ligands and fragments of the constituent ligands.

Table 4 lists the data relating to the main mass losses observed in the thermogravimetric curves and the mass losses and the characteristic temperatures of the decomposition reactions of the $Nd(Btfa)_3Phen$, $Nd(Btfa)_3Bipy$, $Er(Btfa)_3Phen$ and $Er(Btfa)_3Bipy$, complexes are measured. The assignments were made by relating the mass losses to the molecular masses of the fragments from the structure of the complexes.

Table 4. Results of the thermogravimetric analysis decomposition of complexes $Ln(Btfa)_3L$.

Complexes	Events	Temperature Range (°C)	Mass Loss		Probably removed groups
			%	mg	
$Nd(Btfa)_3Phen$	1	25 – 167.2	15.7	0.47	$C_2H_5OH + H_2O$ Free
	2	167.2 – 400	56.8	1.70	Phen + 2 Btfa
	3	>400	27.5	0.83	
$Nd(Btfa)_3Bipy$	1	25 – 163.2	21.2	0.64	$C_2H_5OH + H_2O$ Free
	2	163.2 – 400	49.3	1.48	Bipi + 2 Btfa
	3	>400	29.5	0.88	
$Er(Btfa)_3Phen$	1	25 – 184.3	27.3	0.82	$C_2H_5OH + H_2O$ Free
	2	184.3 – 296.7	12.6	0.38	Phen
	3	296.7 – 400	39.4	1.18	2 Btfa
	4	>400	20.7	0.62	
$Er(Btfa)_3Bipy$	1	25 – 166.4	33.7	1.01	$C_2H_5OH + H_2O$ Free
	2	166.4 – 400	44.7	1.34	Bipi + 21/10 Btfa
	3	>400	21.5	0.64	

Source: Research Data.

According to the data obtained by overlapping the TGA and DSC curves and the values obtained in Table 3 and 4, we can suggest the following order of thermal stability:

$Er(Btfa)_3Phen$ > $Nd(Btfa)_3Phen$ > $Er(Btfa)_3Bipy$ > $Nd(Btfa)_3Bipy$

3.5 Determination of Melting/Decomposition Intervals

According to the data shown in Table 5, it can be seen that the melting/decomposition temperature ranges of the free binders are different from the temperature ranges of the synthesized complexes, being an indication of the formation of new substances and the success of the complexation.

Table 5. Melting/Decomposition intervals of ligands (β-diketone and Heterobiaris) and complexes.

Compounds	Temperature (ºC)	Observation
Btfa	38 - 40	Melting
Phen	114 - 117	Melting
Bipy	73 - 77	Melting
Nd(Btfa)3Phen	159.3 - 162.7	Melting/Decomposition
Nd(Btfa)3Bipy	172.8 – 179.1	Melting/Decomposition
Er(Btfa)3Phen	186.3 - 187.7	Melting/Decomposition
Er(Btfa)3Bipy	203.0 - 208.2	Melting/Decomposition

Source: Research Data.

It can be seen that in the complexes the presence of lanthanides increased the initial melting/decomposition temperatures, and that the $Er(Btfa)_3Bipy$ complex has greater thermal stability when compared to the others, whereas $Nd(Btfa)_3Phen$ is the less thermally stable.

The data obtained in the DSC curves validate the data obtained in the determination of the melting / decomposition intervals and in the thermogravimetric curves. For a better visualization of the data obtained in the three mentioned tests, Table 6 contains the values obtained in the fusion / decomposition tests in the Fisatom equipment and the values obtained in the DSC.

Table 6. Values of the Melting/Decomposition Points of the assay for determining the melting/decomposition intervals and the values obtained in the DSC.

Complexes	Temperature (°C)		
	Range Fisatom	Range DSC	Peak DSC
$Nd(Btfa)_3Phen$	159.3 - 162.7	141 – 196	180
$Nd(Btfa)_3Bipy$	172.8 – 179.1	125 – 169	150
$Er(Btfa)_3Phen$	186.3 - 187.7	154 – 187	159
$Er(Btfa)_3Bipy$	203.0 - 208.2	191 - 231	212

Source: Research Data.

Comparing the values of the tests contained in Table 6 we found that the intervals of both tests were also contained in the other test. Only the peaks of the events observed in the DSC test that are different from the test intervals to obtain the melting/decomposition intervals obtained using the FISATOM equipment.

4. Conclusions

The complexes $Ln(\beta\text{-}dik)_3L$ had been synthesized and characterized by several techniques. Based on the results obtained in the study, it can be concluded that in the visual analysis it is verified that the complexes obtained in the form of powder presented different coloring of the isolated ligands, which suggests the occurrence of coordination between the lanthanide ions and the organic ligands. Solubility tests show that all complexes are insoluble in water and chloroform. Scanning electron microscopy found the formation of crystalline structures. The results of the melting/decomposition temperatures of the binders when compared to the complexes proved to be quite different, which indicates the formation of new substances. The values obtained in the differential exploratory calorimetry ratified the values of the melting/decomposition intervals found in the assay of determination of

Melting/Decomposition Intervals.

In view of the possibilities that the results found offer, it is of interest to all authors to suggest for future work a study of biological applicability such as cytotoxicity and anti-microbial activity of the complexes synthesized in this work.

References

Assunção, F. C. R., Almeida, M. F. L., Arraes, T. M., Lins, F. A. F., Santos, R. L. C., Soares, P. S. M., Nascimento, M., Masson, I. O. C., Silva, C. F. C., Moraes, C. A. C., Pitta, F. M., Nomeline, R., Guerra, E. A., Lima, D. A., Aguiar, E. F. S., Zotin, F. M. Z., Landgraf, F. J., Appel, L. G., Cremona, M., Wendhausen, P. A. P. (2013). Usos e Aplicações de Terras Raras No Brasil: 2012-2030.

Lehn, J. M. (1990). Perspectives in Supramolecular Chemistry—From Molecular Recognition towards Molecular Information Processing and Self-Organization. Angewandte Chemie International Edition in English, 29(11), 1304–1319.

Sabbatini, N., Casnati, A., Fischer, C., Girardini, R., Guardigli, M., Manet, I., Sarti, G., Ungaro, R. (1996). Luminescence of Eu3+ and Tb3+ Complexes of New Macrobicyclic Ligands Derived from P-Tert-Butylcalix[4]Arene. Inorganica Chimica Acta, 252(1–2), 19–24.

Werts, M. H. V., Hofstraat, J. W., Geurts, F. A. J., Verhoeven, J. W. (1997). Fluorescein and Eosin as Sensitizing Chromophores in Near-Infrared Luminescent Ytterbium(III), Neodymium(III) and Erbium(III) Chelates. Chemical Physics Letters, 276(3–4), 196–201.

Momani, W. M. A., Taha, Z. A., Ajlouni, A. M., Shaqra, Q. M. A., Zouby, M. A. (2013). A Study of in Vitro Antibacterial Activity of Lanthanides Complexes with a Tetradentate Schiff Base Ligand.” Asian Pacific Journal of Tropical Biomedicine, 3(5), 367–70.

Ji, T., Liu, Z., Wang, G., Guo, X., Khan, S. A., Lai, C., Chen, H., Huang, S., Xia, S., Chen, B., Jia, H., Chen, Y., Zhou, Q. (2020). Detection of COVID-19: A Review of the Current Literature and Future Perspectives. Biosensors and Bioelectronics, 166(March),112455.

Bouras, K., Rehspringer, J. L., Schmerber, G., Rinnert, H., Colis, S., Ferblantier, G., Balestrieri, M., Ihiawakrim, D., Dinia, A., Slaoui, A. (2014) Optical and structural properties of Nd doped SnO2 powder fabricated by the sol–gel method. Journal of Materials Chemistry C, 2, 8235–8243.

Kajihara, K. (2013). Recent advances in sol–gel synthesis of monolithic silica and silicabased glass. Journal of Asian Ceramic Societies, 1, 121-133.

Rai, S., Fanai, A. L. (2016). Effect ofannealing and dopants concentration on the optical properties of Nd3+:Al3+ co-doped sol–gel silica glass. Journal of Luminescence, 170, 325–329.

Lukowiak, A., Chiappini, A., Chiasera, A., Ristic, D., Vasilchenko, I., Armellini, C., Carpentiero, A., Varas, S., Speranza, G., Taccheo, S., Pelli, S., Battisha, I. K., Righini, G. C., Strek, W., Ferrari, M. (2015). Sol–gel-derived photonic structures handling erbium íons luminescence. Optical and Quantum Electronics, 47, 117–124.

Silva, H. C., Morais, C. R. S., Morais, S. A., Lira, B. F. (2012). Synthesis, characterization, and thermal properties of an europium (III) nanocomplex. Materials Science Forum, 727–728, 1913–1918.

Frey, S. T., Gong, M. L., Horrocks, W. D. (1994). Synergistic Coordination in Ternary Complexes of Eu3+ with Aromatic β-Diketone Ligands and 1,10-Phenanthroline. Inorganic Chemistry, 33, 3229–3234.

Morais, C. R. S., Gameiro, C. G., Santa-Cruz, P. A., Alves Jr, S., Soledade, L. E. B., Souza, A. G. (2007). Thermal decomposition of lanthanide(III) complexes with 4,4,4-trifluoro-1-phenyl-1,3-butanedione. Journal of Thermal Analisys and Calorimetry, 87, 887–891.

do Nascimento, R. S. T. R., Morais, C. R. S., Lira, H. L., Morais, S. A., de Athayde Filho, P. F., Lucena, L. F. L. (2010). Synthesis and characterization of nanocomplexes of Eu(III) and Er(III) coordinate with 2(4-clorophenil)-3-phenyl-1,3,4-thiadiazoleo-5-tiolate mesoionic. Journal of Alloys and Compounds,495, 603–605.

Lehn J. (1990) Perspectives in Supramolecular Chemistry-From Molecular Recognition towards Molecular Information Processing and Self-organization. Angewandte Chemie International, 29, 1304–1319.

Boyd, J. W., Cobb, G. P., Southard, G. E., Murray, G. M. (2004) Development of molecularly imprinted polymer sensors for chemical warfare agents. Johns Hopkins APL Tech Dig, 25, 44–49.

Shriver, D. F., Atkins, P. W. (2008). Química Inorgânica, (4a ed.). Ed São Paulo: McGraw-Hill.

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