

# Synthesis and Characterization of Nanocomplex of Erbium with Mesoionic 2(4-chlorophenyl)-3-methyl-4(methoxyphenyl)1,3-tiazolium-5-thiolate and 2,2-Bipyridine

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## ABSTRACT

Considering the technological interest in developing materials that associate properties and allow to diversify its applicability, the coordination compounds with organic ligands such as complexes of lanthanides with mesoionic (MI-1) and 2,2-bipyridine (bipy), which have biological properties, may serve as excellent light molecular converter device with possible application in the field of photonics and health. This perspective was synthesized and carried out a study of thermal behavior and spectroscopic of complex  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot x\text{H}_2\text{O}$  From ethanolic solution of the salt of lanthanide ( $\text{Er}^{3+}$ ), mesoionic of the group 1,3-tiazolium-5-thiolate and 2,2-bipyridine, in stoichiometric proportions, was obtained a nanometric powder with reddish color and formula  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot x\text{H}_2\text{O}$  The complex was characterized by spectrometric and thermal analysis. The analysis of DSC was performed in nitrogen atmosphere, flow  $50\text{mL}\cdot\text{min}^{-1}$  and ambient temperature range to  $500^\circ\text{C}$  and the rates of heat at  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The IR spectra indicate that coordination of MI-1 with the ion  $\text{Er}^{3+}$  probably occurs through the exocyclical sulfur atom ( $\text{S}^-$ ) and 2,2-bipyridine is evidentially coordinated by the nitrogen atom. The decomposition of the complex occurred in six stages with curves profiles similar to organic ligands. The DSC curves

showed that the studied complex began the reaction of thermal decomposition in solid form, before the merger.

**Key words:** synthesis, characterization, lanthanide, mesoionic, nanocomplex.

## 1. INTRODUCTION

The search for materials that associate desirable optic and biological properties, for photonic ends and possible applications in the area of the health is growing each time more and increasing the interest of researchers on the subject [1,2]. Materials that can be obtained of fast form, with processing facilities and that mainly they present a low cost are the objective of study of many scientists. In this sense, the development of research involving lanthanides increased significantly in function of the exploitation of the luminescent properties of these elements, making possible its applicability for the production of light converters molecular devices, which can find diverse applications the example of luminescent markers in fluoro-imunoensaios [3,4,5]. Parallel, stand out scientific studies of organic compounds that present biological properties, amongst which are distinguished mesoionics compounds [6], that present structural characteristics, that have attracted considerable interest of involved researchers in the

area of Medicinal Chemistry [2,4,7]. Such biological potential is attributed to the aromatic character of the compound, formed of heterocyclic rings of small sizes with variation of electronic density and to some possibilities of the presence of different heteroatoms [7,8], taking to diverse mesoionic systems, that are recognized for presenting vast biological activity and antitumoral action [7].

In this sense, the possibility to coordinate and to associate the properties of lanthanides ions with mesoionic compounds in order to preserve the structural characteristics of these, have attracted the attention of researchers, consequence of the luminescence of ions and the biological activities detected in the various classes of mesoionics [4,6]. However, the coordination compounds containing lanthanide ions present its luminescent properties affected by coordinated water molecules, which reduce the intensity of emission due the resonance between its vibrational states and the emitting states of the metallic ion [9]. In the attempt to contour the favoring of a non-radiative way becomes essential the use of the second organic ligand of the heterobiaril type (bipiridina), since, the same it presents high coefficient of molar absorptivity, and is capable to efficiently transfer energy to the ion lanthanide, favoring the increase in the luminescence intensity and potentiate the biological activity of the new complex [10].

In this perspective, this paper has as main objective to synthesize crystalline powders from the coordination of the lanthanide ion Er(III) with mesoionic of the group 1,3-thiazolium-5-thiolate and the bipiridina, beyond characterizing it through the thermal analysis techniques (Thermogravimetry and Differential Scanning Calorimetry) and Spectroscopic (Infra-

## 2. EXPERIMENTAL

### Synthesis

The complex of  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$  was synthesized from an ethanolic solution of erbium chloride with the mesoionic compound 2(4-chlorophenyl)-3-methyl-4(methoxyphenyl)1,3-thiazolium-5-thiolate (MI-1) and the 2,2-bipiridina (bipy) as second ligand, in stequiometric proportions of 1:3: 1, based on the molar weight of the reactants, to prevent the reaction product contamination with the ligand excess, under magnetic agitation and refluxo  $60^\circ\text{C}$ , for the period of 6 hours. The pH 6,0 was controlled with a solution of NaOH [10]. After evaporation was gotten a crystalline powder of reddish coloration.

### Spectroscopy Characterization

The infrared spectra were achieved in a Perkin Elmer FTIR spectrophotometer model Spectrum 400 MIR/NIR with Mid-IR and NIR detectors DTGS for infrared, and registering amplitude waves ranging from  $8.890$  a  $4.200\text{ cm}^{-1}$ .

### Thermal Measures

Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance with alumina crucible, and with heating rates of  $10^\circ\text{C}\cdot\text{min}^{-1}$  in a temperature range from ambient one to  $900^\circ\text{C}$  and under a nitrogen atmosphere with a flow rate of  $50\text{mL}\cdot\text{min}^{-1}$ . The sample mass was  $2.5 \pm 0.5\text{ mg}$ . The TG curves were analyzed with the aid of the TASY software from Shimadzu.

The DSC curves were achieved in a SHIMADZU, DSC-50 calorimeter. The analysis were realized in an aluminum crucible with a nitrogen atmosphere, flux  $50\text{mL}\cdot\text{min}^{-1}$ , temperature range from ambient one to  $500^\circ\text{C}$  and heat rates  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The sample mass was  $4.0 \pm 0.5\text{ mg}$ .

## 3. RESULTS AND DISCUSSION

The overlap of the vibrational spectra ( $4000 - 400\text{ cm}^{-1}$ ) absorption in the infrared region of the compound MI-1, 2,2-bipiridina and the complex  $\text{Er}(\text{MI-1})_3\text{bipy}$  are shown in Figure 1. The main absorption bands in the infrared region are shown in Table 1.

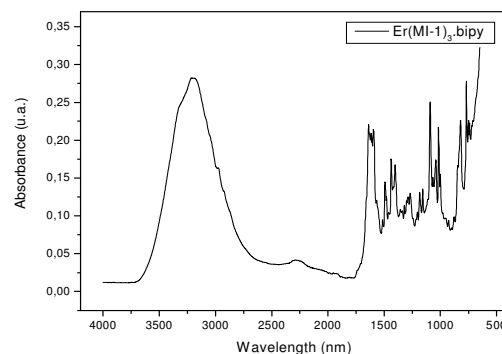


Figure 1 – Spectrum of absorption in the infrared region of the mesoionic MI-1, bipy and  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$  complex.

Table 1 - Infrared absorption bands of mesoionic compound MI-1, 2,2-bipiridina and  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$  complexes

	Attributions $\nu(\text{cm}^{-1})$							
	C-S	C-S <sup>-</sup>	C <sub>(ar)</sub> -Cl	C-O-C (s/as)	C <sub>(ar)</sub> -N	N-CH <sub>3</sub>	C=N	O-H
MI-1	1026	1301	1098	1022/1188	-	1438	1487	-
Bipy	-	-	-	-	1244	-	1453	-
$\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$	1039	1286	1087	1019/1182	1271	1435	1490	3204

Analyzing the spectrum of the complex  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ , can be observed that the same it presents a band of wavelength of  $3204\text{cm}^{-1}$  referring the vibrations of the O-H group, decurrent of ethanol used in the synthesis, what it is not observed in the spectrum of the pure ligands. Between  $1490$  and  $1435\text{cm}^{-1}$  it is observed the presence of bands of axial deformation referring to groups C=N and N-CH<sub>3</sub>, the first band present in all the samples analyzed and the second only in the MI-1 and the complex  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ . The bands of stretching in the region of  $1244\text{cm}^{-1}$  (for the ligand bipy) and  $1271\text{cm}^{-1}$  (for the complex of  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ ) are characteristics of C-N bonds. The bands of symmetric axial deformation ( $1022\text{ cm}^{-1}$  and  $1019\text{cm}^{-1}$ ) and asymmetric ( $1188\text{cm}^{-1}$  and  $1182\text{cm}^{-1}$ ) demonstrate to the presence of the group C-O-C only in compound MI-1 and the complex of  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ , as well as the bands of vibration of stretching between  $1098\text{cm}^{-1}$  and  $1087\text{cm}^{-1}$  that indicate the presence of the groups =C(A<sub>r</sub>)-Cl. Observing the spectrum of mesoionic MI-1 and the complex of  $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ , is possible to identify the presence of the absorption band characteristic of the thiolate exocyclical group (C-S<sup>-</sup>) mid  $1301\text{cm}^{-1}$  and  $1286\text{cm}^{-1}$ . These datas corroborate with the values found for Athayde-Filho (1999), Lira (2004) and Morais (2008). Analyzing comparatively the absorption bands of ligands and of the complex, verifies that the occurrence of coordination between the lanthanide cation and the ligands, may be proven by the displacement of the bands referring to C-S<sup>-</sup> and C-N bonds, in pure ligands and after coordination, what it indicates that the same one if gave through the sulfur atom of the compound MI-1, that it finds outside of the cycle, as well as through nitrogen atoms of the 2,2-bipiridina.

The Figure 2 present the profiles of the thermogravimetric curves for the ligands (MI-1 and bipy) and the synthesized complex ( $\text{Er}(\text{MI-1})_3\text{bipy}\cdot\text{xH}_2\text{O}$ ), obtained at a heating rate of

10°C.min<sup>-1</sup>, being possible to observe that the ligands had presented 1 (one) stage and 3 (three) stages of thermal decomposition, for the 2,2-bipyridine and mesoionic MI-1, respectively, whereas the complex presented 6 (six) stages of thermal decomposition.

The Table 2 presents the datas of thermal decomposition of the samples obtained through the curves TG for the ligands (MI-1 and bipy) and the complex (Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O), measure the mass loss and the characteristic temperatures of the decomposition reactions.

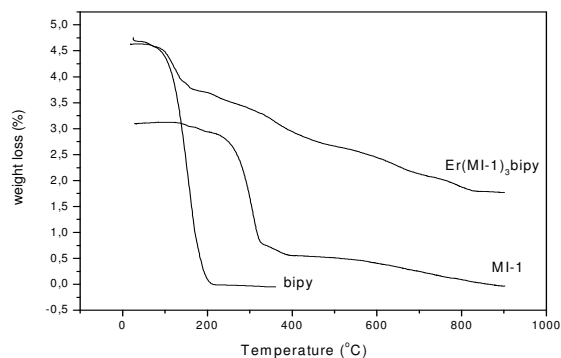


Figure 2 - TG curves of the mesoionic compound MI-1, 2,2-bipyridine and Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O complex obtained using a heating rate of 10°Cmin<sup>-1</sup>.

Table 2 - Thermal decomposition data for mesoionic compound MI-1, 2,2-bipyridine and Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O complex at 10°C.min<sup>-1</sup>.

Compounds	Stage	Temp.		Mass-loss	
		Range (°C)	Peak (°C)	(%)	(mg)
MI-1	1	92 – 186	154	4.52	0.14
	2	186 – 421	295	77.36	2.43
	3	421 – 898	683	18.46	0.58
Bipy	1	77 – 181	153	100.00	4.62
Er(MI-1) <sub>3</sub> bipy.xH <sub>2</sub> O	1	26 – 225	108	19.79	0.92
	2	225 – 323	282	8.48	0.39
	3	323 – 422	350	9.51	0.44
	4	422 – 561	466	5.62	0.26
	5	561 – 742	658	16.05	0.75
	6	742 – 898	782	5.23	0.24

The mesoionic compound MI-1 presented loss of mass approximately at 4,52% (0.14mg) in a band of temperature that varied between 92°C until 186°C, in the first stage, whereas it presented 77.36% (2.43mg) of loss of mass in a band of temperature between 186°C and 421°C, followed of a loss of 18,46% (0.58mg) in a temperature band that varied between 421°C and 898°C.

For the second ligand (bipy) can observe a loss of mass of the 100% (4.62mg) in the band of temperature of 77°C until 181°C, referring to the volatilization of the same.

The complex of Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O presented six stages of loss of mass that were: of 19.79% for the band of temperature of 26°C to 225°C; of 8.48% for temperatures between 225°C and 323°C; 9,51% for temperatures between 323°C and 422°C; 5,62% for temperatures between 422°C and 561°C; 16,05% for temperatures between 561°C and 742°C and finally of 5.23% for the band of temperature of 742°C to 898°C, all referring a thermal decomposition of the complex, being the first loss attributed to the exit of the solvent and the volatilization of the bipyridine, and the other to the decomposition of three molecules of mesoionic MI-1.

The figure 3 shows the overlapping of the curves DSC of the ligands (MI-1 and 2,2-bipyridine) and of the complex Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O under a heating rate of 10°C.min<sup>-1</sup>.

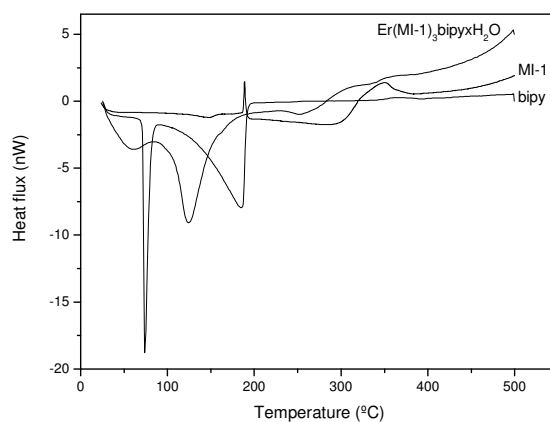


FIGURE 3 - DSC curves of the mesoionic compound MI-1, 2,2-bipyridine and Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O complex obtained using a heating rate of 10°Cmin<sup>-1</sup>.

Analyzing the DSC curve of compound MI-1, it is possible to observe the presence of two exothermic peaks in 147°C and 189°C, referring to the thermal decomposition of the compound, as we can prove in TG curve.

The DSC curve of the 2,2-bipyridine presents endothermic peaks at 73°C and 185°C, the first characteristic of the fusing of the material and the second to the process of volatilization of the same.

The calorimetric profile of the complex Er(MI-1)<sub>3</sub>bipy.xH<sub>2</sub>O presents a band between 25°C and 83°C with maximum in 60°C, referring the volatilization of ethanol, followed of other bands endothermic with maximums in 123°C and 252°C referring to the decomposition reactions.

#### 4. CONCLUSION

The IR vibrational spectra indicate that the coordination of the MI-1 with the lanthanide ion (Er<sup>3+</sup>) probably occurs through the exocyclic sulfur atom (S<sup>-</sup>) and the second ligand (2,2-bipyridine) is essentially coordinated by the nitrogen atom to the lanthanide, favoring, possibly, the increase in the luminescence intensity and potentiate the biological activity of the synthesized complex. The complex presented low thermal stability with decomposition occurred in six stages.

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