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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

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ABSTRACT

The solids achieved in nanometric scale have been demanding scientific and technological interest due to the significant alterations in physical and chemical properties observed in such kind of materials, potentializing their technological applications. The nanocomplexes produced by lanthanide ions with the mesoionic compounds 2(4-clorophenil)-3-phenyl-1,3,4-thiadiazole-5-tiolate (M-1) were achieved in a powdered yellowed way. These compounds were characterized through X-ray diffraction, infrared (IR) spectroscopy and differential scanning calorimetry (DSC). The X-ray diffractograms of the M-1 compound and of $Er(M\text{-}1)_3{\cdot}3H_2O$, $Eu(M\text{-}1)_3{\cdot}3H_2O$ complexes, presented more than one phase and a crystalline structure. The disappearance and appearance of new peaks, as well as the variation on the intensity of the M-1 majoritary peaks as compared to the complexes' peaks can also be observed. The IR spectra indicate that the coordination of M-1 with the cations Eu^{+3} e Er^{+3} probably happens due to the sulfur exocyclic atom, where a considerable displacement in the carbon–sulfur (C–S)-ligation can be perceived. Comparing the DSC curves of the M-1, $Er(M\text{-}1)_3{\cdot}3H_2O$ and $Eu(M\text{-}1)_3{\cdot}3H_2O$, a displacement of the complexes peaks in relation to M-1 can be observed, suggesting the achievement of new specimens. Thus, it can be concluded that the formation of two new organic nanocomplexes with crystalline characteristics which may be used as a pharmacy, is quite evident.

1. Introduction

The solids achieved in nanometric scale have been demanding scientific and technological interest due to the significant alterations in physical and chemical properties observed in such kind of materials, potentializing their technological applications. Considering the importance of the development of nanomaterials with application conducted to the health area, both following classes present excellent possibilities [1]. The mesoionic composites, which are recognized by presenting a vast biological activity and recently, an antitumoral action [2,3]. As well as, the lanthanide ions, consequence of the exploitation of the luminescent properties of these elements that may allow the development of light converters molecular devices which can be applied as luminescent markers in immunoassays [1,4,5].

Although the literature shows just a few registers of any kind of mesoionic compounds with lanthanide ions, the possibility of the occurrence of coordination between these ions is real, mainly with the tiolate group of the mesoionic compounds [6]. Amongst the lanthanides, the europium is the most commonly used ion in the development of immunohistochemistry techniques [7,8].

Thus, aiming the attainment of a material that can preserve, simultaneously, the luminescent properties of the lanthanide ions and the biological activity of the mesoionic, it was synthesized from salts of Eu(III) and Er(III) with the mesoionic compound 2(4-clorophenyl)-3-phenyl-1,3,4-thiadiazole-5-tiolate (M-1) and characterized through X-ray diffraction (XRD), infrared (IR) spectroscopy and differential scanning calorimetry (DSC), nanocomplexes $Ln(M)_3{\cdot}3H_2O$, in powder form with yellowish color, aiming the application in immunoassays or as pharmacs [1,9,10].

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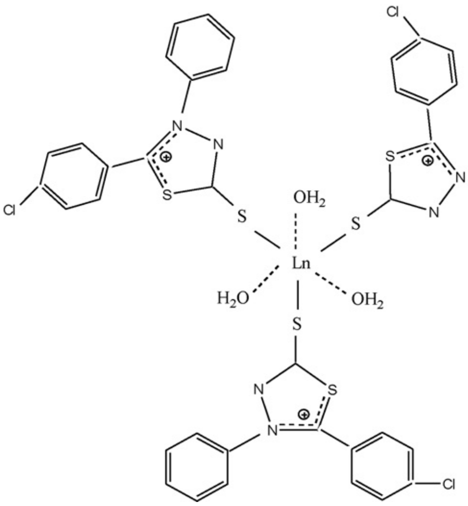

Fig. 1. Structural formula of the Ln(M-1)$_3$·3H$_2$O complex.

2. Experimental

2.1. Synthesis of the complexes

The complexes Eu(M-1)$_3$·3H$_2$O and Er(M-1)$_3$·3H$_2$O were synthesized by reacting the corresponding metal salt of chloride, prepared from the lanthanide oxides, with the mesoionic compounds 2(4-clorophenil)-3-phenyl-1,3,4-thiadiazole-5-tiolate (M-1). In an ethanolic solution of LnCl$_3$ the ligand was added. After reflux at 65 °C, under constant magnetic agitation, a solution of NaOH at 0.1 M was added to reach pH 6, maintaining the reflux for four hours. The resulting solution was left at room temperature for drying [1,9–11]. The mesoionic compounds were added in exact stequiometric proportions, based on the molar weight of the reactants, to prevent the reaction product contamination with the ligand excess [11]. Two structure formula complexes were synthesized as shown in Fig. 1.

The nanocomplexes produced by lanthanide ions with the mesoionic compounds were achieved in a powdered yellowed way.

2.2. Structure characterization

The X-ray diffractograms were achieved in a SHIMADZU XRD-6000 diffractogram meter model, with CuKα radiation and amplitude wave λ = 15,406 Å working with a 40 kV voltage and 30 mA current and ranging from 2° < 2θ < 80°, pass of 0.02/seg, ambient temperature of de 25 °C, small Soller fend and graffiti monochromator through the glass laminas smears technique. The crystallites size has been achieved from the enlargement of the most intense X-ray's reflection peaks of each sample using the Scherrer equation [12].

2.3. Thermal measurements

The DSC curves were achieved in a SHIMADZU, DSC-50 calorimeter. The analyses were realized in an aluminum crucible with a nitrogen atmosphere, flux 50 mL min^{-1}, temperature range from ambient one to 500 °C and heat rates 10 °C min^{-1}.

2.4. Spectroscopy

The infrared spectra were achieved in a FTIR spectrophotometer Modelo IF66, employing KBr pellets and registering amplitude waves ranging from 400 to 4000 cm^{-1}.

3. Results and discussion

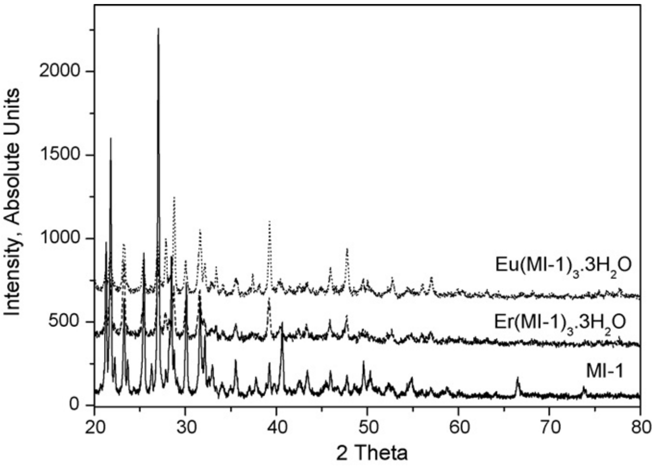

Fig. 2. DSC curves of the mesoionic compound M-1, Er(M-1)$_3$·3H$_2$O and Eu(M-1)$_3$·3H$_2$O complexes, obtained using a heating rate of 10 °C min^{-1}.

Fig. 2 shows the overlapping of the X-ray diffractograms of the M-1 compound, Eu(M-1)$_3$·3H$_2$O and Er(M-1)$_3$·3H$_2$O complexes, where it can be observed comparatively that all the samples presented, possibly, more than one phase and have crystalline characteristics. Also the disappearing and appearing of new peaks, as well as the variation on the intensity of the M-1 majoritary peaks compared to the complexes' peaks can be observed. The majority peaks appear between 20 °C and 30 °C. The other peaks gradually decrease while 2θ increases. Comparing M-1 with their respectively complexes, it can be observed that the lanthanides introduction in the mesoionic compound structure, probably favors the increase in the crystallite of both complexes. Also, it can be observed that the Eu(M-1)$_3$·5H$_2$O (99.13%) presents a higher crystallinity percentual than Er(M-1)$_3$·5H$_2$O (92.38). Considering the crystallite size it can be concluded that M-1 (59.39 nm) presents the biggest one compared to Er(M-1)$_3$·3H$_2$O (23.07 nm) and Eu(M-1)$_3$·3H$_2$O (37.06 nm).

Table 1 presents the level of crystallinity and the size of the crystallite of the M-1 compound and of the complexes Eu(M-1)$_3$·3H$_2$O and Er(M-1)$_3$·3H$_2$O. It can be observed that, for all of the analysed samples, the crystallite size varied from 23.07 to 59.39 nm and presented nanometric dimensions inferior to 100 nm, which potentialize the possibility of the development of a tumoral marker or of a pharmac that may play specific bioactive functions. Comparing the M-1 (87.68%) compound, with the respective complexes, it can be verified that the introduction of the lanthanide on the structure of the mesoionic compound may probably favor the increase in the crystallinity in both complexes. It can also be verified that the complex Eu(M-1)$_3$·3H$_2$O (99.13%) presents a higher crystallinity percentage in comparison to Er(M-1)$_3$·3H$_2$O (92.38%).

The IR vibrational spectra provided good evidence that the metal ion is coordinated to the ligands via the atom of sulfur which is outside the loop (S–C$^-$) [1,6]. The more important IR bands are reported in Table 2.

Fig. 3 shows the overlapping of the DSC curves profiles for M-1 compound, Eu(M-1)$_3$·3H$_2$O and Er(M-1)$_3$·3H$_2$O complexes, at heating rate 10 °C/min where a displacement of the peaks of

Table 1
Absolute crystallinity level and crystallite size of the mesoionic compound M-1, Er(M-1)$_3$·3H$_2$O and Eu(M-1)$_3$·3H$_2$O complexes.

Compounds	Crystallinity level (%)	Crystallite size (nm)
M-1	87.68	59.39
Eu(M-1)$_3$·3H$_2$O	99.13	37.06
Er(M-1)$_3$·3H$_2$O	92.38	23.07

Table 2
Main absorption bands on the infrared spectra of the mesoionic compound M-1, Er(M-1)$_3$·3H$_2$O and Eu(M-1)$_3$·3H$_2$O complexes.

Compounds	νC–S$^-$	νC–S	νC–N	νN=C	νC$_{ar}$–Cl
M-1	1280f	1045	1336	1678	1096
Er(M-1)$_3$·3H$_2$O	1294f	1051	1349	1642	1090
Eu(M-1)$_3$·3H$_2$O	1283f	1064	1336	1637	1141

f – weak.

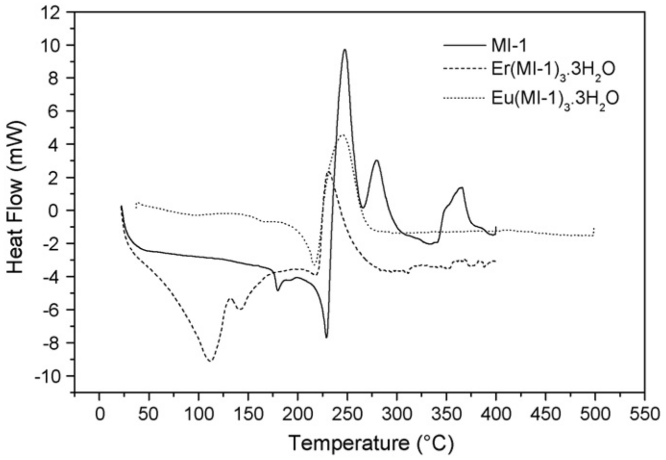

Fig. 3. X-ray diffractograms of the mesoionic compound M-1, $\mathrm{Er(M\text{-}1)_3\cdot 3H_2O}$ and $\mathrm{Eu(M\text{-}1)_3\cdot 3H_2O}$ complexes.

the complexes compared to the compound M-1 can be observed, suggesting the acquisition of new species. The mesoionic DSC curves M-1 present endothermic peak at 229 °C immediately followed by exothermic peaks at 247 °C, characteristics of a fusion process followed by the compounds decomposition. After that, two endothermic bands with a maximum at 279 °C and 365 °C can be observed, which is a characteristic of thermal decomposition.

The DSC curve the $\mathrm{Eu(M\text{-}1)_3\cdot 3H_2O}$ complex presents one endothermic band with maximum at 216 °C, characteristics of a fusion process, followed by exothermic peaks at 245 °C, a characteristic of thermal decomposition.

The DSC curve the $\mathrm{Er(M\text{-}1)_3\cdot 3H_2O}$ complex presents one endothermic band with maximum at 111 °C, characteristic of thermal decomposition, followed by exothermic peaks at 230 °C, characteristic of a possible oxidation.

4. Conclusion

Through X-ray diffraction a crystalline nanocomplex, with the crystallite size inferior to 60 nm and crystallinity higher than 87.68% can be evidenced.

The DSC curves showed that the studied complexes initiate the thermal decomposition reaction in the solid state, before the fusion process.

The IR vibrational spectra provided good evidence that the lanthanides ion is coordinated to the mesoionic compounds by exocíclico sulfur (S^-).

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