Spectroscopic Studies of two novel Eu^{+3} and Gd^{+3} with usnic acid derivative from *Cladonia substellata* Vainio

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Introduction

Lichens are symbiotic associations between fungal (mycobiont) and algal or cyanobacterial (photobiont) partners [1,2]. The secondary metabolites found in Liquens are phenolics which accumulate either on the cortex or on the cell walls of medullar hyphae. Usnic acid (UA) is a substance derivative from liquens pharmaceutically interesting due its high activity against microorganisms [3]. This natural compound has shown a great relevance in pharmacology and clinics. Recently our group have been synthesized of Eu^{+3} and Gd^{+3} ions with organic ligands and suggested as efficient molecular devices light-conversion [4]. In this work we investigate for the first time the synthesis, characterization and spectroscopic properties of the Eu-UA and Gd-UA complexes. The lanthanides ions (Eu^{+3} and Gd^{+3}), have extraordinary photophysical properties and have been widely used in the study of time-resolved, luminescent probes, optical amplification, electroluminescence and diagnostic application. This spectroscopic feature makes the Ln(III) ions as potential local probes in biochemical systems.

Results and Discussion

Luminescence measurements, X-ray diffraction and thermal analysis provide evidence that metal ion is coordinated to the UA. Powder XRD patterns of the UA free and coordinated to metal, present well definite peaks for the AU, reflecting in the crystallinity of this compound. The results showed that crystalline profile for the UA was modified with the formation of composites. The luminescence spectrum of the Eu^{3+} ion in the complex is due to the transition from the $^5D_0$ excited state to the ^7F ground state manifold. The presence of the $^5D_0 \rightarrow {}^7F_0$ transition serves as a good diagnostic of the crystallinity and purity of the Eu-UA complex. The presence of UA The substitution in the first coordination sphere of the europium complex results in an increase in the intensities of the Eu^{3+} ion transitions, as is most evident for the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The high intensity can be associated with the low symmetry of the site.

The emission spectrum of the Gd-UA in the solid form, at 77 K, shows an emission band peaked at 582 nm (17182 cm^{-1}) which is characteristic of a triplet state. This band is not observed on the emission spectrum of Eu-UA indicating the energy transfer from the UA ligand to the Eu^{+3} ion is very efficient. The good emission quantum yield of 41% for the Eu-UA and the value of the relatively high of lifetime of 300.5 μs can be attributed to a considerable resonance of the ligand triplets UA with the excited levels of the Eu^{3+}.The high value of Intensity parameter Ω_2 (39 x 10^{-20} cm^2) compared with the value of Ω_4 (13 x 10^{-20} cm^2) reflect the hypersensitivity $^5D_0 \rightarrow {}^7F_2$ transition. The thermal behavior of the Eu-UA complex shows an increase of the band of water in temperature at 100°C. It is observed also in the DSC curve of the Eu-UA complex the absence of the peak related to the melting of the UA at 201°C, evidencing that there is not free UA. Theses results were confirmed using thermogravimetry.

Conclusion

Thermal analysis and X-ray diffraction, as well as the luminescence spectra indicate the coordination of the Eu^{+3} ion to the AU. The presence of the $^5D_0 \rightarrow {}^7F_0$ transition serves as a good diagnostic of the crystallinity and purity of the Eu-UA complex. The high values of lifetime and emission quantum yield corroborate with the increase in the luminescence intensity the Eu-AU complex.

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