



Synthesis, characterization and spectroscopic study of Eu(III) complexes with 3-aminopicolinic acid derivatives

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Abstract

The synthesis, characterization and spectroscopic properties of lipophilic Eu(III) complexes of 3-aminopicolinic acid derivatives are reported. The stable complexes of Eu(III) with the ligands 3-dodecanoylamino picolinic acid (3-NHCORpic) and 3-dodecanoylamino picolinic acid N-oxide (3-NHCORpicNO) exhibit a remarkably high solubility in most common solvents and have enhanced luminescence and spectroscopic properties when compared with their parent 3-amino complexes. A strong absorption in the UV range, intense emission in the visible range, reasonable quantum yield and a long luminescence lifetime are observed. The results obtained show that these complexes can be used as light-conversion molecular devices either in solid state or in solution.

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1. Introduction

Interest in the synthesis of lanthanide complexes, particularly of Eu(III), with organic ligands has been greatly intensified due to their variety of applications in structural studies as well as in

practical applications, such as efficient phosphors, time-resolved fluoroimmunoassays, photosensitive bioinorganic compounds and high-technology optics [1]. Highly luminescent Eu(III) complexes with pyridinic units and heterobiaryl ligands have been synthesized and strongly suggested as promising light-conversion molecular devices (LCMD) [2]. In these complexes the luminescence is obtained by the antenna effect, which is the result of a strong UV absorption by the ligands

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followed by efficient ligand to lanthanide energy transfer and an intense emission in the visible range by the lanthanide ion [3].

To extend the information on the coordination chemistry of the lanthanide ions with N and O atoms in bidentate chelates, the complexation behavior of the Eu(III) ion towards picolinic acid and its N-oxide has been investigated showing a strong coordination and efficient ligand-to-metal energy transfer [4,5]. Such a characteristic provides the stability and high luminescent properties exhibited by the 3-aminopicolinic acid (3-NH₂pic) or 3-aminopicolinic acid N-oxide (3-NH₂picNO) with Eu(III) and Tb(III) adducts, candidates for efficient LCMD [6–9]. However, they are rather insoluble in organic solvents and water, limiting further purification, characterization and application. We have used the 3-amino group of the ligands as a point of attachment for the introduction of appropriate substitutes aiming at modifying the physical–chemical properties, such as solubility in common organic solvents of luminescent complexes. Presented herein are the results of our first studies in this field, introducing a new class of easily synthesized lipophilic luminescent Eu(III) complexes with 3-aminopicolinic acid and its N-oxide derivatives. In this paper we describe the synthesis, characterization and spectroscopic properties of the new Eu(III) complexes

with the ligands 3-dodecanoylamino picolinic acid (3-NHCORpic) and 3-dodecanoylamino picolinic acid N-oxide (3-NHCORpicNO). The long lipophilic tail (11 carbons) in these ligands provides complexes highly soluble in common organic solvents with an enhanced luminescence when compared with their precursor complexes [10]. Furthermore, the synthesis of the material considered in this context is more direct and simpler than the synthesis of soluble complexes with cryptands and macrocycles [11].

2. Methodology

2.1. Reagents

Commercial solvents (Fluka, Aldrich) were used without further purification. Stock ethanol solution of hydrated Eu(ClO₄)₃ was prepared by dissolving Eu₂O₃ (99.99% purity, Aldrich) in perchloric acid. The pH of these solutions was adjusted to 6 after consecutive evaporations with ethanol.

The ligand and complex structures are given in Fig. 1. The ligands 3-NHCORpic and 3-NHCORpicNO were synthesized as described previously [12].

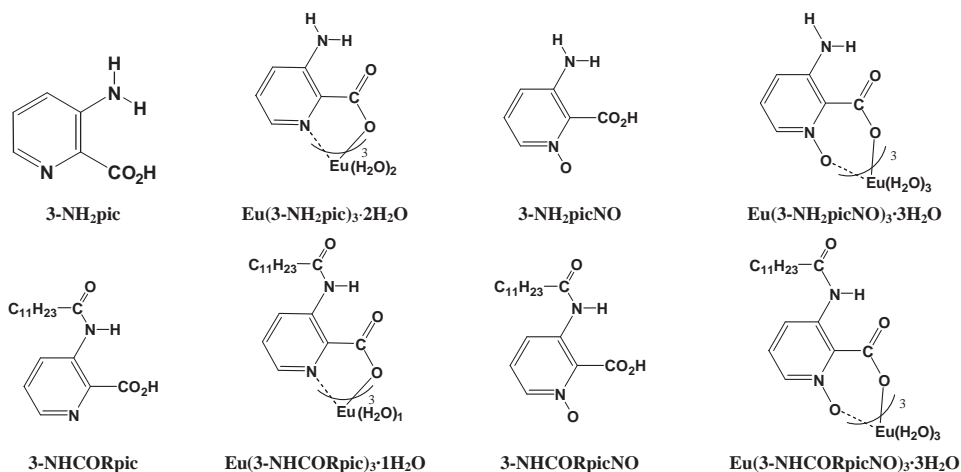


Fig. 1. Structures and abbreviations of the ligands and complexes used in this work.

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