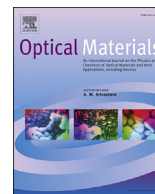




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## Rare earth Ibuprofen complexes: Highlighting a pharmaceutical

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## ABSTRACT

Complexes of  $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  with the widely applied, nonsteroidal, anti-inflammatory drug Ibuprofen (“ibu”) have been prepared and characterized with respect to their photo-physical properties. The native complexes proved to be non-luminescent, but acquired very high quantum efficiencies of up to 75% with  $\text{Eu}^{3+}$  on co-coordination with bidentate ligands (1,10-phenanthroline, 2,2'-bipyridine), accompanied by luminescent life times approaching 2 ms. However, due to energy back transfer to the ligand's triplet and the lack of suitable  $\text{Tb}^{3+}$  receptor states, the long life times could not grant the expected high efficiencies for  $\text{Tb}(\text{ibu})_3\text{phen}$ , the highest value amounting to 27% only despite an accompanying decay of 1.927 ms.

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## 1. Introduction

Complexes of the rare earths have drawn considerable interest not long after the discovery of the intriguing luminescence properties of the native, molecular  $\beta$ -diketonates about five decades ago. The interest was initially stimulated by the observation of laser action [1], then faded somewhat due to the superior performance of inorganic glasses in that area, until the events of (metal) organic electroluminescence [2], polymer based optical amplifiers [3], and medical applications as biomarkers especially [4–7], revived the research efforts on rare earth complexes.

Bidentate and aromatic carboxylates, and  $\beta$ -diketonates of the rare earths are among the most versatile and most frequently used molecular luminescent complexes due to their intriguing optical properties (high efficiencies, long decay times, narrow line emissions). The chelating organic ligands fulfill an at least twofold purpose: on direct coordination in close proximity to the ions they can greatly improve the intrinsically weak absorption of the rare earths (forbidden f-f transitions, intramolecular energy transfer, “antenna effect”) and thermodynamically they initially yield reasonably stable complexes of high coordination numbers either as molecular entities or as coordination polymers. However, in order to completely screen the ions against the adverse entry of additional and unwanted “parasitic” species (e.g. water), co-

coordination with neutral ligands (“ancillary ligands”, e.g. 1,10-phenanthroline (“phen”), 2,2'-bipyridine (“bipy”), tri-octylphosphine oxide, dibenzylsulfoxide) is a convenient and popular countermeasure [8]. In our recent search for sensitive tools to detect widely used pharmaceuticals of ecotoxicologically hazardous potential, we found that several of them are aromatic carboxylates and accessible analytically by luminescence. Diclophenac (2-(2-(2,6-dichlorophenylamino)phenyl)acetic acid) for example could be detected at the ppm level due to complex formation with rare earths ions, especially when supported by co-coordinating ligands. However, the photophysical properties of phen- and bipy-co-coordinated  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  (quantum efficiencies in excess of 40% and long decays of up to 1.7 ms) astounded us and additionally makes them very interesting for incorporation into useful and applicable matrices, e.g. polymers and subsequently into luminescent beads for biophotonics.

Here we would like to report on results obtained on Ibuprofen ((RS)-2-[4-(2-Methylpropyl)phenyl]propanoic acid, “Hibu”, Fig. 1) and complexation of its anion “ibu” with rare earth ions. Although ibu has been evaluated to show a much smaller overall toxicity [9] in comparison to e.g. Diclophenac, it is produced on an even larger technical scale (estimated as 15,000 t/yr [10], approximately 54 mio. users [11]) and is harder to remove naturally by irradiation, as it possesses no absorption overlap with natural sunlight [12]. The focus of the present investigation is, however, stimulated by the exciting photophysics of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes, and their phen and bipy co-coordinated derivatives, respectively.

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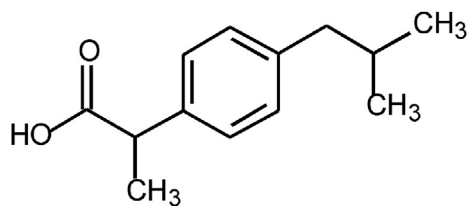


Fig. 1. Structure of Ibuprofen, “Hibu”.

## 2. Experimental

### 2.1. Materials and experimental methods

Rare earth starting solutions ( $\text{LnCl}_3(\text{H}_2\text{O})_n$ ) were prepared from rare earth oxides,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{Tb}_4\text{O}_7$  (99.99%, Treibacher) by dissolution in hydrochloric acid, vaporization of the liquid to near-dryness, re-dissolution in water, and crystallized in an ice bath. Ibuprofen (99%) was purchased from Alfa Aesar. 2,2'-bipyridine (“bipy”, 99%) and 1,10-phenanthroline monohydrate (“phen”, 99%) from Sigma-Aldrich were used as delivered. Carbon analyses were conducted with an Eltra carbon-sulfur analyzer CS-800, in which the resulting gases ( $\text{SO}_2$  and  $\text{CO}_2$ ) from combustion of the samples in oxygen are analyzed by infrared absorption. Due to its high carbon content, 4-aminobenzenesulfonic acid (41.61%C) was used to calibrate the analyzer.

#### 2.1.1. Lanthanoid(III)-2-(4-(2-methylpropyl)phenyl)propionate, $\text{Ln}(\text{ibu})_3$ , $\text{Ln}(\text{C}_{13}\text{H}_{17}\text{O}_2)_3$

Stoichiometric quantities of a 0.5 M, freshly prepared  $\text{LnCl}_3$  ( $\text{EuCl}_3$ ,  $\text{TbCl}_3$  and  $\text{GdCl}_3$ ) solution and ibuprofen were dissolved in ethanol, from which precipitation of a white powder occurs immediately after mixing, the solution was nevertheless aged for another 2 h. The powder was filtered with a Büchner funnel and washed gently with 10 mL of water. The remaining powder was dried at 60 °C in vacuum. To extract the formed sodium chloride, the gained powder was washed with 50 mL of hot water and was dried again under vacuum at 60 °C. The obtained product is anhydrous, which was confirmed by DTA/DTG. Elemental analyses are discussed below, data on carbon contents are summarized in Table 1.

#### 2.1.2. 1,10-Phenanthroline-lanthanoid(III)-tris2-(4-(2-methylpropyl)phenyl)propionate, $\text{Ln}(\text{ibu})_3\text{phen}$ , $\text{Ln}(\text{C}_{13}\text{H}_{17}\text{O}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$

$\text{Ln}(\text{ibu})_3$  was dissolved in hot toluene and an equimolar amount of 1,10-phenanthroline monohydrate added. The hot solution was concentrated until the white  $\text{Ln}(\text{ibu})_3\text{phen}$  started to precipitate. After cooling, the white precipitate was filtered by suction filtration with a Büchner funnel, and dried at 60 °C in vacuum. Elemental analyses are discussed below, data on carbon contents are

summarized in Table 1.

#### 2.1.3. 2,2-Bipyridine-lanthanoid(III)-tris2-(4-(2-methylpropyl)phenyl)propionate, $\text{Ln}(\text{ibu})_3\text{bipy}$ , $\text{Ln}(\text{C}_{13}\text{H}_{17}\text{O}_2)_3(\text{C}_{10}\text{H}_8\text{N}_2)$

The  $\text{Ln}(\text{ibu})_3\text{bipy}$  complex was synthesized analogously to the complexes  $\text{Ln}(\text{diclo})_3\text{phen}$  by exchanging the water with 2,2-bipyridine, also yielding a white powder. Elemental analyses are discussed below, data on carbon contents are summarized in Table 1.

### 2.2. Elemental analyses

The final lanthanide contents proved to be unexpectedly difficult to determine titrimetrically, most likely due to the formation of insoluble polymeric species, and were therefore complemented by differential thermal analyses (DTA, DTG). In brief, complexometric titrations of the lanthanide contents were conducted using either a) 2 M  $\text{HNO}_3$  for dissolution, producing an oily film on the aqueous phase, addition of saturated oxalic acid, filtration of the precipitated oxalates, washing to neutral pH, re-dissolution with 2 M  $\text{H}_2\text{SO}_4$ , hot titration with  $\text{KMnO}_4$ , or b) dissolution in conc.  $\text{HNO}_3$ , boiling down until a solid crust had formed. This procedure was repeated several times, after which the brownish residue was re-dissolved in 2 M  $\text{HNO}_3$ , and titrate as described above (a). The last method (c) also consisted of dissolution in conc.  $\text{HNO}_3$ , but evaporation was interrupted, after the solution had become viscous (to avoid the formation of  $\text{Tb}_4\text{O}_7$ ), was then again diluted with 2 M  $\text{HNO}_3$  and analyzed as before.

Method a) yielded Ln contents typically 25%, method b) typically 20%, method c) typically 7% below the theoretical expectations for the  $\text{Ln}(\text{ibu})_3\text{phen}$  and  $\text{Ln}(\text{ibu})_3\text{bipy}$  complexes; assuming 2 water molecules as evident from the FTIR spectra (see below, Fig. 2) for the  $\text{Ln}(\text{ibu})_3$  complexes, the expected and theoretical contents deviate by less than 1%. As opposed to that, DTG (air, up to 800 °C) conducted on  $\text{Eu}(\text{ibu})_3$ ,  $\text{Eu}(\text{ibu})_3\text{phen}$  and  $\text{Eu}(\text{ibu})_3\text{bipy}$ , now yielded too low mass losses on complete decomposition, (−4.14%,  $\text{Eu}(\text{ibu})_3$ ; −4.85%  $\text{Eu}(\text{ibu})_3\text{phen}$ ; −6.87%  $\text{Eu}(\text{ibu})_3\text{bipy}$ ). The discrepancy is not readily understood, tentatively the data suggest that some unknown Eu-species may form, probably in the polymeric residue in the titrimetric analyses (a–c), and incomplete pyrolysis in DTA. On inspection of the FTIR-spectra (Fig. 3), water can be excluded for the co-coordinated phen and bipy complexes, but is unambiguously contained in the  $\text{Ln}(\text{ibu})_3$  complexes (see below, see Fig. 2).

#### 2.2.1. Spectroscopic measurements

Excitation and emission spectra of the powders were measured with an Acton Research Corporation Spectra Pro<sup>®</sup>-300i, where the samples were placed inside a homemade, UV-fiber coupled brazen chamber. The samples surface is irradiated at an angle of 90° and reflected or emitted radiation is collected at an angle of 45° through a collimating lens with a fiber. The recorded excitation spectra were corrected against Lumogen Red F300 doped (50 ppm) PMMA powder standard. The validity of this measurement was checked against commercial green and red phosphors ( $\text{LaPO}_4\text{:Ce,Tb}$  and  $\text{Y}_2\text{O}_3\text{:Eu}$ ), the relative error being  $\pm 5\%$ .

Reflection spectra were also recorded with same Acton Research Corporation Spectra Pro<sup>®</sup>-300i. The sample is measured in an integrating sphere, the recorded spectra were corrected against a black standard (felt, reflectance 5%) and a white standard ( $\text{BaSO}_4$ ).

#### 2.2.2. Decay times

The powdrous samples were measured with an Edinburgh Instruments FSL 920 and irradiated with a xenon  $\mu\text{F920H}$  flashlamp. Decay times of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes were measured using the

Table 1  
Carbon contents for all compounds.

Compound	Carbon content (theor.) [%]	Carbon content (found) [%]
$\text{Eu}(\text{ibu})_3(\text{H}_2\text{O})_2$	58.2	58.1
$\text{Tb}(\text{ibu})_3(\text{H}_2\text{O})_2$	57.8	61.4
$\text{Gd}(\text{ibu})_3(\text{H}_2\text{O})_2$	57.9	60.5
$\text{Eu}(\text{ibu})_3\text{phen}$	64.6	64.6
$\text{Tb}(\text{ibu})_3\text{phen}$	64.1	67.4
$\text{Gd}(\text{ibu})_3\text{phen}$	64.3	67.4
$\text{Eu}(\text{ibu})_3\text{bipy}$	63.7	60.8
$\text{Tb}(\text{ibu})_3\text{bipy}$	63.0	61.5
$\text{Gd}(\text{ibu})_3\text{bipy}$	63.3	n.d.

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