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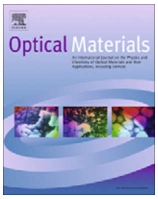

Novel, highly photoluminescent Eu(III) and Tb(III) tetrazolate-2-pyridine-1-oxide complexes

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ABSTRACT

Tetrazole-2-pyridine-1-oxide was prepared from 2-cyanopyridine and sodium azide, followed by oxidation with m-chloroperbenzoic acid. This ligand forms neutral 1:3 complexes with Eu(III) and Tb(III) cations. The complexes are photoluminescent in solution, with photoluminescence quantum yields 13% and 31%, respectively.

1. Introduction

The fascinating optical and magnetic properties of lanthanide ions have promoted the use of their complexes in an increasing number of technological applications ranging from biomedical analysis (fluoroimmunoassays, MRI contrast agents, and cellular imaging) to materials science (lasers, optical fibers, light emitting diodes, and optical displays) [1–5]. Accordingly, numerous studies have been directed toward the design of ligands for the development of highly luminescent and robust lanthanide chelates [2,6]. In particular, lanthanide ions present sharp characteristic emission in the visible and near infrared (NIR) ranges, long luminescence lifetimes, and large Stokes shifts, which makes them very attractive candidates for the development of optical devices. Tetrazolate groups are used as isosteric replacement of carboxylates in medicinal chemistry [7]. In spite of this, and although two recent reports evoke the possibility of using tetrazole as lanthanide binding units [8], the chemistry of lanthanide tetrazolates remains unexplored.

Just as with many scientific discoveries, the preparation of the first tetrazole complex by the Swedish chemist Bladin in 1885 was accidental [9]. Since this discovery, interest in this area of chemistry has remained strong over the last 100 years and to date, studies on the synthesis and applications of tetrazoles remain very popular [10]. This is quite unsurprising in view of the functional group's role in coordination chemistry as a ligand with various coordination modes [11], in medicinal chemistry as a metabolically stable surrogate for a carboxylic acid group [12], and in various materials science applications, including specialty explosives [13]. While Bladin and co-workers established the first synthetic route to tetrazoles, the most widely used method of preparation is [2 + 3] cycloaddition of an azide to a nitrile. The addition of hydrazoic acid to the cyanide group resulting in the formation of 5-substituted tetrazole derivatives was first reported by Hantzsch and Vagt [14] and led to the birth of [2 + 3] cycloaddition as the protocol of choice for the synthesis of tetrazoles.

5-Substituted tetrazoles that contain a free N–H bond are also frequently referred to as tetrazolic acids, and exist as a nearly 1:1 ratio of 1H- and 2H-tautomeric forms. The isomers are essentially different in their chemical and physicochemical characteristics [15]. The compounds readily lose a proton when treated with a base providing the corresponding tetrazolate anions, which are fairly stable against hydrolysis and exist in water solutions predominantly in a ionic form. The free N–H bond of tetrazoles makes them acidic molecules, and not surprisingly it has been shown that both the aliphatic and aromatic tetrazoles have pK_a values that are similar to corresponding carboxylic acids (4.5–4.9 vs. 4.2–4.4, respectively) [16], due to the ability of the tetrazole ring to stabilize a negative charge by electron delocalization. The characteristic feature of the crystals of all NH unsubstituted tetrazoles is the presence of strong intermolecular N–H···N hydrogen bonds, which govern mainly the molecular packing of these compounds. In general, tetrazolic acids exhibit physical characteristics similar to carboxylic acids and are strongly influenced by the effect of substituents at the C5-position [15]. For example, many 5-aryl tetrazoles are highly soluble in water and are best crystallized from

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aqueous alcoholic solvents. The corresponding tetrazolate anionic species, which have a higher capacity for hydrogen bonding than the protic species, are easily generated in hot alcohol or aqueous solutions and these intermediates are more reactive than the corresponding neutral species toward a variety of electrophiles and alkylating agents [15]. Tetrazoles are versatile chelating motifs which can be used in replacement of carboxylate groups because of their similar pK_a values. Moreover tetrazolates have attracted considerable interest in coordination chemistry [16] due to their π-acceptor properties and to their ability to form metal complexes and coordination polymers with high thermal stability and displaying interesting luminescence, non-linear optical, electrochemical or H_2 storage properties [17,18]. Notably tetrazolate-based ligands have been shown to afford iridium and ruthenium based electroluminescent devices with improved efficiency with respect to their polypyridine or picolinate analogs [19,20]. Surprisingly, in spite of the interesting properties of the tetrazole group, very few examples of tetrazole-based ligands for lanthanides have been reported so far. Aime et al. have synthesized [21] in 2002 the H4dotetra ligand, a mixed pendant-arm macrocycle comprising a tetrazole subunit. The resulting gadolinium complex exhibited a satisfactory stability and interesting relaxometric properties. A second example came from Facchetti et al., who prepared [22] neutral Gd(III) and Zn(II) complexes of pyridine- and (pyridine-1-oxide)tetrazole (Hpytz). The Gd(III) 1:3 complexes show a large number of coordinated H_2O molecules and hence a high relaxivity, but their stability remains low due to the small denticity of the ligands. Andrews et al. reported [23] the formation of hydrogels using 2-pyridyl-tetrazole in the presence of lanthanum chloride (1:3 stoichiometry), and later extended the work [24] to other cationic, neutral and hydroxo-bridged lanthanide bis-pyridine-tetrazole complexes. Recently, Mazzanti et al. reported [25] a series of new tetrazole based ligands with terpyridine or bipyridine chromophores appended with two tetrazole units and they also report about photophysical properties of these complexes which is showing quantum yields ranging from 5% to 53% for Eu(III) complexes, 6% to 35% for Tb(III) complexes, and 0.1% to 0.3% for Nd(III) complexes, which is among the highest reported for a neodymium complex. Furthermore, in these compounds the presence of water molecules or hydroxo groups coordinated to the metal center is likely to result in the non-radiative deactivation of the lanthanide excited states by OH oscillators reducing the luminescence emission quantum yield.

In our laboratory, we were the first to report the introduction of the lanthanide 2-pyridine-tetrazole 1:3 complexes. The different geometric and electronic features of these complexes with respect to carboxylate ones [26–28] resulted in very interesting properties, as highlighted by their very efficient luminescence emission. The quantum yields of the europium and terbium complexes of pyridinetetrazolate oxide are 13% and 31% in solution, respectively. The results prompted us to further explore the rich coordination chemistry of the tetrazole ligands.

2. Results and discussion

2.1. Synthesis and characterization

The ligands: 5-(2-pyridyl)tetrazole 5-(2-pyridyl-1-oxide)tetrazole were synthesized according to Scheme 1, using the slightly modified literature procedure [8a].

The synthesis procedure of Eu(III), Gd(III) and Tb(III) complexes **1**–**3** is shown in Schemes 2 and 3. The microanalyses, IR studies of complexes show that lanthanide ions have reacted with HPTO in a metal-to-ligand mole ratio of 1:3. The IR spectrum of complex **1** shows a broad absorption in the region 3000–3500 cm^{-1}, indicating the presence of solvent or water molecules in the complex. The central Eu^{3+} ion is coordinated with three oxygen atoms and three nitrogen atoms from PTO ligand, three from water molecules (either with 2 water molecules and another water molecule is dissipated in lattice as reported in various reviews for tetrazolate complexes [29a,b,c]).

2.2. Spectroscopic studies

2.2.1. UV spectra

UV absorption spectra of the Eu(III) and Tb(III) complexes were measured in CH_3CN are shown in Fig. 1. The maximum absorption bands at 274 nm were found in both europium and terbium complex. The spectral shapes of the complexes in CH_3CN are similar to that of the free ligands, however a small blue shift observed in the absorption maximum of all the complexes is due to the perturbation induced by the metal coordination.

2.2.2. Photoluminescent properties of complexes *1*–*2*

It is clear both from the excitation spectra of complexes **1**–**2** (Fig. 2) and also from the absorption spectra that overlaps exist between the excitation band of each lanthanide complex and the absorption bands of the ligands. This is diagnostic of the typical sensitization of Ln^{3+} ion by organic ligands and therefore confirms that the Ln^{3+} ions are surrounded by HPTO ligand. The excitation spectra for **1**–**2** exhibit a broad excitation band between 250 and 350 nm, which can be assigned to the π–π^* transition of the N and O from PTO. In turn, this proves that luminescence sensitization via excitation of the ligands is more efficient than the direct excitation of the Ln^{3+} ion excitation level. Each complex exhibits a maximum excitation in the range of 260–350 nm hence samples were excited at the wavelengths of 261 and 276 nm respectively.

The room-temperature normalized emission spectra of europium and terbium complexes **1**–**2** (in solution) under the excitation wavelengths that maximize the emission intensity are shown in Figs. 3 and 4. The emission spectrum of the europium complex displays characteristic sharp peaks in the 575–725 nm region associated with the $^5D_0$–^7F_J transitions of the Eu^{3+} ion. The five expected peaks for the $^5D_0$–$^7F_{0-4}$ transitions are well resolved and the hypersensitive $^5D_0$–$^7F_2$ transition is very intense, pointing to a highly polarizable chemical environment around the Eu^{3+} ion that is responsible for the brilliant red emission of these complexes. A relevant feature that may be noted for the complex **1** is the very high intensity of the $^5D_0$–$^7F_2$ transition, relative to the $^5D_0$–$^7F_1$ line, indicating that the Eu^{3+} ion coordinated in a local site without an inversion center. Further, the emission spectra of the complex show only one peak for $^5D_0$–$^7F_0$ transition (half width for $^5D_0$–$^7F_0$ is 1.5 nm) and three stark components for the $^5D_0$–$^7F_1$ transition, indicating the presence of a single chemical environment around the Eu^{3+} ion. All attempts to grow crystals for X-ray analysis failed in all solvent systems.

The room-temperature normalized emission spectrum of Tb^{3+} complex **2** (Fig. 3) shows characteristic emission bands of Tb^{3+} ($\lambda_{ex} = 276$ nm) centered at 490, 545, 585 and 620 nm, resulting from the deactivation of the $^5D_4$ excited state to the corresponding ground state ^7F_J ($J = 6, 5, 4, 3, 2, 1$) of the Tb^{3+} ion. The strongest emission is centered on 545 nm, which corresponds to the hypersensitive transition of $^5D_4$–$^7F_5$. The broad emission peaks obtained may be due to the greater non-homogeneity for Tb^{3+} local coordination site due to the presence of water molecules, or *syn*-, and *anti*- geometric complex isomers.

The luminescence lifetime values (τ_{obs}) of the $^5D_0$ and $^5D_4$ levels are 0.35 and 0.42 for complex 1 and 2 respectively, which were determined from the luminescence decay profiles at room temperature by fitting with a monoexponential curve. The relatively shorter lifetime obtained for complex may be due to dominant