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Mono(pyridine-N-oxide) analog of DOTA as a suitable organic reagent for a sensitive and selective fluorimetric determination of Ln(III) ions

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ABSTRACT

The mono(pyridine-N-oxide) analog of the H₄dota macrocyclic ligand, H₃do3a-py^{NO}, is capable of forming thermodynamically stable and kinetically inert Ln(III) complexes. Its Eu(III) and Tb(III) complexes display a strong long-lived fluorescence as a result of the antenna effect of the pyridine-N-oxide fluorophore in the reagent. It is shown that H₃do3a-py^{NO} can be used as a fluorogenic reagent for the determination of Eu(III) and Tb(III) at pH 6.5 and c_L = 1 mM. At an excitation wavelength of 286 nm, the emission maxima are 615 nm (Eu(III)-complex), and 547 nm (Tb(III) complex). Detection limits are at concentrations around 1.0 μM and linearity of the method spans over 2 orders of magnitude. The method was applied to artificial and real samples (spiked mineral waters, extracts from cathode ray tube luminophore dust) and gave satisfactory results. The method is simple, rapid, and hardly interfered by other metal ions.

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1. Introduction

Ln(III) complexes of H₄dota and its derivatives (Scheme 1) are utilized in many areas of medicine (e.g. complexes of metal radioisotopes as ⁹⁰Y, ¹⁵³Sm, ¹⁶⁶Ho, ¹⁷⁷Lu in nuclear medicine) [1–3], Gd(III) complexes as magnetic resonance imaging (MRI) contrast agents [4], Eu(III)/Tb(III) complexes as luminescence probes [5,6] or sometimes as bimodal probes (e.g. optical-nuclear [7] or optical-MRI [8,9] imaging). The complexes can be attached to a biomolecule (e.g. short peptide, sugar, etc.) to control their distribution in body [1,5,6] and in order to visualize differences between health and diseased tissues [5,6]. Majority of the utilizations in optical imaging relies on complexes of lanthanide(III) ions with organic ligands which serves also as efficient sensitizer of lanthanide(III) fluorescence [5,6].

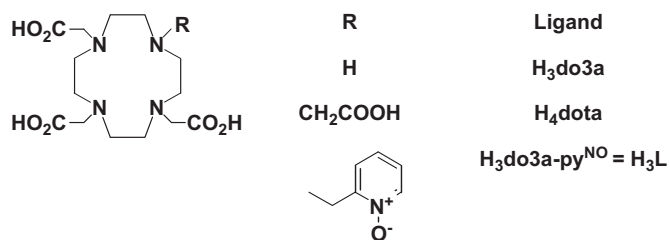
Lanthanides and their compounds have been widely utilized in industry, e.g. as catalysts, high-temperature ceramic superconductors, molecular magnets, oxygen sensors and capacitors, etc. [10,11]. The optical properties of Ln(III) ions have been used for the production of TV screens and PC monitors. Nowadays, their important utilizations involve the active media for the lasers, e.g. Nd-YAG, or phosphors for electroluminescent displays (Tb for

green and Eu for red lights) [10,11]. Recently, the recycling of used screens of color televisions and PC monitors followed by isolation of europium(III) and yttrium(III) from concentrate of luminophore dust or sludge becomes important ecological and economical problem for the society [12,13]. In the applications, there is a strong requirement to check a purity of the input and output materials during the process of manufacturing of lanthanides and their compounds as well as the control of luminophore industrial reprocessing [12,13].

Lanthanide(III) ions can be determined classically by gravimetry in the form of insoluble oxalates, phosphates, oxides or chelates with 8-hydroxyquinoline ligand [11,14] or volumetrically using more general chelatometric and/or redox titrations specific for some Ln(III) ions (e.g. Ce, Eu, Tb or Yb [11,14]). Due to similar physical and chemical properties of Ln(III) ions, they have complex absorption and emission spectra [11]. The first step in analysis of lanthanide-containing materials should be their separation and also preconcentration (for samples with lower metal content) on ion exchange column followed by analysis with a suitable spectroscopic detection/method (UV-vis, fluorescence, mass spectrometry-MS [11,14]). Recently, electromigration techniques mostly in capillary mode (electrophoresis, isotachopheresis) have become very popular although spectroscopic techniques are used for Ln(III) ion determination more frequently [11,15]. Atomic emission spectroscopy in ICP or flame modes is generally preferred; however, the ions might interfere each other due to overlapping atomic/ionic spectral lines generally leading

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Scheme 1. The formulas of macrocyclic ligands discussed in the text.

to increase of the limit of detection [11,16]. This can be eliminated using high-resolution spectrographs or MS detection [11,16]. In addition, X-ray spectrography is more suitable than atomic absorption spectroscopy [11] while neutron activation analysis is capable of low-concentration determination in comparison with other instrumental techniques [11]. Molecular methods using absorption or fluorescence of Ln(III) ions are mostly used more widely due to a high sensitivity, suitable availability and portability in practice and lower cost of analysis in comparison to atomic spectroscopic techniques [11]. Thus, Ln(III) ions are sensitized after formation of their complexes by reaction with an organic reagent (Arsenazo III, PAR and some other azodyes, Morin, Aluminon, Calcein, 1,10-phenanthroline) [11,14,17–23]; however, some interfering ions have to be removed prior such analysis [11,14,17–23]. Other problem from practical point of view is fact that some of sensitive organic reagents (e.g. Arsenazo III, PAR, Calcein) are not selective for Ln(III) ions [11,17–19] and they can be employed only in combination with separation techniques in order to increase the method sensitivity, selectivity and applicability [24].

In this contribution, we present an application of macrocyclic ligand with the pyridine-N-oxide pendant arm ($\text{H}_3\text{do3a-py}^{\text{NO}}$ or H_3L ; Scheme 1) for determination of Ln(III) ions by fluorescence spectroscopy. The ligand and its complexes [25–27] or its conjugates with dendrimers [28] or calixarenes [29] have been already investigated during development of new MRI contrast agents. It was proved the lanthanide(III) ions are tightly bound inside the ligand cavity and they are coordinated by eight ligand donor atoms in the O_4N_4 fashion and one water molecule in the apical position [27].

Tetraazamacrocyclic ligands have not been commonly used for metal ion analysis; however, there are many analytical applications for other macrocyclic ligands, e.g. crown-ethers, calixarenes, etc. [30]. The application of cyclam (the fourteen-membered tetraazamacrocyclic ligand) having phosphonate pendant arms for sensitive and selective copper(II) determination was already described recently [31,32]. This pilot paper is dealing with the first application of new synthesized twelve-membered tetraazamacrocyclic ligand (Scheme 1) for Eu(III) and Tb(III) luminescence determination. In comparison with other methods using fluorogenic reagents, the formed complex is kinetically inert which can be treated in slightly acidic medium without its decomposition for several hours. Thus Ln(III) complex can be employed for its separation from other interferents, e.g. other interfering anions and/or metal ions.

2. Experimental

The title ligand, 1,4,7,10-tetraazacyclododecane-1-[(N-oxido-pyridine-2-yl)methyl]-4,7,10-triacetic acid ($\text{H}_3\text{do3a-py}^{\text{NO}} = \text{H}_3\text{L}$), was synthesized according to procedure described in literature [25–27]. Stock solutions of the individual metal cations were prepared by dissolving hydrates of LnCl_3 (99.9%; Strem, www.strem.com or Alfa, www.alfa.com). The Ln(III) contents in the solutions were determined by titration with a standard $\text{Na}_2\text{H}_2\text{edta}$ solution with visual

detection on xylenol orange in pH 5.5–6.0 [11]. The sample of a mineral water (“Vincentka”) was spiked by addition of the Eu(III) or Tb(III) stock solution. Prior to analysis, the sample was acidified to $\text{pH} \approx 4$ and carbon dioxide was removed from the solution in ultrasound bath since it can cause some solubility problems. The proposed analytical procedure for determination of Eu(III) ion concentration was verified in a high excess of other Ln(III) or transition metal ions (Cu(II), Mn(II), Co(II), Fe(II), Ni(II)) in 50-times higher excess under optimal experimental conditions discussed in the article.

The kinetic study was followed by means of a HP-8453A diode array (Hewlett-Packard, USA) spectrophotometer (<http://www.agilent.com>). The fluorescence spectroscopy employed for thermodynamic study of Eu(III) ion complexation by the title ligand and spectroscopic study of the organic reagent for determination of Eu(III) and Tb(III) ions was carried on Aminco-Bowman AB2 spectrofluorimeter (Aminco-Bowman, USA) in 1-cm cells ($\lambda_{\text{exc}} = 286$ or 394 nm). The experimental conditions are given in text. The thermodynamic data were measured with solutions equilibrated for the time required from kinetic measurement (see Table 1) and the experimental fluorescence data were treated by OPIUM program [34]. The quantum yield for Eu(III) complex was determined as described elsewhere [35] using recommended secondary standards [35,36].

The real samples were obtained from industrial extraction process of cathode ray tubes (CRT) giving powder lanthanide-containing samples as described elsewhere [12] and they were analyzed by analytical method developed in this paper. The results of chemical analysis were verified by capillary isotachopheresis (CITP) with EA 101 equipment (Villa Labeco, Slovakia, www.villalabeco.sk) and inductively-coupled plasma atomic emission spectrometry (ICP-AES) with JobinYvon 170 Ultratrace equipment (www.horiba.com) using optimized experimental conditions given there [15,16].

3. Results and discussion

In analytical chemistry, the organic reagents for determination of metal ions should form thermodynamically and kinetically stable complexes. The experimental conditions (e.g. concentration of organic reagent, pH, reaction time, etc.) are then optimized in order to reach a quantitative formation of the metal complexes exhibiting the desired physico-chemical properties [17,18].

3.1. Thermodynamic and kinetic study

The title ligand belongs to macrocyclic ligands which form complexes with Ln(III) or transition metal ions rather slowly if it

Table 1
Formation kinetic data of $[\text{Eu(L)}]$ complex ($l = 0.1 \text{ mol dm}^{-3}$ (KCl), $t = 25.0 \pm 0.1$ °C).

pH	$k_2^{\text{f}} (\text{M}^{-1} \text{s}^{-1})^{\text{a}}$	$k_{\text{obs}} (\text{s}^{-1})^{\text{b}}$ $t(99.9\%) (\text{min})$	$k_{\text{obs}} (\text{s}^{-1})^{\text{c}}$ $t(99.9\%)$
4.5	20.3	567	5.7 min
5.0	121	95.2	57 s
5.5	713	16.2	9.7 s
6.0	1504 ^d	7.7	4.6 s
6.5	4900 ^d	2.4	1.4 s

^a $c(\text{Eu}^{3+}) = 5 \times 10^{-5} \text{ mol dm}^{-3}$, $c(\text{H}_3\text{L}) = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, the experimental data were processed by PRO-K II software [33].

^b $c_{\text{L}} = 10^{-5} \text{ mol dm}^{-3}$.

^c $c_{\text{L}} = 10^{-3} \text{ mol dm}^{-3}$.

^d values in italics were estimated from extrapolation from $k_{2,\text{f}} = f(\text{pH}, K_{\text{p},\text{f}})$ dependence [37].

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