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Spectroscopic study, thermal investigation and evolved gas analysis (EGA) during pyrolysis and oxidative decomposition of new binuclear complexes of La(III), Ce(III), Pr(III) and Nd(III) with *N*-phenylanthranilic acid

Lidia Zapała[a,*], Małgorzata Kosińska[a], Elżbieta Woźnicka[a], Łukasz Byczyński[b], Wojciech Zapała[c], Jan Kalembkiewicz[a]

[a] Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszow, Poland
[b] Department of Polymers and Biopolymers, Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland
[c] Department of Chemical and Process Engineering, Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

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ABSTRACT

New binuclear complexes of La(III), Ce(III), Pr(III) and Nd(III) ions with *N*-phenylanthranilic acid of general formula $Ln_2(NFA)_5(OH)\cdot nH_2O$ (where NFA–*N*–phenylanthranilic acid) were synthesized and characterized by elemental analysis, infrared spectroscopy, XRD technique and thermogravimetric analysis. The obtained results show that in complexes only the carboxyl group is involved in the coordination of the rare earth ions in the bidentate mode. Coordination does not occur through the nitrogen atom.

The detailed TG–DSC analysis provided previously unreported information concerning the thermal behaviour of these binuclear compounds in nitrogen and air atmosphere. Thermogravimetric analysis shows that decomposition processes are multistage and dehydration is the first step of decomposition. The calculated dehydration enthalpies are low for all studied complexes what indicates that it is crystallization water. Moreover, the thermal stability and the decomposition path of these compounds depend on the metal ion and the used atmosphere. The TG–FTIR–MS technique was employed in order to study a decomposition pathway of the obtained compounds. The EGA data allowed for the identification and comparison of gaseous products evolved during pyrolysis and oxidative decomposition of the considered compounds.

1. Introduction

The lanthanide coordination chemistry attracts much attention due to diversity of the promising properties and various applications of lanthanide complexes. Lanthanide complexes with organic ligands are used for producing the luminophore (in particular the compounds with Sm^{3+}, Eu^{3+}, Tb^{3+} ions) and lasers (especially the compounds with Nd^{3+}, Ho^{3+}, Er^{3+} ions). One of the newer applications of complex compounds of lanthanide ions exhibiting good luminescence properties is the production of organic light-emitting diodes (OLEDs) and solar cell components. Lanthanides complexes may also be used as suitable luminescent chemosensors [1,2]. Moreover, the importance of lanthanide complexes and chelates in medicine should also be emphasized. Unique photo-physical properties enable to use them as diagnostic probes, contrast agents in diagnostic X-ray as well as contrast enhancing agents for magnetic resonance imaging [3]. Lanthanides ions coordinate to some essential drugs are also in the area of interest as potential therapeutic agents [4]. They exhibit a wide spectrum of biological activities: antitumor, antifungal, antibacterial, anti-inflammatory and antioxidant [5]. Furthermore, coordination compounds of rare earth elements and drug may exhibit higher biological activity than that of metal or ligand because of synergetic effects [6,7]

N-Phenylanthranilic acid (2-(phenylamino)benzoic acid, diphenylamine-2-carboxylic acid, 2-anilinobenzoic acid) belongs to fenamates: N-substituted anthranilic acid derivatives. The most known mefenamic acid, tolfenamic acid, meclofenamic acid are used clinically as nonsteroidal anti-inflammatory drugs

* Corresponding author.
E-mail address: lzapala@prz.edu.pl (L. Zapała).

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Table 1
Analytical (complexometric), thermoanalytical (TG) and elemental (EA) analyses data of Ln(III) complexes with N-phenylanthranilic acid.

Compound	Molecular mass/ g mol^{-1}	Ln			C		H		N		H_2O	
		EDTA	TG	calc.	EA	calc.	EA	calc.	EA	calc.	TG	calc.
$La_2(C_{13}H_{10}NO_2)_5(OH)\cdot 3.5H_2O$ (La-NFA)	1418.98	18.84	19.46	19.58	56.59	55.02	3.93	4.12	5.04	4.94	4.28	4.44
$Ce_2(C_{13}H_{10}NO_2)_5(OH)\cdot 4H_2O$ (Ce-NFA)	1430.40	20.29	20.37	19.59	55.01	54.58	3.93	4.16	4.90	4.90	5.01	5.04
$Pr_2(C_{13}H_{10}NO_2)_5(OH)\cdot 3.5H_2O$ (Pr-NFA)	1422.98	20.23	20.51	19.80	53.34	54.86	3.83	4.11	4.69	4.92	4.13	4.43
$Nd_2(C_{13}H_{10}NO_2)_5(OH)\cdot 4H_2O$ (Nd-NFA)	1438.66	19.80	20.15	20.05	54.23	54.26	3.93	4.13	4.80	4.87	4.59	5.01

(NSAIDs) for the treatment of fever, pain, and inflammation [8,9]. N-Phenylanthranilic acid was established as the minimum structural requirement for achievement the biological properties of fenamates [10]. Many applications of this aromatic amino acid are known. It is widely used in medicine and pharmacy as starting material for synthesis of pharmaceutically important molecules such as antimalarials, anti-inflammatory and antineoplatics [8] and comparative medical research as well as in analytical chemistry for metal ion determination [11].

In the literature there is not much information about lanthanide ions complexes with fenamate ligands, especially *N*-phenylanthranilic acid. Until now descriptions of binary and ternary mononuclear lanthanide complexes with *N*-phenylanthranilic acid and 1,10-phenanthroline can be found in relatively few papers [2,12]. Furthermore, there are no data about thermoanalytical studies of binuclear lanthanide complexes with N-phenylanthranilic acid under pyrolysis and oxidizing conditions. Considering biologically active metal complexes, thermal analysis data play also an important role for estimating the thermal stability and shelf life of these compounds as potential drugs [13]. In addition, the thermal analysis coupled on-line with FTIR and MS spectroscopy provides valuable information about the relevant gaseous products and allows to correctly characterize decomposition steps as well as to confirm proposed decomposition mechanisms for complexes [14,15]

Therefore, the aim of this work was to obtain binuclear binary complexes of La (III), Ce(III), Pr(III) and Nd(III) ions with N-phenylanthranilic acid in solid state as well as study their properties and thermoanalytical behaviour. For this purpose elemental analysis, gravimetry, infrared spectroscopy and X-ray powder diffraction (XRD) as well as simultaneous TG/DTG–DSC analysis coupled with MS and FT-IR spectrometry were applied.

2. Experimental

2.1. Materials and measurements

All the chemicals were of analytical grade and used without further purification. *N*-phenylanthranilic acid was obtained from Sigma-Aldrich. The rare earth(III) chlorides ($1\cdot10^{-2}$ mol dm^{-3}) were prepared from the rare earth(III) oxides (except for cerium, where cerium nitrate $Ce(NO_3)_3\cdot 6H_2O$ was used). Methanol, sodium hydroxide and hydrochloric acid were acquired from POCH, Poland while DMSO was from Merck.

Elemental analyses (C, H and N) were performed on a Vario EL elemental analyzer (Elementar, Germany). The content of the lanthanide ions was determined by complexometric method using Na_2EDTA and xylenol orange as indicator. The water content was calculated on the basis of the results obtained by the thermogravimetric method. The chlorine content was determined by the Schöniger method. The FT-NMR spectra for N-phenylanthranilic acid and La(III) complex were recorded on a FT-NMR spectrophotometer, 500 MHz (Bruker). FT-IR spectra were carried out in the range 4000–400 cm^{-1} on Alpha FT-IR spectrophotometer (Bruker, Germany) using a KBr pellets. The X-ray powder analysis of solid complexes samples was carried out by means of a Bruker D2 Phaser powder diffractometer, using Cu Kα radiation (λ = 1.5406 Å). The measurements of 2θ were carried out in the range of 0–28°. The differential scanning calorimetry (DSC) of the synthesized complexes was performed with a Mettler Toledo DSC-822e calorimeter in nitrogen atmosphere at a heating rate of 10 °C min^{-1} from −30 to 250 °C.

Thermogravimetric analysis of the obtained lanthanide complexes was carried out using TGA/DSC1 apparatus (Mettler Toledo) in dynamic nitrogen and air atmospheres (50 mL min^{-1}) in the temperature range of 25–1000 °C with a heating rate of 20 °C min^{-1}. Evolved gas analysis was performed by applying combined TG-FTIR-MS technique. TG-FTIR analyses were performed in nitrogen and air atmosphere at 20 °C min^{-1} with the use of Mettler Toledo TGA/DSC1 apparatus, which was online coupled with FTIR spectrometer Nicolet iS10 (Thermo Scientific) by a transfer line heated at 220 °C. The FTIR spectra of the evolved gases were acquired in the range 400–4000 cm^{-1} with resolution of 4 cm^{-1}. The evolved gases were then transferred by a quartz capillary heated at 200 °C into mass spectrometer ThermoStar^{TM} (Pfeiffer Vacuum) where the selected *m*/*z* signals were monitored.

2.2. Preparation of the complexes

The synthesis of La(III), Ce(III), Pr(III), Nd(III) complexes with N-phenylanthranilic acid was carried out in aqueous–methanol solution according to the molar ratio of Ln^{3+} to ligand 1:2 at 70 °C under stirring. A stock solution of appropriate lanthanide ions (1×10^{-2} mol dm^{-3}) was added into a hot solution of N-phenylanthranilic acid in methanol (1×10^{-2} mol dm^{-3}) and then diluted with water to the ratio of methanol to water 1:1. Afterwards, pH of the mixture was adjusted to 6–6.5 by addition of 0.5 mol dm^{-3} NaOH solution. The resulting solid complexes appeared as coloured precipitates. The temperature of the mixture was maintained at 70 °C for 1 h and then left at room temperature for 24 h. Next, the precipitates were filtered, washed with deionized water and methanol until no chloride ions could be found and finally dried in air at room temperature.

3. Result and discussion

3.1. Elemental analysis of the complexes

The composition of the prepared complexes was determined based on elemental (EA), complexometric (EDTA) and thermoanalytical (TG) analyses. The results are presented in Table 1.

All complexes were obtained as hydrates. They are amorphous, insoluble in water and sparingly soluble in methanol, DMSO and other polar solvents. The molecular formula of the obtained complexes (generally labeled Ln-NFA) is $Ln_2(C_{13}H_{10}NO_2)_5(OH)\cdot 3.5H_2O$ for La(III) and Pr(III) ions and $Ln_2(C_{13}H_{10}NO_2)_5(OH)\cdot 4H_2O$ for Ce(III) and Nd(III) ions, where Ln is the lanthanide cation.