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LASER DESORPTION/IONIZATION (LDI MS) AND THERMOPROGRAMMED DESORPTION MASS SPECTROMETRY (TPD MS) OF EUROPIUM(III) COORDINATION COMPOUND WITH N-{*BIS*[METHYL(PHENYL)AMINO]PHOSPHORYL}-BENZENESULFONEAMIDE

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The coordination compound EuL$_3$Phen (where L$^-$ = N-{bis[methyl(phenyl)amino]phosphoryl}-benzenesulfoneamidate anion) has been synthesized and studied by laser-desorption and temperature-programmed mass spectrometry in the condensed phase and on the surface of a standard metal substrate. The temperature dependence of the main mass spectrum components in the method of temperature-programmed desorption mass spectrometry (TPD MS) is defined and interpreted, components of the laser desorption/ionization (LDI) mass spectrum of the synthesized substance have been identified. A comparative analysis of mass spectra obtained by both methods for the studied coordination compound has been carried out. A possibility of both mass spectrometric methods using for the investigation of metal-containing polymer components is discussed.

Keywords: *laser desorption/ionization (LDI MS), temperature-programmed desorption mass spectrometry (TPD MS), lanthanides, phosphorylic ligands*

INTRODUCTION

The growing interest of researchers to the synthesis and comprehensive study of the properties of lanthanide-containing compounds is caused by wide possibilities of their practical applications, especially those related to their useful magnetic and optical properties [1, 2]. Coordination compounds of lanthanides with chelating ligands of β-diketonate type, which contain N,N-chelating additional neutral ligands, lately have attracted especial attention due to the advancement of technology MOLED (metal organic light emitting devises) for the creation of color flexible displays and laser devices, as well as the possibility of using such compounds in biomedical research and as contrast reagents for NMR tomography studies [3–6]. It is well known that direct excitation of the 4*f*- levels of the emitting lanthanide ion leads to a very low quantum yield of luminescence. In the case of coordination compounds the much more likely the process of excitation of the electronic system of the ligand environment (chromophore) is realized, followed by transfer of excitation energy to the emitting metal center (antenna effect). From this standpoint, the selection of appropriate ligands, which are effective sensitizers of lanthanide luminescence and form thermodynamically stable complexes, is especially important.

The development of film luminescent materials is one of the priorities of the novel technologies. The chromophores belonging to the polymers of different nature and controlled by optimal concentrations of the lanthanide ions chemically bounded with the surface are of particular interest. Lanthanide coordination compounds with O, O'-chelating sulfamide acido-ligands and N, N-chelating neutral additional ligands are promising model systems for such tasks.

In present work, the results of mass-spectrometric studies of the coordination

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compound of europium(III) with the ligand *N*-{*bis*[methyl(phenyl)amino]phosphoryl}benzenesulfoneamide («ligand – antenna») selected as a model have been presented.

The different methods of soft ionization such as matrix activated laser desorption/ionization (MALDI), its modifications – LDI (laser desorption ionization) and GALDI (graphite activated laser desorption/ionization) are widely employed for the investigation of complexes [7–9]. These methods allow us to get the information about the composition of complex (stoichiometric ratio of the components), to estimate the nature and stability of the complex particle and the character of intramolecular bonds due to analysis of the fragments and associates.

The main preference of the «soft ionization» methods is the possibility of unfragmented ions registration. On the other hand, the TPD MS quantifies the changes in some physical and chemical characteristics of the complexes at the thermolysis, which give an idea about the features of their structure. Thus, a combination of MALDI and MS TPD methods provides fairly complete information about the properties of substances.

APPARATUS AND INSTRUMENTS

IR spectrum was recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer over the frequency range 4000–400 cm^{-1} (KBr pellets). ^{1}H, ^{31}P NMR spectra were recorded on a Varian AMX 400 spectrometer with frequencies 400 MHz for ^{1}H and 162.1 MHz for ^{31}P respectively in deutero- dimethylsulfoxide solution. As an internal standard tetramethylsilane was used and as external standard 85 % orthophosphoric acid in D_2O was used. The X-ray diffraction patterns were obtained with a DRON-3 diffractometer (CuK_α radiation).

MALDI TOF. Mass analysis was performed by the method of laser desorption/ionization in linear mode for positive ions on a Autoflex II (Bruker Daltonics, Germany) mass spectrometer with nitrogen laser (λ = 337 nm).

Samples were prepared for laser desorption mass analysis as follows: 1 mg of complex was dissolved in 1 ml of methanol. Small aliquots of mixture were applied to the steel probe tips and dried. Spectra were obtained for the mass range 50 to 2 000 a.m.u. by summing the data of 100 laser shots. Processing of the data was performed by the software FlexAnalysis (Bruker Daltonics, Germany).

TPD MS. Investigation of the thermolysis was performed by temperature-programmed desorption mass spectrometry (TPD MS) on a monopole mass analyzer MX-7304A (Sumy, Ukraine) equipped for the ionization of gaseous samples by electron impact and facilities for the programmed heating of the sample and the computer system of registration of mass spectra.

The resolution of the instrument was 1 M at 10 % height, heating rate 10 °C/min, mass range 1–200 Da. The method allows us to determine the thermal stability of systems, both in the thermal desorption and thermal decomposition of bulk sample in the temperature range up to 800 °C.

RESULTS AND DISCUSSION

Preparation of Eu(L)$_3$Phen. The ligand and its sodium salt were synthesized as reported in literature [10] with some modification. NaL (3 mmol) was dissolved in 5 ml of 2-propanol and was added to a solution of 1.10-phenanthroline (1 mmol) in 2 ml of 2-propanol. The mixture was poured into a solution of $Eu(NO_3)_3{\cdot}5\,H_2O$ (1 mmol) in 5 ml of 2-propanol. The precipitated $NaNO_3$ was filtered off and kept undisturbed during a few days, until crystals were formed. The yield was 87 %. The single-crystals were obtained from 2-propanol. To identify the impurities in the crystal powder, the X-ray diffraction patterns method have been used.

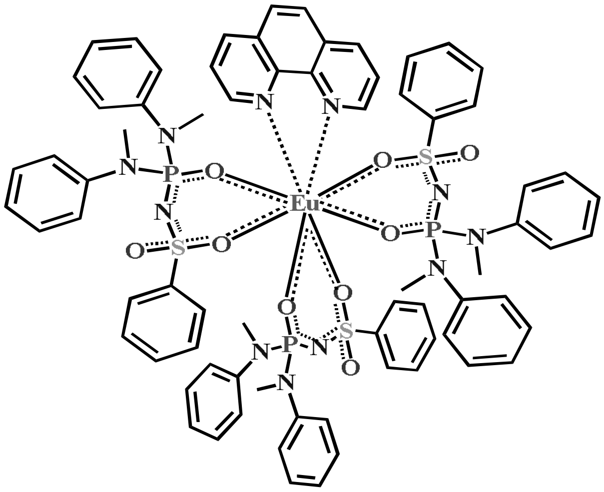


Fig. 1. Schematic representation of the neutral europium(III) complex based on phosphorosulfamidic type ligand

MALDI TOF. Method of laser desorption/ionization – 'soft' ionization method is more useful for identification of non-covalent complexes. This method allows us to generate unfragmented molecular ions for the respective determination of the complex composition. But in our case the mass spectra do not content the molecular ion peak (calculated mass for the complex under consideration is equal to 1575 Da).

In the mass spectra of the complex (Fig. 2) there are peaks which can be refer to the fragments with different ratio of europium/metal/phenantroline and their short-lived adducts with alkali metals ions (Na^+ and K^+) and water molecules formed in gaseous phase. Experimental values and theoretically calculated mass of the core fragments are presented in Table.

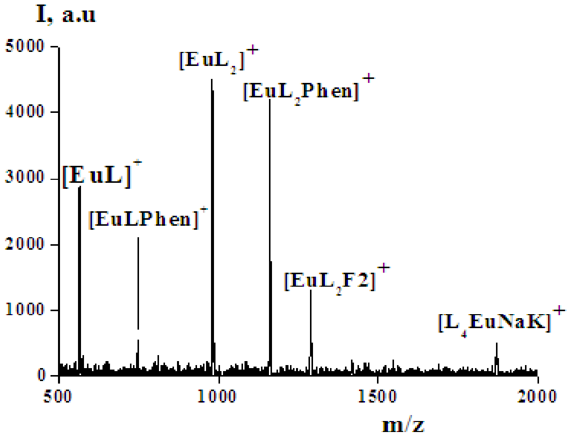
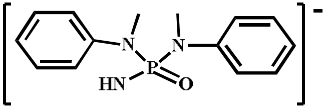
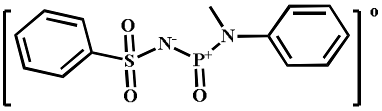


Fig. 2. Representative mass spectrum of europium(III) complex under consideration

Table. Fragmentation of europium(III) complex under conditions of MALDI ToF mass spectrometric experiment in the linear mode of positive ions

Fragment	Theoretical values, Da	The experimental mass values, m/z
$[EuL]^+$	567.0	566.6
$[EuLPhen]^+$	746.6	746.5
$[EuL_2]^+$	980.8	979.9
$[EuL_2Phen]^+$	1161.0	1160.4
$[EuL_2F2]^+$	1288.1	1287.3
$[EuL_4 NaK]^+$	1871.2	1869.5

The highest relative intensities have two series of peaks 566.6, 746.5, 979.9 m/z and 1160, 1287.3 m/z, which correspond to fragments of $[EuL]^+$, $[EuLPhen]^+$ and $[EuL_2]^+$, $[EuL_2Phen]^+$, $[EuL_2F_2]^+$, respectively. Also, in the mass spectrum there is a peak corresponding to the $[EuL_4NaK]^+$ fragment. These fragments are the most stable under mass spectrometry experiment conditions.

The low-intensity peaks with m/z 1019.1, 1418.4, 1435.0, 1454.6, 1457.8, 1547.7, 1959.8 were also detected in the mass spectrum. These peaks correspond to the following fragments: $[EuLPhenF1]^+$, $[EuL_3Na]^+$, $[EuL_2PhenF1]^+$, $[EuL_2PhenF1+H_2O]^+$, $[EuL_2PhenF1Na]^+$ (last three fragments are the most similar to the molecular ion composition), and $[Eu_2L_3]^+$, $[Eu_2L_4]^+$, where F1 – a fragment of the ligand with the structure  and F2 – a fragment of the ligand with the structure , respectively.

Low ionization capability of the formed fragments leads to low intensity of the respective peaks.

TPD MS. Investigation of thermolysis process of the complex studied allows us to conclude that the emission of volatile products occurs in three stages. In the first stage, at temperatures up to 200 °C, a cleavage of the ligand terminal fragments has been observed in the mass range from 28 to 65 Da.

When the temperature reaches 200 °C, in the temperature interval 200–400 °C, fragments with mass numbers 77, 93, 106 m/z are detected, as it is shown in Fig. 3. Characteristic feature of all those fragments are their synchronous appearance in mass spectra, with invariable ratio of signal intensities. Two maxima of thermally stimulated evolution of decomposition products are distinctly observed in thermograms, with maxima located at approximately 260 and 340 °C.

Thermal decomposition of the ligand is illustrated by the scheme presented in Fig. 3.

The attention is to be paid to the fact that evolution of fragments occurring at the low temperature stage of thermolysis in our experiments was observed in wider temperature range than those observed at high temperature.

Such behavior of fragments evolution testifies in favor of discrepancy of activation energy distribution usually observed in thermal desorption and thermal decomposition on the surface of the support, whereas narrow temperature interval points at presence of cooperative effects typical for bulk co-ordination compounds [11, 12].

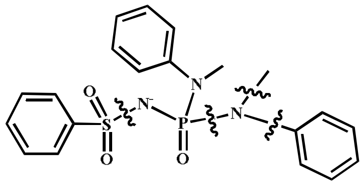


Fig. 3. Possible pathways of thermal bond rupture of the complex

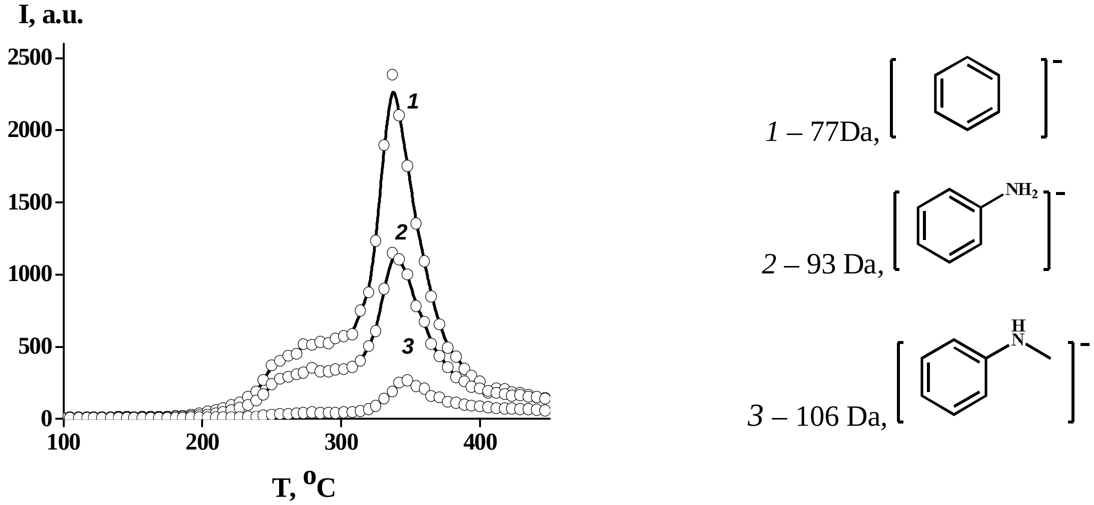


Fig. 4. Characteristic thermograms of europium(III)-containing complex decomposition (*1* - 77 Da, *2* -93 Da, *3* - 106 Da)

Besides, TPD MS data, concerning thermolysis of the ligand, confirm indirectly the assumptions about the decomposition mechanisms of sulfamide ligand coordinated to lanthanides under conditions of laser desorption experiment.

Thus, a possibility of investigation of Eu(III)-containing compounds by combined LDI MS and TPD MS methods has been proposed as an example of complement approach to studies of such complexes.

LDI mass spectra of the complex under investigation has been obtained and interpreted. It has been shown that the absence of molecular ion peaks testifies that the loss of one electron by complex molecule results in destruction of excited molecular ion and formation of positively charged ion-fragments which intensity probably corresponds to that of molecular ions in mass spectra.

Characteristic thermograms of europium(III) complexes have been obtained and it has been shown that thermal decomposition of the compound occurrs in two stages, which correspond to certain type of intermolecular interactions.

Лазерна десорбція/іонізація (ЛДІ МС) і термо десорбційна мас-спектрометрія (ТПД МС) координаційної сполуки європію(III) з N-{*bis* [метил(феніл)аміно]фосфорил}бензенсульфонамідом

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Синтезовану координаційну сполуку EuL_3Phen (де L^- = N-{bis [метил(феніл)аміно]фосфорил}-бензенсульфонамідний аніон) в конденсованій фазі та на поверхні стандартної металевої підкладки досліджено методами температурно-програмованої та лазерно-десорбційної мас-спектрометрії. Визначена та інтерпретована температурна залежність основних компонент одержаних мас-спектрів в методі термопрограмованої десорбційної мас-спектрометрії (ТПД МС), ідентифіковано компоненти мас-спектра, одержаного методом лазерної десорбції/іонізації (ЛДІ) синтезованої речовини.

Проведено порівняльний аналіз мас-спектрів, одержаних обома методами, та обговорено можливості їх застосування для дослідження компонентів металовмісних полімерів.

***Ключові слова**: лазерна десорбція/іонізація (ЛДІ МС), температурно-програмована десорбційна мас-спектрометрія (ТПД МС), лантаніди, фосфорильні ліганди*

Лазерная десорбция/ионизация (ЛДИ МС) и термодесорбционная масс-спектрометрия (ТПД МС) координационного соединения европия(III) с N-{*bis* [метил(фенил)амино]фосфорил}бензенсульфонамидом

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Синтезированные координационные соединения EuL_3Phen (где L^- = N-{bis [метил(фенил)амино] фосфорил}бензенсульфонамидный анион) исследованы в конденсированной фазе и на поверхности стандартной металлической подложки методами температурно-программируемой и лазерно-десорбционной масс-спектрометрии. Определена и интерпретирована температурная зависимость основных компонентов полученных масс-спектров в методе термопрограммированной десорбционной масс-спектрометрии (ТПД МС), идентифицированы компоненты масс-спектра, полученного методом лазерной десорбции/ионизации (ЛДИ) синтезированного вещества.

Проведен сравнительный анализ масс-спектров, полученных обоими методами, и обсуждены возможности их применения для исследования компонентов металлосодержащих полимеров.

***Ключевые слова**: лазерная десорбция/ионизация (ЛДИ МС), температурно-программированная десорбционная масс-спектрометрия (ТПД МС), лантаниды, фосфорильные лиганды*

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