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LASER DESORPTION/IONIZATION (LDI MS) OF POLYMERIC SILVER(I) COORDINATION COMPOUND BASED ON N-[BIS(DIETHYLAMINO)PHOSPHORYL]-BENZENESULFONAMIDE

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The polymeric coordination compound $(AgL)_n$ (where $L^- = N\text{-}\{bis[diethylamino]phosphoryl\}benzenesulfonamidate$ anion) has been synthesized and studied by laser-desorption spectrometry. The components of the laser desorption/ionization (LDI) mass spectrum of the synthesized coordination compound has been identified. It has been shown that ionization of $(AgL)_n$ is accompanied by protonation of fragments and associates.

Keywords: laser desorption/ionization (LDI MS), silver(I), sulfonamidophosphates

INTRODUCTION

The ampolydentate sulfonylamido-phosphate (SAPh) ligands – compounds, containing the –S(O)₂N(H)P(O)– core, have been proved to be very powerful ligands for the construction of various coordination compounds [1, 2]. Furthermore, some of SAPh containing complexes have potentially useful electrochemical, magnetic, catalytic properties, which may be introduced for the creation of polyfunctional luminescent materials [3, 4]. Polymeric silver complex $(AgL)_n$ (where $L^- = N\text{-}\{bis[diethylamino]\text{-phosphoryl}\}$ benzenesulfonamidate anion) is attractive due to its interesting luminescent properties [5]. On the other hand, novel transition metal complexes may be used as metal containing drugs for their application in different types of therapy [6].

An analysis of those compounds may be carried out by mass spectroscopy (MS) of «soft ionization» techniques, such as MALDI (matrix-assisted laser desorption/ionization) and its variations (LDI, laser desorption/ionization, for example).

Traditional ionization methods, such as EI (electron impact ionization), were not applicable due to intensive fragmentation of molecules studied [7]. In present work, the results of MS study of synthesized compound allow to estimate its capability to associate with different hydrocarbonaceous fragments of ligands and its

affinity to alkaline metals in «traumatic» conditions of MS experiment. Thus, analysis of results obtained provides additional information about the structure and properties of polymeric complex under investigation.

APPARATUS AND INSTRUMENTS

The sample was prepared for the MALDI-TOF analysis as follows: 1 mg of studied complex was dissolved in 1 ml of acetonitrile. Aliquots of mixture were applied to the steel tips and dried.

MS analysis was performed by the method of laser desorption/ionization on an Autoflex II (Bruker Daltonics, Germany) mass spectrometer with nitrogen laser ($\lambda = 337$ nm). Experiments were carried out in reflectron mode for positive ions in the mass range 50 to 2000 a.m.u. Resulting mass spectra were obtained by assuming the data of 150 laser shots and processing by the software FlexAnalysis (Bruker Daltonics, Germany).

IR spectrum was recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer over the frequency range 4000–400 cm^{-1} (nujol mull or KBr pellets). The X-ray diffraction patterns were obtained with an Xcalibur-3 diffractometer (graphite monochromator, MoK_α radiation).

RESULTS AND DISCUSSION

Preparation of $(AgL)_n$. The syntheses of ligand HL and its sodium salt NaL were carried out according to the modified literature procedure [8]

(diethylamine was used instead of aziridine). AgNO_3 (0.097 g, 0.56 mmol) was dissolved in 10 ml of acetonitrile and then added to 10 ml of NaL solution (0.21 g, 0.56 mmol) in *i*-PrOH. After 30 min the precipitate of NaNO_3 was filtered and washed by small amount of acetonitrile. The resulting clear solution was left for crystallization in a dark vacuum desiccator over CaCl_2 . The colorless crystals of $(\text{AgL})_n$ were collected after several days. The complex is light sensitive. IR for $(\text{AgL})_n$ (nujol mull, $\nu \text{ cm}^{-1}$): 1150 (PO); 1270, 1090, 1060 (SO_2), for HL (KBr, $\nu \text{ cm}^{-1}$): 1222 (PO); 1323, 1177 (SO_2), for NaL (KBr, $\nu \text{ cm}^{-1}$): 1130 (PO); 1210, 1040, 1075 (SO_2). The IR spectra of the sodium salt NaL and $(\text{AgL})_n$ reveal shifts of the characteristic stretching vibrations in comparison with the neutral ligand HL which indicate a significant delocalization of π -electron density in the SO_2NPO fragment ($\Delta\nu_{\text{as}}(\text{SO}_2) = 50\text{--}115 \text{ cm}^{-1}$, $\Delta\nu_{\text{s}}(\text{SO}_2) = 50\text{--}120 \text{ cm}^{-1}$ and $\Delta\nu(\text{P}=\text{O}) = 80\text{--}120 \text{ cm}^{-1}$) [9, 10].

X-ray diffraction study was carried out for $(\text{AgL})_n$. The complex has a polymeric structure (Fig. 1). The ligand is coordinated to the two Ag^+ ions in the tridentate bridging manner. As a result, one-dimensional polymeric chains are formed in complex $(\text{AgL})_n$: the ligand is coordinated to the Ag^+ ion in the bidentate manner *via* the oxygen atoms of sulfonyl and phosphoryl groups with an additional bridging coordination *via* the nitrogen atom to the neighboring Ag^+ ion.

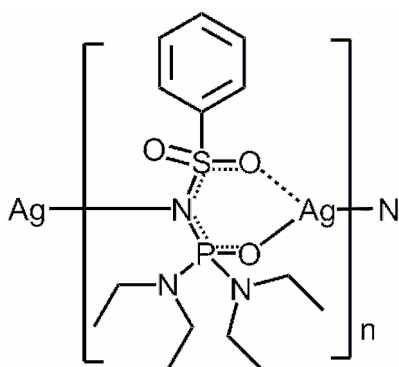


Fig. 1. Schematic representation of the polymeric coordination $\text{Ag}(\text{I})$ complex based on *N*-{bis[diethylamino]phosphoryl}benzenesulfonamide ligand

The fragment of mass spectrum of complex $(\text{AgL})_n$ in mass range from 650 to 900 Da is presented in the Fig. 2.

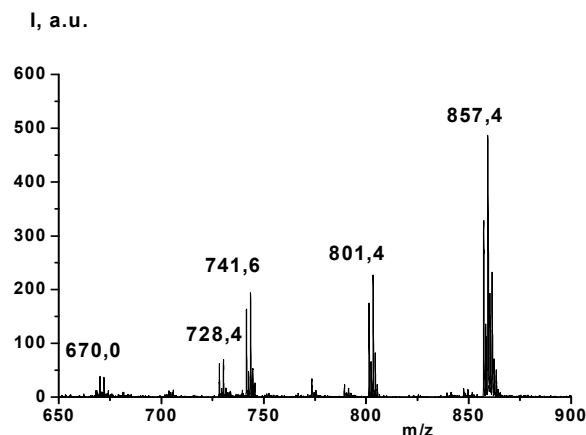


Fig. 2. Representative fragment of mass spectrum of studied complex under consideration in mass range 650–900 Da

In the general mass spectra of the complex, a series of peaks with masses from 348.4 to 389.4 Da with a pitch 14 Da ($-\text{CH}_2-$), according to cation-radical of ligand $([\text{HL}]^+)$ and their derivatives are presented. The next series of peaks are presented in mass range from 437.4 to 465.5 Da and belong to silver-containing fragments whereas the peak with mass 454.2 m/z corresponds to base unit ionized of proclaimed compound $([\text{AgL}]^+)$. The peaks with masses 493.5 and 517.5 m/z accord to adducts of AgL with alkaline metal ions (K^+ and Na^+) corresponding to formulae $([\text{AgLK}]^+)$ and $([\text{AgLKNa}]^+)$ (Fig. 3). The formation of such associates is characteristic for various classes of coordination compounds [11, 12].

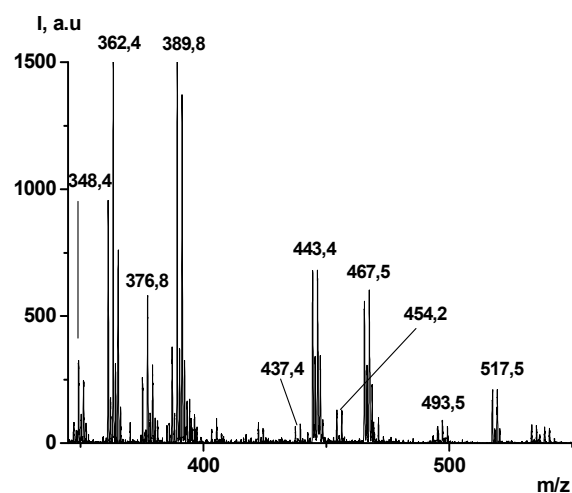


Fig. 3. Representative fragment of mass spectrum of studied complex under consideration in mass range 345–500 Da

According to various ionized associates of ligand and silver ($[\text{Ag}_3\text{L}]^+$ with mass value 670 m/z ; $[\text{AgL}_2]^+$ with mass value 801.1 m/z and its fragments with masses 728 and 741 m/z peaks are observed as well as peaks with low intensity according to its associates with K^+ and Na^+ ; $[\text{Ag}_4\text{L}]^+$ with mass 775 m/z and the most intensive peak with mass 857.4 m/z $[\text{Ag}_4\text{LK}_2]^+$) (see Table).

Thus, interpreted peaks show that ionization of complex is accompanied by protonation of fragments and associates. This fact allows to assume high proton affinity in gas phase for the complex under investigation.

Presence of the fragments with various amount of silver atoms, as well as ligand molecules, can be

explained by polymeric structure of complex studied $(\text{AgL})_n$.

Table. Fragmentation of silver complex under conditions of LDI mass spectrometric experiment in reflectron mode of positive ions

Fragment	Theoretical values, Da
$[\text{Ag}_3\text{L}]^+$	670.0
$[\text{Ag}_4\text{L}]^+$	775.1
$[\text{AgL}_2]^+$	801.4
$[\text{Ag}_4\text{LK}_2]^+$	857.4

Besides, it can be note like a peculiarity of complex studied to form adducts with alkaline metals of various structure under MS experiment conditions; this fact testifies in favor of its high ion – acceptor properties in gas phase.

Лазерна десорбція/іонізація (ЛДІ МС) полімерної координаційної сполуки срібла(I) на основі N-*бис*[диетиламіно]фосфорил}бензенсульфонаміду

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Синтезовану полімерну координаційну сполуку $(\text{AgL})_n$ (де $\text{L}^- = \text{N-}\{бис[диетиламіно]фосфорил\}$ бензенсульфонамідний аніон) на поверхні стандартної металевої підкладки досліджено методом лазерно-десорбційної мас-спектрометрії. Ідентифіковано компоненти мас-спектра, одержаного методом лазерної десорбції/іонізації (ЛДІ) синтезованої речовини. Було показано, що іонізація супроводжується протонуванням фрагментів та асоціатів.

Ключові слова: лазерна десорбція/іонізація (ЛДІ МС), срібло(I), сульфониламідфосфат

Лазерная десорбция/ионизация (ЛДИ МС) полимерного координационного соединения серебра(I) на основе N-*бис*[диэтиламино]фосфорил}бензолсульфонамида

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Синтезированное полимерное координационное соединение $(\text{AgL})_n$ (где $\text{L}^- = \text{N-}\{бис[диэтиламино]фосфорил\}$ бензолсульфонамидный анион) исследовано на поверхности стандартной металлической подложки методом лазерно-десорбционной масс-спектрометрии. Идентифицированы компоненты масс-спектра, полученного методом лазерной десорбции/ионизации (ЛДИ) синтезированного вещества. Было показано, что ионизация сопровождается протонированием фрагментов и ассоциатов.

Ключевые слова: лазерная десорбция/ионизация (ЛДИ МС), серебро(I), сульфониламидфосфат

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