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ARTICLE TYPE

Studies of the complexation behavior of tetramorpholinyl-PNP-lariat ether with Ag(I), Ca(II), Cd(II), Cu(II) and Pb(II) by Electrospray Ionization Mass Spectrometry

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In this publication the cationic metal complexes of tetramorpholinyl-PNP-lariat ether have been studied by electrospray ionization mass spectrometry (ESI-MS). The tandem mass spectra (MS/MS) of these complexes have also been tested to evaluate the stability of the different types of the complexes formed. As occurred each of the selected metal cations forms, with the investigated ligand, the complex with the stoichiometry equal 1:1. Only silver ions create a “sandwich” type complex. Furthermore the divalent cations form complexes with the nitrate anion adduct. In the case of Ca(II), Cd(II) and Pb(II) we also observed another type of the species with additional water molecule attached to the parent complex.

Introduction

Electrospray ionization mass spectrometry (ESI-MS)¹⁻⁴ is currently an effective tool for analysis of a wide variety of noncovalent complexes⁵⁻¹⁶, such as those formed in host-guest chemistry. Many studies show that equilibrium distribution of complexes in solution is reflected in the intensities of host-guest complexes observed in the ESI mass spectra¹⁷⁻²³. ESI-MS analysis enables us to direct determination of the complexes formed in the solution, as well as to study the equilibrium states, carry out quantitative analysis of stability constants or evaluation of the binding selectivities²⁴⁻³⁹. This method is considered to be a „soft ionization” process (involving transfer of solution ions into the gas phase), and therefore typically yields molecular ions with little or no fragmentation at all. The simplicity of spectra obtained by this technique is of great benefit. Conventional techniques such as infrared spectroscopy, X-ray diffraction and NMR have several drawbacks. The use of ESI-MS for studying metal-ligand interactions and metal complexes is readily recognized. The MS is more sensitive than conventional techniques and opens up the possibility to screen the complex samples. Moreover, MS enables simultaneous monitoring of the response of ligand-exchange reactions and additionally obtaining chemical information about the specific compound. Furthermore, ions generated by the electrospray ionization process can be easily fragmented using techniques such as tandem mass spectrometry (MS/MS). In this method, an ion (called precursor ion) is selected on the basis of the first stage of MS measurements and activated to produce fragment ions which are then analysed in the second stage of MS^{40, 41}. ESI-MS can provide important information concerning the structure, stoichiometry, and metal oxidation state of dissolved metal complexes^{42, 43}.

Macrocyclic ligands built on a cyclotriphosphazene ring are compounds which bind cyclophosphazene chemistry with macrocyclic chemistry. The combination of these two fields gives the compounds which have high possibility of modification of their structure through the nucleophilic substitution reaction, polycondensation or creation of possible binding centres for cations, anions or neutral species. In this way, the design of various compounds with potential practical use can be realized. Lariat ethers are derived from the group of crown ethers having a side chain attached to the crown moiety by the so-called pivot atoms (C, N or P). The sidearms contain atoms or groups with a lone pair of electrons that can cooperate with the heteroatom's electrons from the macrocyclic ring, thus providing a three-dimensional coordination of the guest cation⁴⁴⁻⁴⁶. Three types of lariat ethers are known depending on the atom to which the side arm is attached: C- (carbon-pivot lariat ethers)⁴⁷⁻⁴⁹, N- (nitrogen-pivot lariat ethers)^{50, 51} or P- (phosphorus-pivot lariat ethers)⁵². The object of the presented publications is the P-pivot lariat ether derivative. This compound is derived from the group of reactive crown ethers which was formed by incorporation of a chloro-substituted cyclotriphosphazene unit into the macrocyclic polyether skeleton to give mono- and bis-cyclosubstituted derivatives⁵³. By substitution of the reactive chloride substituents with various nucleophiles we can obtain a whole series of PNP-lariat ethers. There are known PNP-lariat ether derivatives substituted with different amines⁵⁴⁻⁵⁸ and sodium arylates⁵⁹⁻⁶⁰. These compounds exhibit very good abilities toward complexation. Due to the presence of the binding sites in the form of both oxygen and nitrogen donor atoms, these ligands form stable complexes with alkali metals and alkaline earth metal cations as well as transition metal cations^{61, 62}. Macrocyclic derivatives of cyclotriphosphazenes and their complexes are recognized as compounds of proven antitumor

activity⁶³ as well as anti-AIDS activity⁶⁴. Anti-proliferative activity may be modified by the formation of complexes with metal ions. These types of compounds form selective bindings with silver ions⁶⁵⁻⁶⁶. Additionally, recent investigations showed that silver compounds exhibit antibacterial properties⁶⁷. It has been proved that the thio-substituted PNP-lariat ethers are commonly used to remove highly toxic heavy metal pollutants and for recovery of silver from the industrial wastes⁶⁸. Complexing abilities of these compounds give the possibility of modelling biological systems, in which sulphur-organic compounds are involved⁶⁹⁻⁷⁰. The PNP-crown amino ethers can be potentially useful as "pH-controlled active ion carriers" in liquid membranes⁷¹. However bis-PNP-lariat ethers were found to behave as efficient ion carriers for heavy metal (Zn^{2+} , Cd^{2+} , Pb^{2+}) transport carriers across polymer inclusion membranes, in particular for lead (II), due to the formation of "sandwich" type complexes with the macrocyclic compounds⁷².

In the present paper we report the ESI-MS studies of the tetramorpholinyl-PNP-lariat ether complexes with Ca (II), Ag (I), Cd (II), Cu (II) and Pb (II) ions. The tandem mass spectra (MS/MS) of these complexes were also examined to evaluate the stability of the different complex types. The tetramorpholinyl-PNP-lariat ether has a few structural units with the potential ability to take part in binding of metal cations: the polyether oxygen donors of the macrocyclic PNP-crown skeleton, the endocyclic nitrogen atom of the cyclotriphosphazene ring and the exocyclic nitrogen atoms and oxygen donor atoms of the morpholinyl substituents. This ligand is capable of complexing „hard” and „soft” cations.

Experimental

Synthesis

The synthesis of tetramorpholinyl-PNP-lariat ether has been previously reported⁶⁵. The investigated ligand is presented in Fig.1.

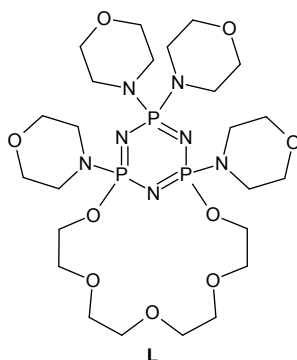


Fig.1 Investigated ligand L

Materials

$AgNO_3$ (Sigma Aldrich), was used as received. Nitrates of Ca(II), Cd(II), Cu(II) and Pb(II) were purchased from POCh Gliwice and used without further purification.

Methanol (HPLC - grade) was purchased from J.T. Baker (POCh Gliwice) and used without purification.

Stock solutions of the ligand and metals salts in methanol (10^{-3} M

each) were prepared prior to dilution to 10^{-4} M for mass spectrometric investigation (ligand/metal salt ratio 1:1). In each case freshly prepared solutions were used.

Instrumental methods

ESI-MS and MS/MS were recorded using a Varian 500-MS LC ion-trap mass spectrometer (Palo Alto, CA, USA). Whole sample was introduced into ESI-MS source by continuous infusion by means of the instrument syringe pump at a rate of $10 \mu l \text{ min}^{-1}$. The ESI-source was operated at 5.00 kV and the capillary heater was set to $300 \text{ }^\circ\text{C}$. The cone voltage was set within the range 40-260 V. Scanning was performed from $m/z = 100$ to 1500. For fragmentation experiments, mass-selected monoisotopic molecular ions were isolated in the ion trap and collisionally activated using helium damping gas present in the mass analyser as a collision gas. The experiments were performed in positive ion-mode.

Results and discussion

The ESI-MS spectrum of L revealed the presence of the protonated molecule, at m/z 672.6, and a less abundant ion corresponding to the Na^+ adduct of the parent compound Fig.2.

ESI-MS fragmentation analysis of L is shown on Scheme 1. In the first step we observed the loss of morpholinyl substituent ($m/z = 585.4$), probably from the exomacrocyclic P atom. Such behaviour for tetrapyrrolidiny cyclophosphazene derivative was described previously⁶². There were also whole substituents loss observed without the cleavage of the ring. In the following steps the loss of successive fragments of the polyether chain was noticed. After detachment of the two $-OCH_2CH_2$ fragments we observed two concurrent fragmentation patterns. First involved a stepwise loss of one morpholinyl substituent ($m/z = 412.2$) and subsequent $-OCH_2CH_2$ group ($m/z = 368.2$). The second one showed two major fragment ions with $m/z = 453.3$ due to the loss of $-OCH_2CH_2$ moiety and with $m/z = 368.2$ caused by the loss of morpholinyl substituent. In the last stage splitting-off of the third morpholinyl substituent is observed.

The ESI mass spectra of the mixture of L with metals ions (Ca, Ag, Cd, Cu and Pb) indicate the presence of many different forms of coordination compounds. The experiments were done using nitrate salts because the stability constants of the investigated ligand with silver (I) ions (with nitrate as counter ions) had been reported earlier in the literature⁶⁵. The resulting complexes were presented in Table 1. As occurs from the analysis of mass spectra - all the metal ions (apart from of calcium ion) are bounded with the endocyclic nitrogen atom. The nitrogen atom build-in the structure of the polyether is representing „soft” electron donor place to which the „soft” transition metals cations as well as heavy metals cations are preferably bound. The oxygen atoms from crown ether moiety are „hard” donors having the affinity toward „hard” cations of I and II group of the periodic table of elements⁷³.

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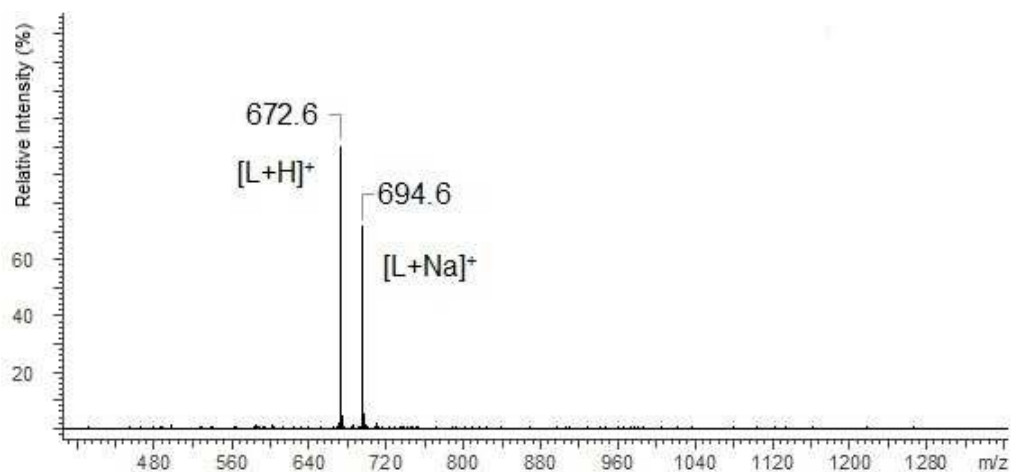
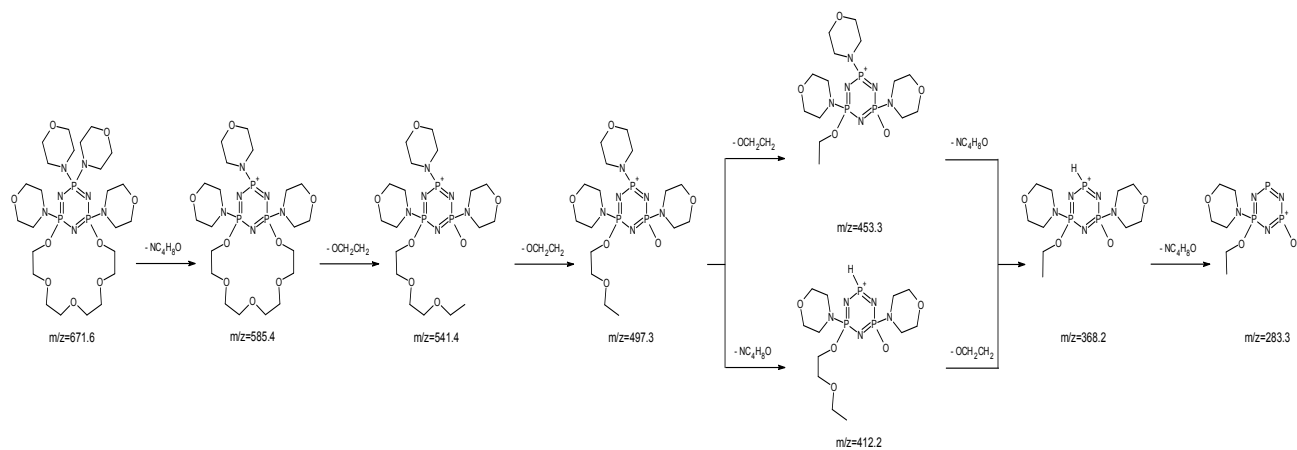


Fig.2 The mass spectrum of investigated ligand L



Scheme 1. Fragmentation pattern of the free ligand.

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Table 1. Positive ion ESI-MS data for the complexes

| Metal salt | Ions (m/z) |
|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| AgNO ₃ | [Ag(I)L] ⁺ (778.5) [Ag(I)L ₂] ⁺ (1449.7) |
| Ca(NO ₃) ₂ | [Ca(II)L] ²⁺ (355.7) [Ca(II)L+NO ₃] ⁺ (773.5) [Ca(II)L+OH] ⁺ (728.5) |
| Cu(NO ₃) ₂ | [Cu(I)L] ⁺ (734.6) [Cu(II)L] ²⁺ (367.3) [Cu(II)L+NO ₃] ⁺ (796.5) |
| Cd(NO ₃) ₂ | [Cd(II)L] ²⁺ (392.8) [Cd(II)L+NO ₃] ⁺ (847.6) [Cd(II)L+H ₂ O] ⁺ (802.5) |
| Pb(NO ₃) ₂ | [Pb(II)L] ²⁺ (439.8) [Pb(II)L+NO ₃] ⁺ (941.6) [Pb(II)L+H ₂ O] ⁺ (896.6) |

The mass spectrum of L with AgNO₃ was dominated by the [Ag(I)L]⁺ complex. Among other investigated metal ions only the silver ion form a „sandwich” type complex with two molecules of the ligand (peak at m/z=1449.7). The interesting fact about the system with Ag(I) ion was no signal of the uncomplexed ligand (no peak at m/z = 672.6), what probably may confirm the very strong binding of silver ions by the investigated ligand. The complexes of AgL and AgL₂ type obtained during the ESI-MS measurement are in accordance with the results obtained by potentiometric method⁶⁵. Divalent cations form complexes with the nitrate anion or with water molecule attached to parent compound, such behaviour was observed for Cd (II), Pb (II) and Ca (II) ions. For the complexes with divalent cations, the loss of one counter ion (NO₃⁻) seems to be the predominated ionization process. The ESI-MS spectra of L with Cd(II), Cu(II) and Pb(II) show the presence of [Cd(II)L]²⁺, [Cu(II)L]²⁺ and [Pb(II)L]²⁺ complexes. The relative intensity of these complexes were very

low (RI<5%). The situation is different in the case of calcium ion - because in this case the formed [Ca(II)L]²⁺ complex exhibit much higher relative abundance of 31%.

In the case of copper ion due to the measurement conditions we observed the reduction process Cu(II) → Cu(I). This type of process is a phenomenon observed in ESI⁷⁴⁻⁷⁷ and is usually not an electrochemical redox reaction. This process can be explained as an electron transfer between a Cu complex and a solvent molecule in the gas phase.

In the case of silver ions we observed two types of complex [Ag(I)L]⁺ and [Ag(I)L₂]⁺ - **Fig.3**. The ESI-MS for [Ag(I)L]⁺ show two main peaks at m/z 778.5 and 780.5, which are expanded in Fig.4 (b), and compared well with the corresponding calculated (Fig.4 (a)) isotope pattern. The isotope patterns in Fig.4 are consistent with a molecular cation containing one silver atom and exhibits the natural intensity ratio for silver isotopes.

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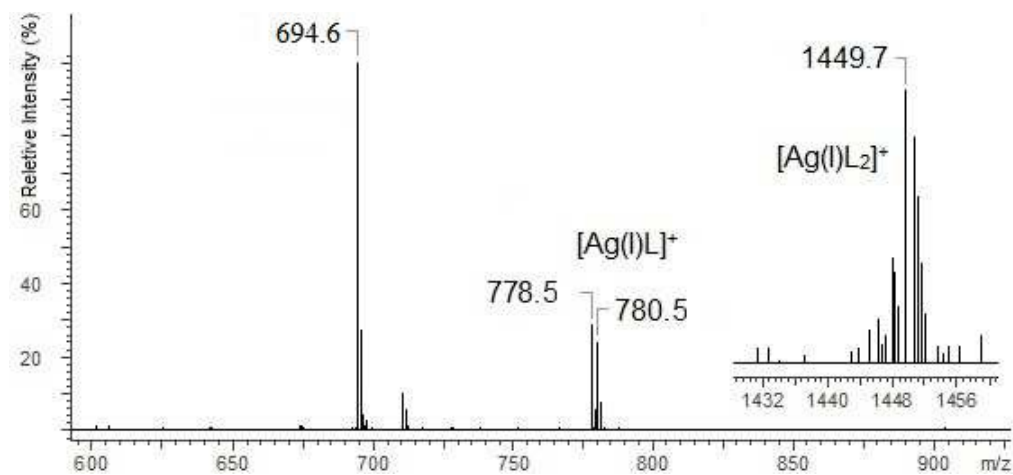


Fig.3 The mass spectrum of L with $AgNO_3$ (the attached fragment of AgL_2 spectrum had $RI < 5\%$)

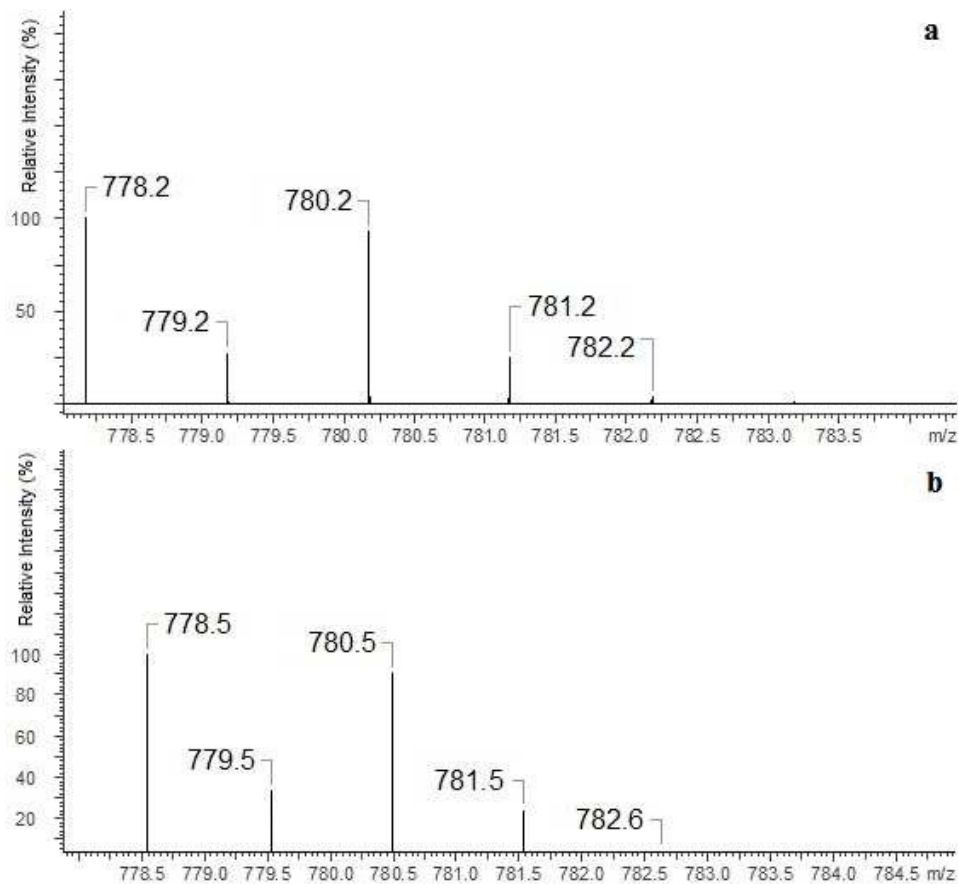


Fig.4 Comparison of the theoretical isotope pattern calculation (a) for $[Ag(I)L]^+$ with the one observed experimentally (b)

We made the fragmentation of the peak $m/z = 778.5$. The fragmentation pattern for $[\text{Ag(I)L}]^+$ show the same fragmentation pattern as in the case of the ligand **Fig.5**. This suggests that

binding of silver ions by the ligand molecule is reasonably strong and complex formed does not completely disintegrate under the influence of ionization process.

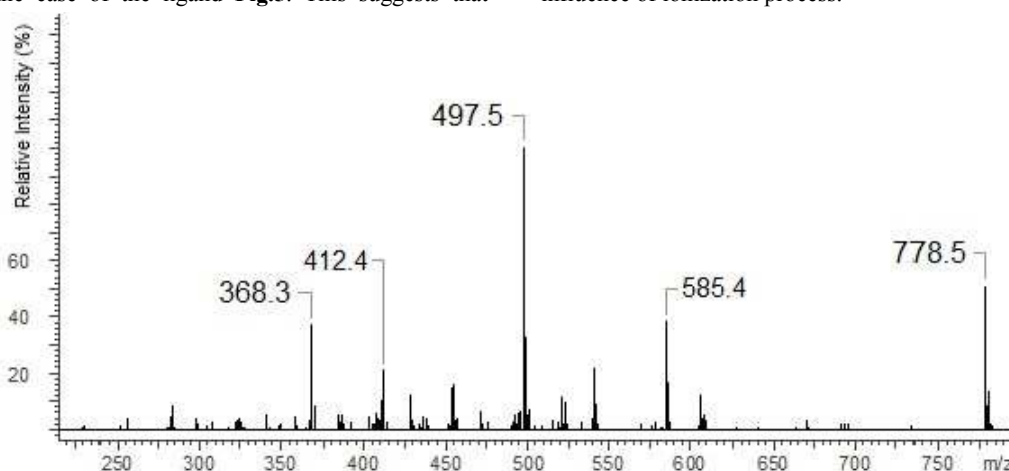


Fig.5 The ESI-MS/MS spectrum of ion $^{107}\text{Ag(I)L}^+$ - $m/z = 778.5$

The ESI-MS of an equimolar mixture of L and $\text{Ca}(\text{NO}_3)_2$ shows three types of complexes: $[\text{Ca(II)L}]^{2+}$, $[\text{Ca(II)L}+\text{NO}_3]^+$ and $[\text{Ca(II)L}+\text{OH}]^+$ (**Fig.6**). The most abundant peak at $m/z 773.5$ is the one corresponding to $[\text{Ca(II)L}+\text{NO}_3]^+$ complex. The ESI-MS/MS spectrum of $[\text{Ca(II)L}+\text{NO}_3]^+$ complex is shown in **Fig.7**. For this complex we observed the loss of nitrate anion and one proton ($m/z = 710.5$). The MS/MS fragmentation analysis of calcium complex revealed at the first stage the loss of one morpholinyl substituent (probably from exomacrocyclic P atom) and $-(\text{CHCH}_2)$ group ($m/z = 597.4$) Then we saw an intense peak at $m/z 552.5$, corresponding to the loss of fragment of the polyether chain $-(\text{OCH}_2\text{CH}_2)$. From this step two concurrent

fragmentation paths were observed. In the first one - two less abundant peaks at $m/z = 465.4$ and $m/z = 406.2$, corresponding to the loss of second morpholinyl group from exomacrocyclic P atom and another fragment of the crown ether ring and H_2O molecule. The second fragmentation pattern involves a stepwise loss of $-(\text{OCH}_2\text{CH}_2)$ and OH moiety to an ion with $m/z 491.4$, followed by losses of morpholinyl substituent to an ion with $m/z 406.2$. These two fragmentation patterns are presented on **Scheme 2**. The region within the peak at $m/z 406.2$, which is expanded in **Fig.8 (b)**, compare well with the corresponding calculated (**Fig.8 (a)**) isotope pattern.

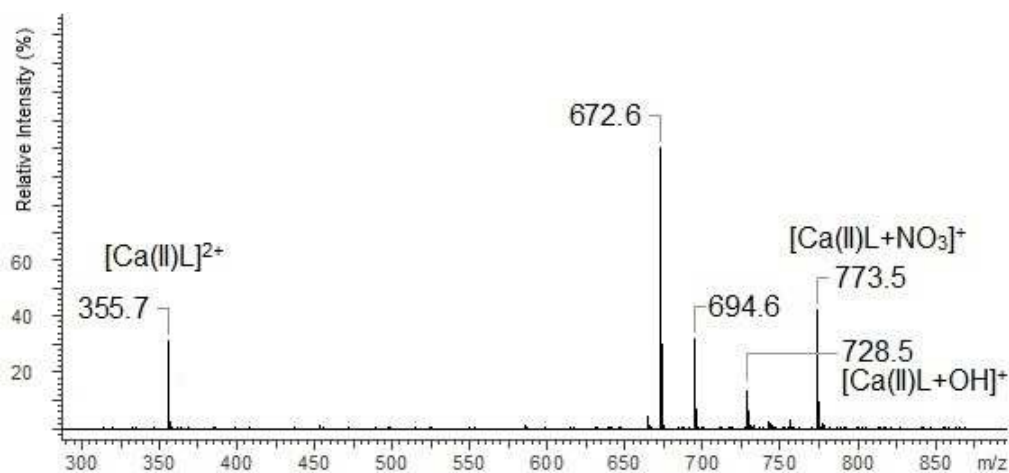
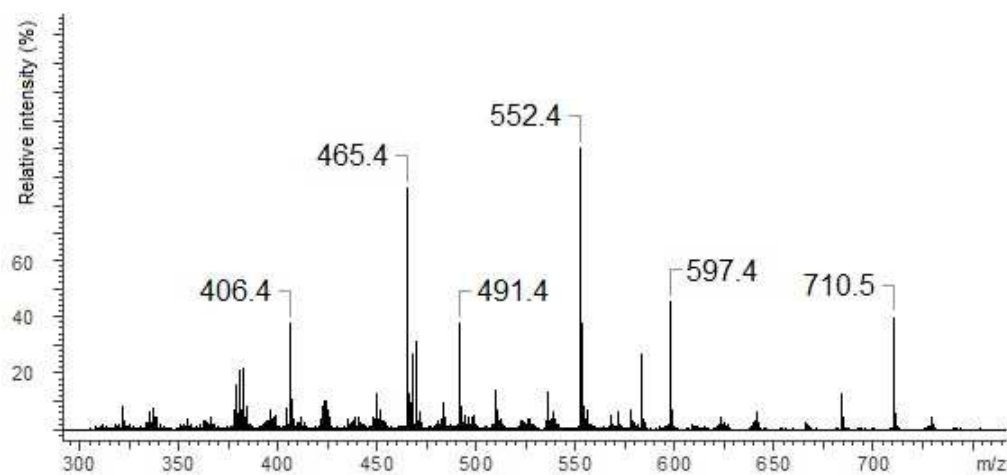
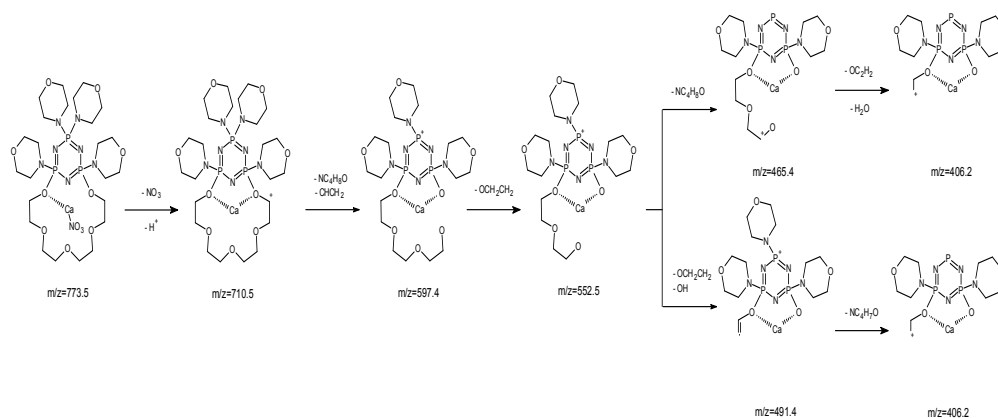


Fig.6 The mass spectrum of L with $\text{Ca}(\text{NO}_3)_2$

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ARTICLE TYPE**Fig.7** The ESI-MS/MS spectrum of ion $[Ca(II)L+NO_3]^+$ - $m/z = 773.5$ **Scheme 2.** Fragmentation pattern of calcium (II) complex

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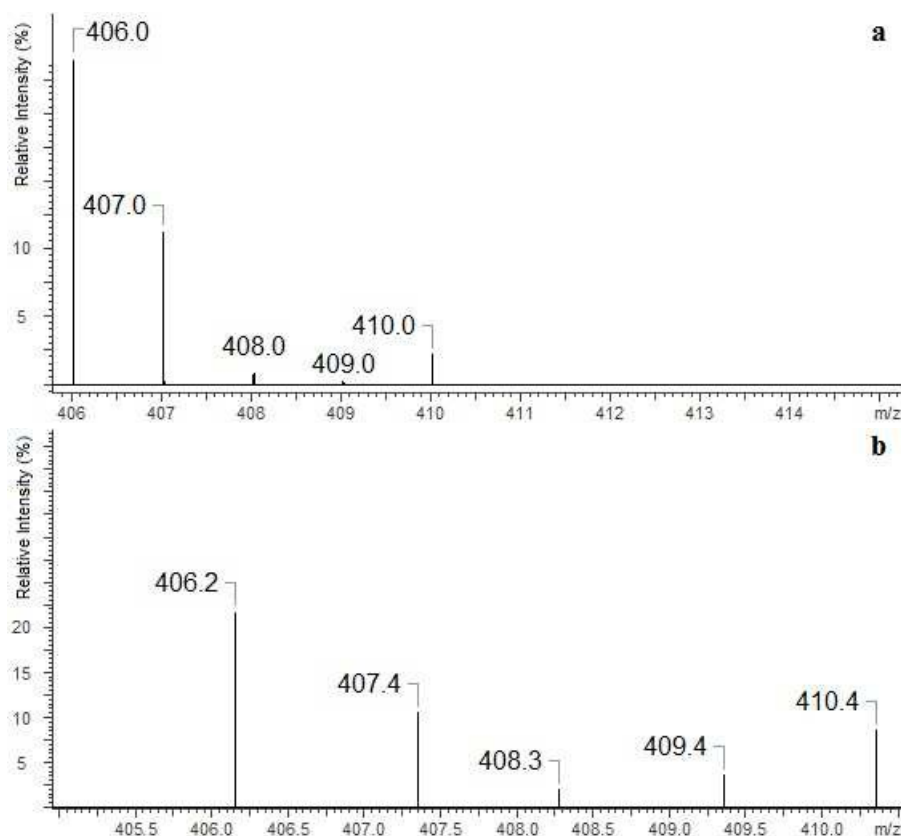


Fig.8 Comparison of the theoretical isotope pattern calculation (a) for calcium complex at m/z = 406.2 with the experimentally observed pattern (b)

5 Additionally the fragmentation of $[\text{Ca}(\text{II})\text{L}+\text{OH}]^+$ complex was checked (Fig.9). In this case we also noticed two fragmentation patterns. At the beginning we observed the loss of $-\text{OH}$ fragment as H_2O molecule (18 Da) to an ion with m/z = 710.5. The most intense peak m/z 684.5 is connected with the loss of $-(\text{C}_2\text{H}_2)$

10 group which was followed by the loss of 44 Da $-(\text{OCH}_2\text{CH}_2)$. The less intense signal (m/z = 666.6) is originated from the loss of $-(\text{OCH}_2\text{CH}_2)$ and that with m/z 640.4 due to subsequent loss of $-(\text{C}_2\text{H}_2)$. The proposal of fragmentation pattern is presented on Scheme 3.

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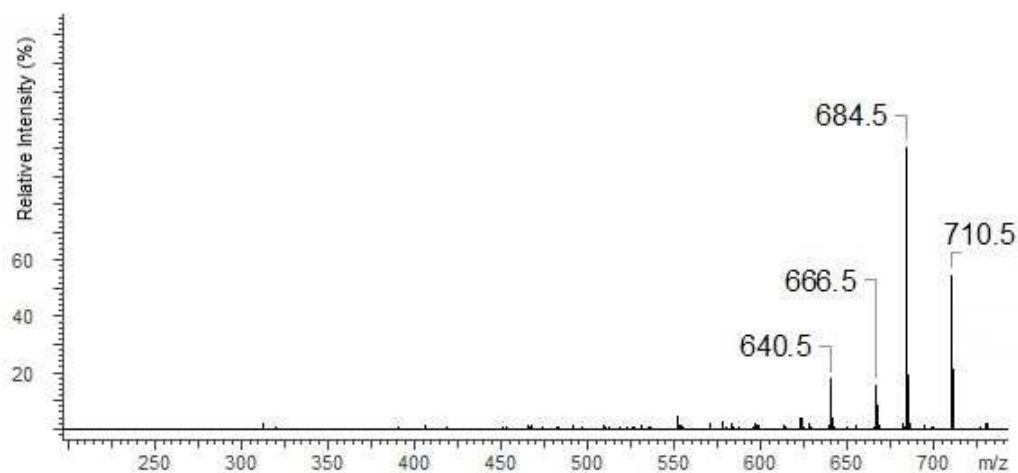
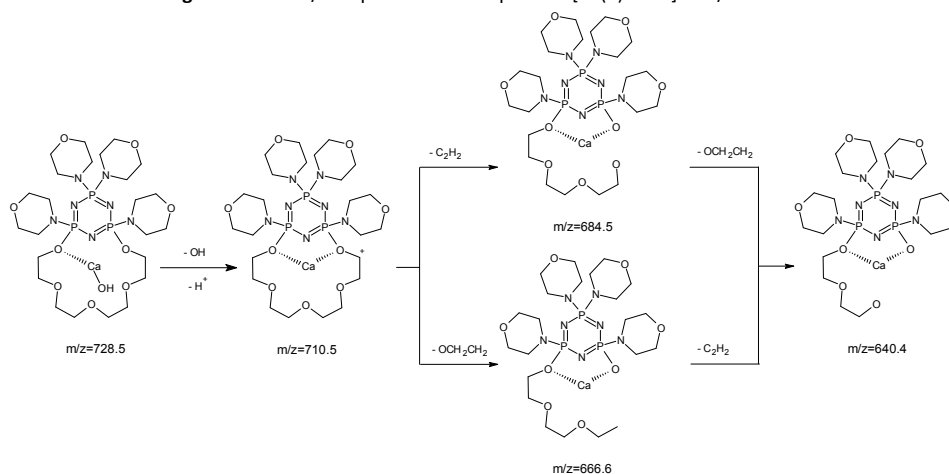


Fig.9 The ESI-MS/MS spectrum of complex ion $[\text{Ca}(\text{II})\text{L}+\text{OH}]^+$ - $m/z = 728.5$



Scheme 3. Fragmentation pattern of $[\text{Ca}(\text{II})\text{L}+\text{OH}]^+$ complex

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The ESI-MS spectrum of L and $\text{Cd}(\text{NO}_3)_2$ show three types of complexes: $[\text{Cd}(\text{II})\text{L}]^{2+}$, $[\text{Cd}(\text{II})\text{L}+\text{NO}_3]^+$ and $[\text{Cd}(\text{II})\text{L}+\text{H}_2\text{O}]^+$ (Fig.10). We made the fragmentation of the peak $m/z = 847.6$ and we observed the same fragmentation pattern as in the case of the

free ligand Fig.11. This fact proves that the cadmium (II) complex is very unstable structure. A similar situation was observed during the fragmentation of the $[\text{Cd}(\text{II})\text{L}+\text{H}_2\text{O}]^+$ complex.

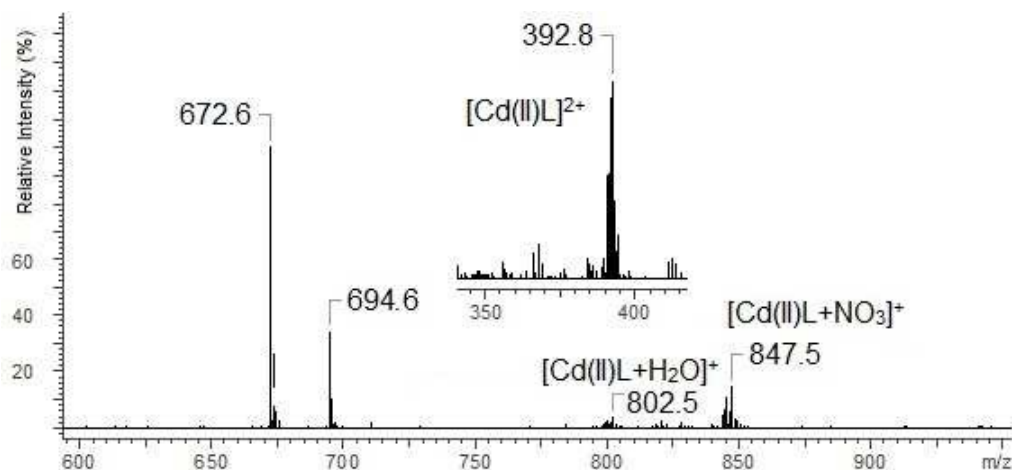


Fig.10 The mass spectrum of L with $\text{Cd}(\text{NO}_3)_2$ (the attached fragment of CdL spectrum had $\text{RI} < 5\%$)

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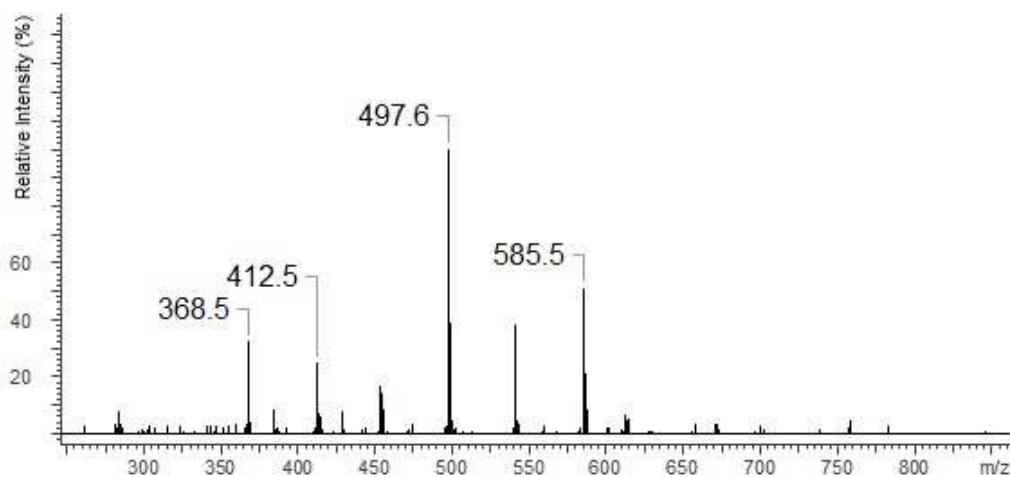


Fig. 11 The ESI-MS/MS spectrum of ion $[\text{Cd(II)L+NO}_3]^+$ - $m/z = 847.6$

The copper ions create three types of complexes: $[\text{Cu(I)L}]^+$, $[\text{Cu(II)L}]^{2+}$ and $[\text{Cu(II)L+NO}_3]^+$ (Fig.12). The MS/MS fragmentation pattern for $[\text{Cu(II)L+NO}_3]^+$ complex ($m/z = 796.5$) show the loss of $-\text{NO}_3$ to an ion with $m/z = 734.6$ (Fig.13). During the next step the loss of morpholinyl group with $m/z = 647.6$ was noticed. Then we observed the loss of another morpholinyl substituent together with the $-(\text{CH}_2\text{CH}_2)$ group with $m/z = 534.6$. In the last step the splitting-off the fragments of polyether moiety was observed (Scheme 4). Fragmentation of $[\text{Cu(I)L}]^+$ with $m/z 734.6$ (Fig.14) proceeds with the loss of two morpholinyl substituents ($m/z = 562.4$). The most abundant

fragment observed at $m/z = 477.4$ was formed due to the loss of another morpholinyl group. Then the losses of 28 Da $-(\text{CH}_2\text{CH}_2)$ peaks with $m/z = 448.3$ and with $m/z = 363.2$ due to subsequent loss of the last morpholinyl group were observed. This fragmentation pattern is shown on Scheme 5. Analysing the ionic radii of Cu(I) and the probable ligand cavity size we can notice that the copper ion fits well into crown moiety. Crown size (170 – 220 pm) and copper (I) ion (182 pm)⁷⁸ are comparable, while the copper (II) ion (144 pm) is much smaller hence almost whole fragment of the polyether chain decay is observed.

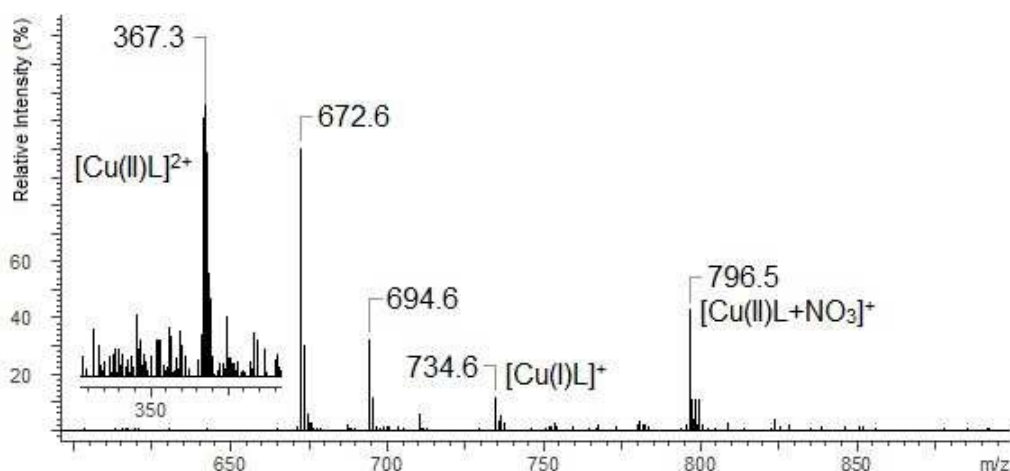


Fig.12 The mass spectrum of L with $\text{Cu(NO}_3)_2$ (the attached fragment of Cu(II)L spectrum had $\text{RI} < 5\%$)

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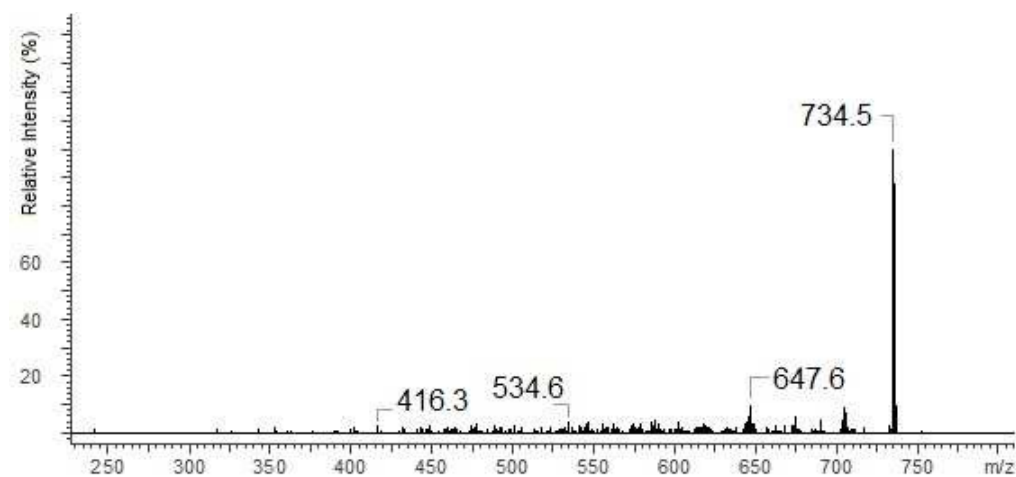
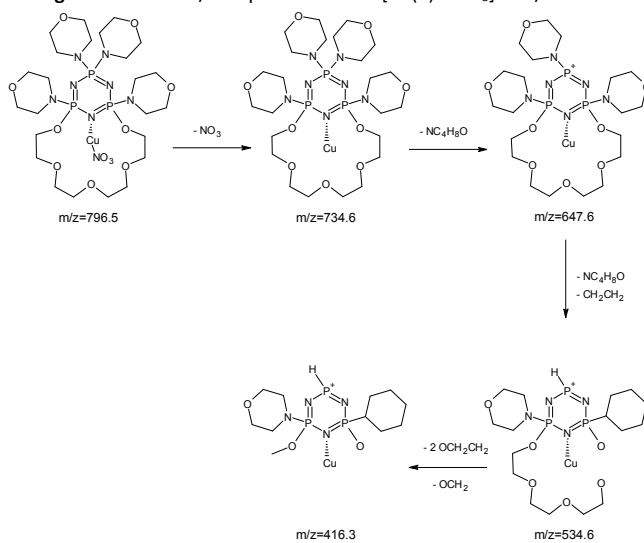


Fig. 13 The ESI-MS/MS spectrum of ion $[\text{Cu(II)L}+\text{NO}_3]^+$ - $m/z = 796.5$



Scheme 4. Fragmentation pattern of $[\text{Cu(II)L}+\text{NO}_3]^+$ complex

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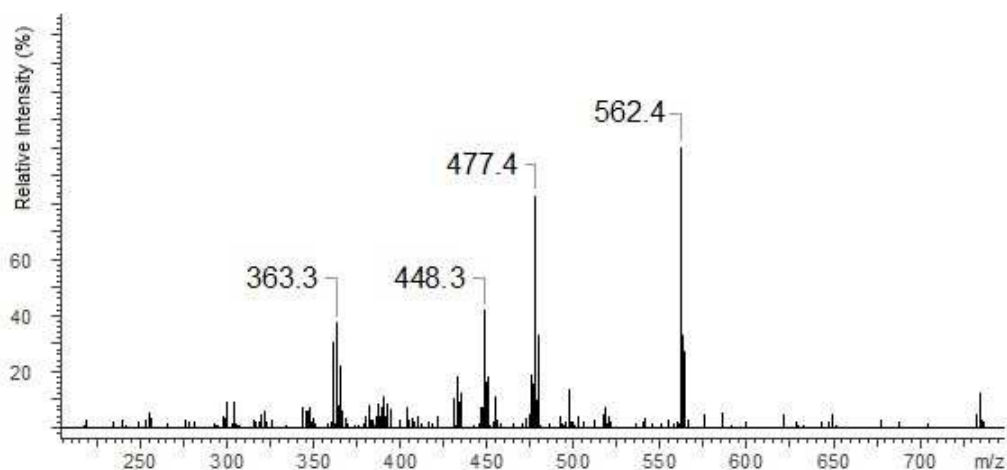
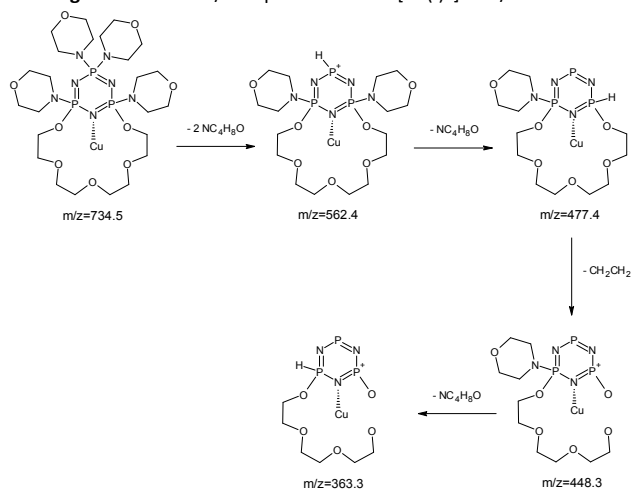


Fig. 14 The ESI-MS/MS spectrum of ion $[Cu(I)L]^+$ - $m/z = 734.5$



Scheme 5. Fragmentation pattern of $[Cu(I)L]^+$ complex

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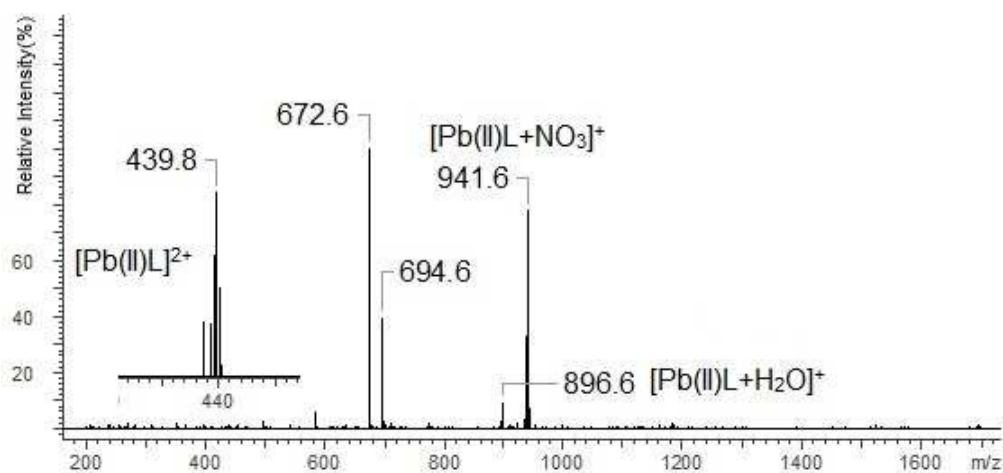
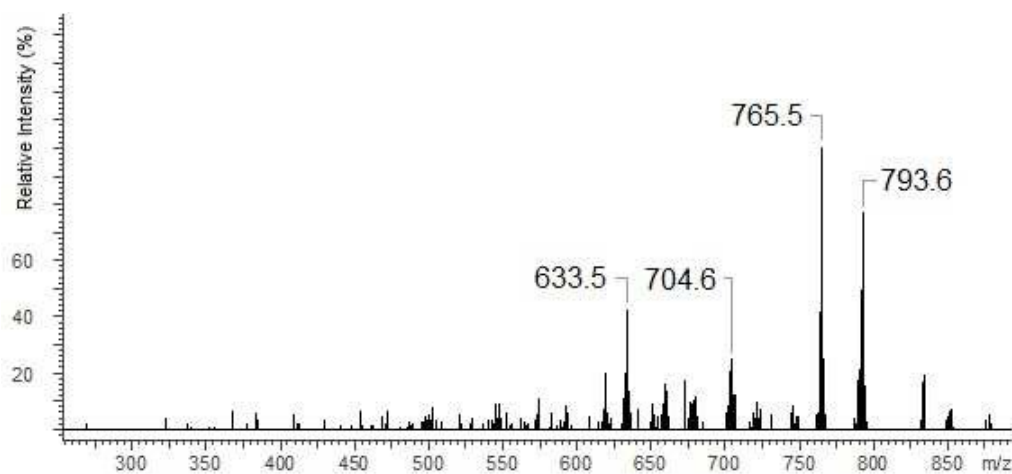
In the case of lead (II) ions we observed three types of complexes: $[Pb(II)L]^{2+}$, $[Pb(II)L+NO_3]^+$ and $[Pb(II)L+H_2O]^+$ (Fig.15). The fragmentation pattern of $[Pb(II)L+NO_3]^+$ shows (as in the case of copper derivative) the loss of $-NO_3$ group to an ion with $m/z = 878.7$. Then the loss of one morpholinyl substituent giving the peak at $m/z = 793.6$ was observed. The most intense

peak at $m/z = 765.5$ is related to the fragment which remained after $-(CH_2CH_2)$ loss. The further decomposition was realized through the stepwise splitting-off almost all parts of the polyether moiety ($m/z = 633.5$). In the final step the morpholinyl group was detached giving the peak at $m/z = 546.3$ (Fig.16), (Scheme 6).

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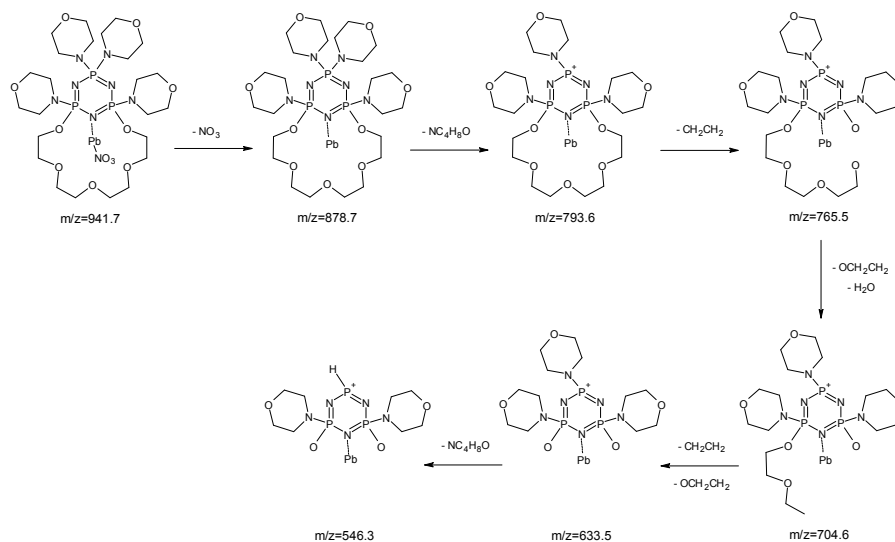
Fig.15 The mass spectrum of L with Pb(NO₃)₂Fig.16 The ESI-MS/MS spectrum of ion [Pb(II)L+NO₃]⁺ - m/z = 878.7

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Scheme 6. Fragmentation pattern of $[\text{Pb}(\text{II})\text{L}+\text{NO}_3]^+$ complex

Conclusion

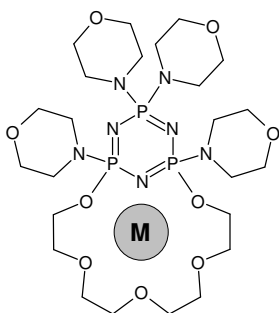
Electrospray ionization mass spectrometry was used to probe the complexation behaviour of tetramorpholinyl-PNP-lariat ether with a wide range of metals ions. All selected metal cations form the complexes with 1:1 stoichiometry with the investigated ligand. Only silver ions create the „sandwich” type complex ($[\text{Ag}(\text{I})\text{L}_2]^+$). Furthermore divalent cations form complexes with the nitrate anion adduct. In the case of Ca (II), Cd (II) and Pb (II) we noticed also another type of complex species where water molecules are involved in the formation of the molecular ion observed during the measurements: $[\text{Ca}(\text{II})\text{L}+\text{OH}]^+$, $[\text{Cd}(\text{II})\text{L}+\text{H}_2\text{O}]^+$ and $[\text{Pb}(\text{II})\text{L}+\text{H}_2\text{O}]^+$. Additionally, as far as copper ions are concerned, what we observed during the ionisation process was the reduction of $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$ and formation of the complexes with both copper(I) and copper(II) ions. As we noticed from the fragmentation pattern, the complex with cadmium ion is unstable under the measurement conditions. Calcium, copper and lead forms of complexes in MS/MS fragmentation pattern of $[\text{M}(\text{II})\text{L}+\text{NO}_3]^+$ show the loss of $-\text{NO}_3$ anion. In the case of tandem MS/MS for all investigated complexes - at the beginning we always observed the loss of morpholinyl substituent and subsequent splitting-off the polyether chain. Breaking of the chain and loss of the $-(\text{CH}_2\text{CH}_2)$ and $-(\text{OCH}_2\text{CH}_2)$ group fragments were observed in the literature in case of common crown ethers derivatives⁷⁹. Only in the case of copper (I) we observed the loss of four morpholinyl substituent. This fact suggests that the copper (I) is strongly accommodated inside the polyether ring. The obtained results suggest that ESI-MS technique seems to be a promising tool for characterization of

complexes which are existing in the solution, despite the differences in the phase of the measurement conditions.

Notes and references

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M = Ag(I), Ca(II), Cd(II), Cu(II) or Pb(II)

In this paper we present identification of complexes containing tetramorpholinyl-PNP-lariat ether with Ag(I), Ca(II), Cu(II), Cd(II) and Pb(II) by ESI-MS technique. The tandem mass spectra of these complexes were done in order to evaluate the stability of the different types of the complexes formed.