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Short communication

Formation of organometallic species from complexes of *N*-phenylaza-crown ether conjugates with lead cations in CID-MS/MS conditions

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ABSTRACT

Gas phase decomposition of the ions $[M + PbNO_3]^+$ (M stands for fluoro-substituted *N*-nitrophenylaza-crown ether conjugate), has been studied by the electrospray ionization-collision induced dissociation-tandem mass spectrometry (ESI-CID-MS/MS). The conjugates containing hydrogen atom at *ortho* position to the crown moiety, form abundant fragment ions which can be assigned as complexes of deprotonated conjugates and lead cation, thus the ions $[M - H + Pb]^+$ (fragment ions formed as a result of HNO_3 loss). Interaction between the nitro group (present at the second *ortho* position to the crown moiety) and the metal cation affects the formation of fragment ion $[M - H + Pb]^+$ (but does not prevent its formation). Ions $[M - H + Pb]^+$ are very rare example of the organometallic species (containing metal-carbon bond), in which metal cation is also complexed by crown ether moiety.

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1. Introduction

The gas phase study of organometallic species, so in the absence of solvent, provides some insight into the intrinsic properties of the species [1–5]. Many experiments have been performed in gas phase, including simple CID-MS/MS ones (collision induced dissociation-tandem mass spectrometry). Literature provides a number of reports on non-organometallic ions subjected to CID-MS/MS experiment which formed organometallic fragment ions [6–15]. In other words the ion containing a covalent metal-carbon bond may be formed upon gas phase decomposition of the complex of organic molecules with metal cations.

The organometallic compounds in which the metal cation (this metal cation which forms covalent metal-carbon bond) is also complexed by crown ether are rare. Examples of such compounds are organosilver polymer [16], organometallic complexes of rubidium and ceasium [17], and organopotassium compound of cyclic radical anion $[C_8H_6]^{\bullet -}$ [18]. In this paper we show that organometallic ions (containing metal-carbon bond), in which the metal cation is also complexed by crown ether moiety, are formed upon the gas phase decomposition of metal complexes of *N*-phenylaza-crown ether conjugates (Scheme 1). Formation of abundant organometallic ions has been observed for complexes of **1** and **2**, and with less efficiency also for complexes of **3** and **4**. Complexes of **5–8** are analyzed in this study for comparison.

Fluoro-substituted *N*-nitrophenylaza-crown conjugates **1–7** contain one, relatively acid, hydrogen atom at the phenyl ring. As demonstrated further in the manuscript, the conjugates containing hydrogen atom at *ortho* position to the crown moiety, form abundant fragment ions which can be assigned as a complexes of deprotonated conjugates and lead cation.

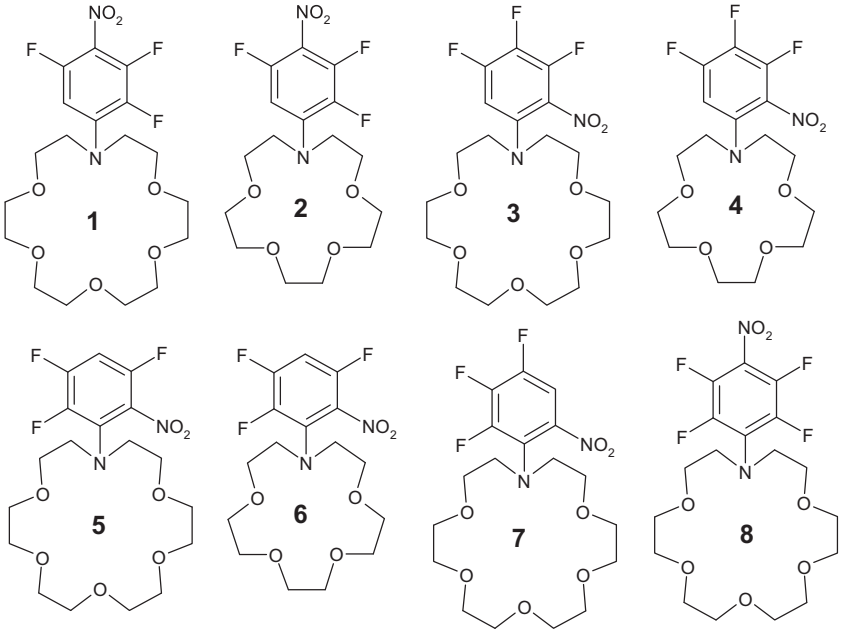
2. Experimental

N-Phenylaza-crown ether conjugates (**1–8**) are new compounds that were synthesized as follows. To a solution of 3.8 mmol of an appropriate aza-crown ether (1.00 g of 1-aza-18-crown-6 or 0.83 g of 1-aza-15-crown-5) in 50 ml of dry diethyl ether, a portion of 3.8 mmol of fluoronitroarene was added (0.81 g of pentafluoronitrobenzene (for ligand **8**), 0.74 g of 2,3,4,6-tetrafluoronitrobenzene (for ligands **1–6**) or 0.74 g of 2,3,4,5-tetrafluoronitrobenzene (for ligand **7**)). The mixture obtained was refluxed over 24 h. Then the solvent was evaporated and the products were purified by column chromatography on silica, using hexane-chloroform (1:1 v/v) or chloroform as eluents.

1: Orange-brown solid, m.p. 55–57 °C. Yield: 0.12 g (7%; minor isomer). ^{1}H NMR ($CDCl_3$): δ 3.65 (m, 16H); 3.75 (m, 8H); 6.63 (ddd, 1H; 1.8, 7.4 & 14.7 Hz). ^{19}F ($CDCl_3$): δ −121.7 (dddd, 1F; 4.4, 7.4,

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Scheme 1. *N*-Phenylaza-crown ether conjugates.

12.9 & 14.7 Hz); −140.6 (dd, 1F; 4.4 & 17.0 Hz); −155.8 (dt, 1F; 7.4 & 17.0 Hz).

2: Yellow solid, m.p. 98–101 °C. Yield: 0.23 g (15%; minor isomer). ^{1}H NMR ($CDCl_3$): δ 3.63 (s, 4H); 3.65 (s, 8H); 3.68 (t, 4H; 6.0 Hz); 3.76 (t, 4H; 6.0 Hz); 6.52 (dd, 1H; 7.2 & 14.4 Hz). ^{19}F ($CDCl_3$): δ −123.5 (dddd, 1F; 4.4, 7.2, 12.9 & 14.4 Hz); −141.1 (dd, 1F; 4.4 & 17.0 Hz); −156.7 (dt, 1F; 7.2 & 17.0 Hz).

3: Orange crystals, m.p. 62–64 °C. Yield: 0.43 g (26%; minor isomer). ^{1}H NMR ($CDCl_3$): δ 3.40 (t, 4H; 5.4 Hz); 3.59 (m, 12H); 3.68 (m, 8H); 7.28 (ddd, 1H; 1.7, 6.5 & 11.7 Hz). ^{19}F ($CDCl_3$): δ −129.1 (m, 1F); −143.5 (dd, 1F; 6.5 & 20.2 Hz); −166.1 (t, 1F; 20.0 Hz).

4: Orange crystals, m.p. 48–51 °C. Yield: 0.35 g (23%; minor isomer). ^{1}H NMR ($CDCl_3$): δ 3.39 ppm (t, 4H; 5.8 Hz); 3.60 (m, 12H); 3.66 (s, 4H); 7.26 (dd, 1H; 6.5 & 11.7 Hz). ^{19}F ($CDCl_3$): δ −128.0 (m, 1F); −144.5 (dd, 1F; 6.5 & 20.2 Hz); −167.7(t, 1F; 20.0 Hz).

5: Red oil. Yield: 0.74 g (44%; major isomer). ^{1}H NMR ($CDCl_3$): δ 3.41 (t, 4H; 5.4 Hz); 3.65 (m, 20H); 6.86 (td, 1H; 6.1 & 9.0 Hz). ^{19}F ($CDCl_3$): δ −125.8 (ddd, 1F; 3.6, 9.0 & 12.2 Hz); −128.8 (ddd, 1F; 3,6, 9.0 & 20.1 Hz); −146.0 (ddd, 1F; 6.1, 12.2 & 20.1 Hz).

6: Orange oil. Yield: 0.65 g (43%; major isomer). ^{1}H NMR ($CDCl_3$): δ 3.36 (t, 4H; 5.9 Hz); 3.63 (m, 8H); 3.67 (m, 8H); 6.86 (td, 1H; 6.5 & 9.1 Hz). ^{19}F ($CDCl_3$): δ −126.8 (ddd, 1F; 3.6, 9.1 & 12.2 Hz); −129.0 (ddd, 1F; 3.6, 9.1 & 20.1 Hz); −145.5 (ddd, 1F; 6.5, 12.2 & 20.1 Hz).

7: Red oil. Yield: 0.07 g (4%; minor isomer). ^{1}H NMR ($CDCl_3$): δ 3.38 (t, 4H; 5.4 Hz); 3.61 (m, 4H); 3.68 (m, 16H); 7.40 (ddd, 1H; 2.3, 7.6 & 9.4 Hz). ^{19}F ($CDCl_3$): δ −135.7 (d, 1F; 20.0 Hz); −136.9 (d, 1F; 20.0 Hz); −150.6 (td, 1F; 7.6 & 20.0 Hz).

8: Orange-brown solid, m.p. 48–51 °C. Yield: 1.23 g (71%; major isomer). ^{1}H NMR ($CDCl_3$): δ 3.66 (m, 16H); 3.77 (t, 4H; 5.0 Hz). ^{19}F ($CDCl_3$): δ −147.9 (m, 2F); −149.6 (m, 2F).

All NMR spectra were recorded at 298 K on a Bruker Avance 500 spectrometer, operating at frequencies 500.25 MHz (^{1}H) and 470.71 MHz (^{19}F). The chemical shifts were referred to internal TMS (^{1}H; 0.00 ppm) and $CFCl_3$ (^{19}F; 0.00 ppm).

CID-MS/MS spectra were taken on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK) equipped with an electrospray ion source (ESI). The sample solutions were infused into the ESI source by a syringe pump at the flow rate of 5 ml/min. The electrospray voltage was 2.7 kV and the cone voltage −30 V. The source temperature was 80 °C and the desolvation temperature was 250 °C. Nitrogen was used as the cone gas and desolvating gas at the flow-rates of 50 and 300 l h^{-1}, respectively. Argon was used as a collision gas at the flow-rate 0.5 ml/min in the T-wave collision cell. The applied collision energy (CE, laboratory frame), the most important parameter for CID-MS/MS experiments, is indicated in each CID-MS/MS spectrum shown. In each CID-MS/MS spectrum the abundance of the most abundant ion (arbitrary units) is also given. The ion selected for MS/MS experiment is indicated in each CID-MS/MS spectrum shown, for lead complexes the selected ion contained isotope ^{206}Pb. Because of a wide window, the selected ion beam and as a consequence the fragment ions, contained all isotopes characteristic of a given metal in appropriate abundances. In all mass spectra shown, for Pb-containing ions, the ions containing ^{208}Pb are labeled.

The sample solutions were prepared in methanol. The concentration of **1**–**8** was 10^{-5} mol/dm^3. In order to generate the abundant ions of interest (e.g. $[\mathbf{1} + PbNO_3]^+$) the $Pb(NO_3)_2$ was added, its concentration was about 5×10^{-5} mol/dm^3. Abundant complexes of sodium and potassium cations were generated without adding sodium or potassium salts (it is well known that crown ethers are very prone to form complexes with alkali metal cations and sodium and potassium cations are common contaminants which are difficult to remove) but these complexes are not of interest for this study. Especially conjugates **3** and **4** gave very abundant complexes with alkali metal cations (it is difficult to rationalize why these very conjugates), as a consequence the lead complexes had low abundances.

3. Results and discussion

Fig. 1 shows the CID-MS/MS spectra of ions $[\mathbf{1} + PbNO_3]^+$, $[\mathbf{3} + PbNO_3]^+$ and $[\mathbf{5} + PbNO_3]^+$ (conjugates of aza-18C6). As clearly result from Fig. 1, the conjugates containing hydrogen atom at *ortho* position to the crown moiety, form abundant fragment ions which can be assigned as complexes of deprotonated conjugates and lead cations, thus ions $[\mathbf{1}\text{-H} + Pb]^+$ and $[\mathbf{3}\text{-H} + Pb]^+$ (fragment ions formed as a result of HNO_3 loss). Analogous fragment ions occurred in low abundances for the conjugates which did not contain hydrogen atom at *ortho* position (Fig. 1 bottom for **5** and Supplementary material for **7** and **8**).

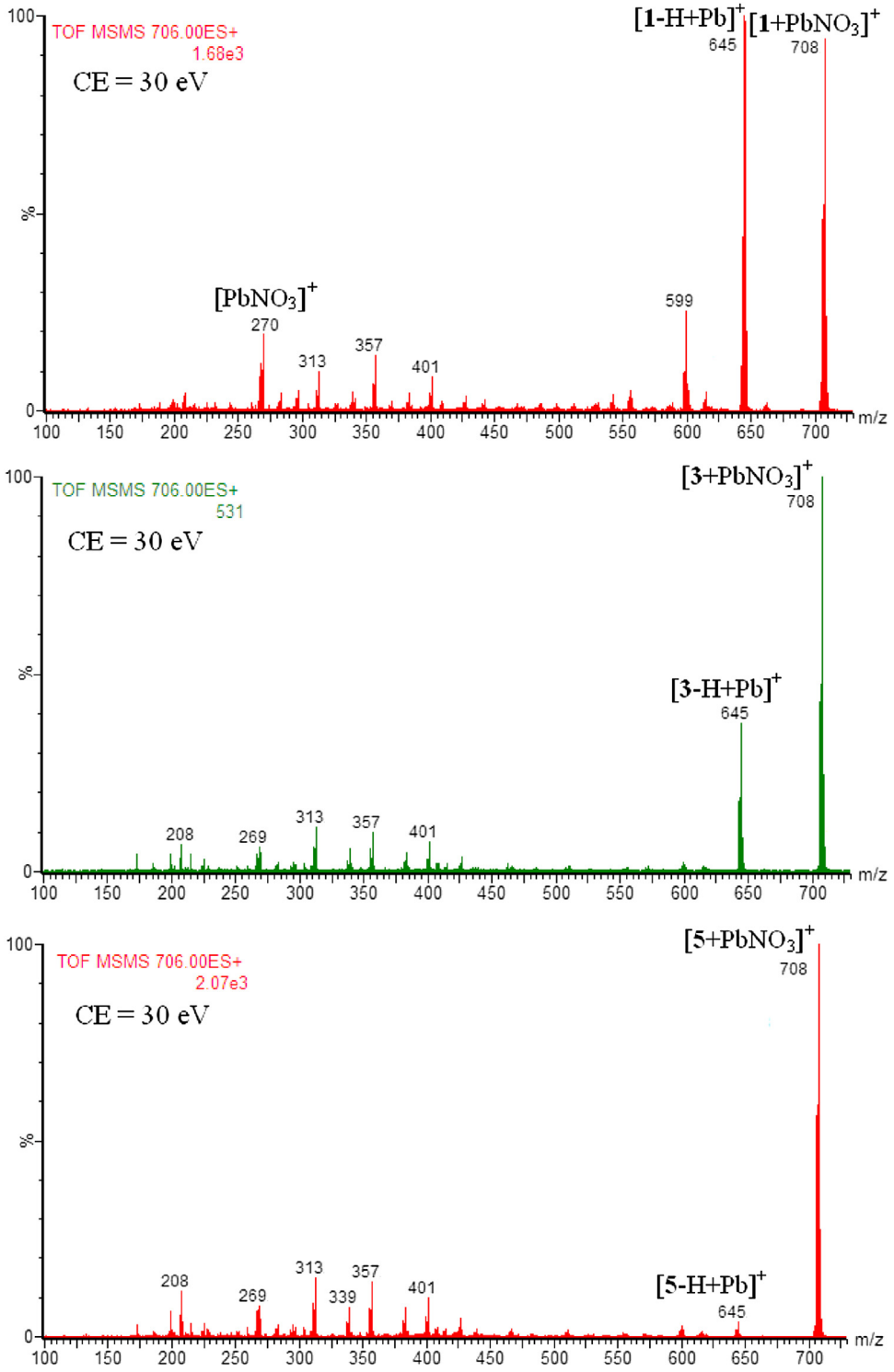


Fig. 1. CID-MS/MS spectra of ions $[\mathbf{1}+PbNO_3]^+$, $[\mathbf{3}+PbNO_3]^+$ and $[\mathbf{5}+PbNO_3]^+$.

Fig. 2 shows the CID-MS/MS spectra of ions $[\mathbf{2}+PbNO_3]^+$, $[\mathbf{4}+PbNO_3]^+$ and $[\mathbf{6}+PbNO_3]^+$ (conjugates of aza-15C5). The spectra confirm that the conjugates containing a hydrogen atom at *ortho* position to the crown moiety, form abundant fragment ions which can be assigned as complexes of deprotonated conjugates and lead cation, thus the ions $[\mathbf{2}\text{-}H+Pb]^+$ and $[\mathbf{4}\text{-}H+Pb]^+$.

Taking into account the size of Pb^{2+} and the size of the crown ether cavity (132 pm for radii of Pb^{2+} and 130–160 pm for radii of 18C6) [19,20], the conjugates of aza-18C6 are able to form real inclusion complex with Pb^{2+} (Pb^{2+} has almost identical radii as K^+ and it is well known that K^+ fits very well into 18C6 cavity), however, the conjugates of aza-15C5 are not able to do this (radii of 15C5 is 85–110 pm). On the other hand, it has to be emphasized, that although **2** and **4** are not able to form real inclusion complex with Pb^{2+}, they form organometallic ions ($[\mathbf{2}\text{-}H+Pb]^+$ and $[\mathbf{4}\text{-}H+Pb]^+$) in which the metal cation interacts with the crown moiety. It is reasonable that ions $[\mathbf{1}\text{-}H+Pb]^+$ and $[\mathbf{2}\text{-}H+Pb]^+$ have the

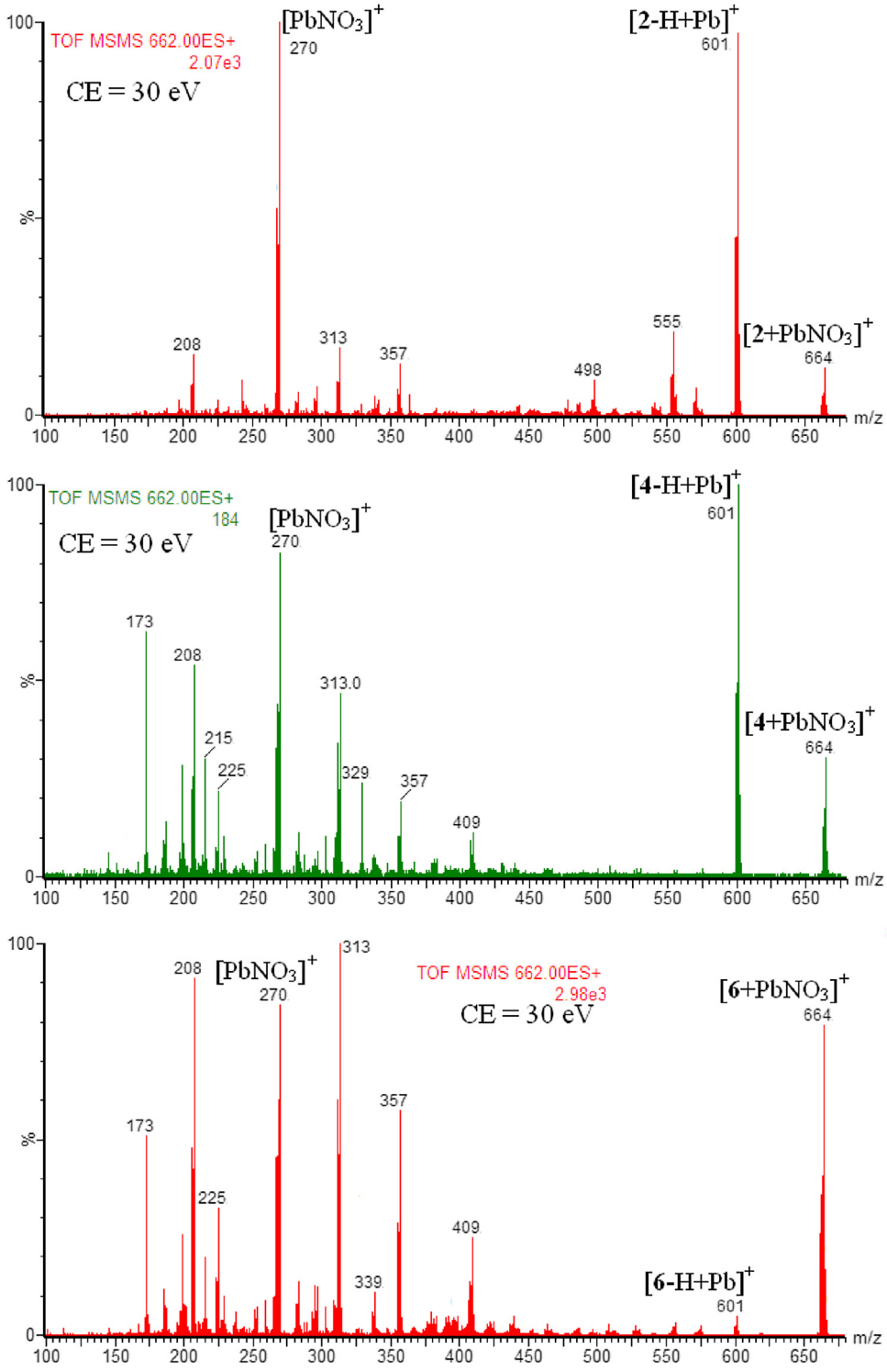
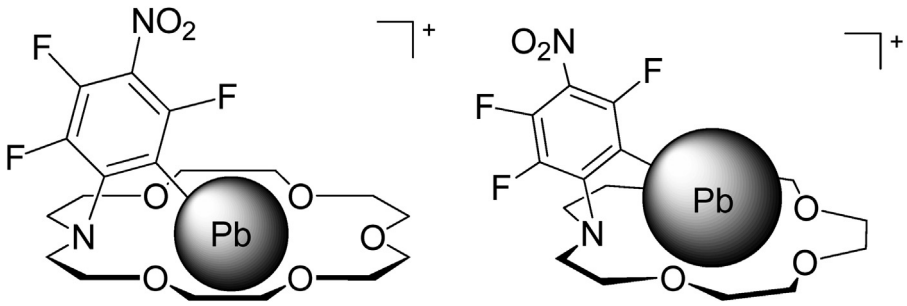


Fig. 2. CID-MS/MS spectra of ions $[\mathbf{2} + PbNO_3]^+$, $[\mathbf{4} + PbNO_3]^+$ and $[\mathbf{6} + PbNO_3]^+$.

organometallic structures shown in Scheme 2 and the structures of ions $[\mathbf{3}\text{-H} + Pb]^+$ and $[\mathbf{4}\text{-H} + Pb]^+$ are analogous.

Fragment ion $[\mathbf{3}\text{-H} + Pb]^+$ is less abundant than fragment ion $[\mathbf{1}\text{-H} + Pb]^+$ (Fig. 1). It is reasonable that interaction between the nitro group and the metal cation in the complex of **3** affects the formation of fragment ion $[\mathbf{3}\text{-H} + Pb]^+$ (but does not prevent the formation of fragment ion $[\mathbf{3}\text{-H} + Pb]^+$). The CID-MS/MS spectra shown in Fig. 2 were obtained at the collision energy 30 eV (the same as for the spectra shown in Fig. 1). The CID-MS/MS spectra obtained at lower collision energy clearly indicate that the formation of $[\mathbf{4}\text{-H} + Pb]^+$ is less efficient than that of $[\mathbf{2}\text{-H} + Pb]^+$ (Supplementary material). Similarly as for conjugate **3**, the interaction between the nitro group and the metal cation for the complex of **4** affects the formation of fragment ion $[\mathbf{4}\text{-H} + Pb]^+$.

As shown in Figs. 1 and 2, besides fragment ions $[\mathbf{M} - H + Pb]^+$ there are also other ones. As a detailed description of mass spectrometric fragmentation pathways of ions $[\mathbf{M} + PbNO_3]^+$ is not the



Scheme 2. Reasonable structure of ions [**1**-H + Pb]$^+$ and [**2**-H + Pb]$^+$.

purpose of this work, thus the other fragment ions are not discussed.

The only other fragment ion which is worth noting is $[PbNO_3]^+$, since the abundance of this fragment ions reflects the strength of interaction between the metal cation and *N*-phenylaza-crown ether molecule. Taking into account the conjugates **1**, **3**, **5**, **7** and **8** (derivatives of 18C6), the fragment ion $[PbNO_3]^+$ is the most abundant for **1** and **8** (Fig. 1 and Supplementary material). Conjugates **1** and **8** do not contain nitro group at *ortho* position. Thus, the conclusion can be drawn that the interaction between the nitro group and the metal cation in the complexes of **3**, **5** and **7** increases the strength of the interaction between the metal cation and *N*-phenylaza-crown ether molecule. The conjugates of aza-18C6 are able to form real inclusion complex with Pb^{2+}, however, the conjugates of aza-15C5 are not able to do this. Therefore, the interaction between the conjugates of aza-15C5 and Pb^{2+} is weaker than that of the interaction between the conjugates of aza-18C6 and Pb^{2+}. As a consequence in the spectra of ions [**2** + $PbNO_3$]$^+$, [**4** + $PbNO_3$]$^+$ and [**6** + $PbNO_3$]$^+$ there are abundant signals of fragment ions $[PbNO_3]^+$ (Fig. 2). Ion [**2** + $PbNO_3$]$^+$ do not have nitro group at *ortho* position, therefore for this ion the fragment ion $[PbNO_3]^+$ is the most abundant.

Formation of the discussed organometallic ions, in which the metal cation is also complexed by crown ether moiety, have been observed not only for the lead-containing ions but also for the ions containing other metals (namely mercury and alkali earth metals). Formation of the discussed complexes has been also observed for the ions containing anions other than nitrate. The examples are briefly discussed in Supplementary material.

4. Conclusion

Formation of abundant fragment ions [**M** − H + Pb]$^+$ from ions [**M** + $PbNO_3$]$^+$ (**M** stands for fluoro-substituted *N*-nitrophenylaza-crown ether conjugate) is observed for conjugates containing hydrogen atom at *ortho* position to the crown moiety. In other words this process is regiospecific, as it clearly results from comparison of the mass spectra of the complexes of respective isomers (Scheme 1). The fragment ions [**M** − H + Pb]$^+$ (for **M** = **1**, **2**, **3** and **4**, Scheme 1) are very rare examples of organometallic species (containing metal-carbon bond), in which metal cation is also complexed by crown ether moiety. It is worth adding that the interaction between the nitro group (present at the second *ortho* position to the crown moiety) and the metal cation affects the formation of fragment ion [**M** − H + Pb]$^+$ (but does not prevent its formation).

Furthermore, the complexes shown in Scheme 2 can be called "scorpionate"- like by analogy to the complexes of cyclams containing nitrophenyl or nitrobenzyl substituents in *ortho* position [21,22]. To the best of our knowledge, organometallic "scorpionate" complexes like this shown in Scheme 2, or similar, have not been observed yet.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2017.07.009.

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