
Anion- π Interactions—Interactions Between Benzo-Crown Ether Metal Cation Complexes and Counter Ions

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The loss of X \cdot radical from [M + Cu + X] $^+$ ions (copper reduction) has been studied by the so called in-source fragmentation at higher cone voltage (M = crown ether molecule, X $^-$ = counter ion, ClO $_4^-$, NO $_3^-$, Cl $^-$). The loss of X \cdot has been found to be affected by the presence/lack of aromatic ring poor/rich in electrons. Namely, the loss of X \cdot occurs with lower efficiency for the [NO $_2$ -B15C5 + Cu + X] $^+$ ions than for the [B15C5 + Cu + X] $^+$ ions, where NO $_2$ -B15C5 = 3-nitro-benzo-15-crown-5, B15C5 = benzo-15-crown-5. A reasonable explanation is that Anion- π interactions prevent the loss of X \cdot from the [NO $_2$ -B15C5 + Cu + X] $^+$ ions. The presence of the electron-withdrawing NO $_2$ group causes the aromatic ring to be poor in electrons and thus it enhances its interactions with anions. For the ion containing the aromatic ring enriched in electrons, namely [NH $_2$ -B15C5 + Cu + ClO $_4$] $^+$ where NH $_2$ -B15C5 = 3-amino-benzo-15-crown-5, the opposite situation has been observed. Because of Anion- π repulsion the loss of X \cdot radical proceeds more readily for [NH $_2$ -B15C5 + Cu + X] $^+$ than for [B15C5 + Cu + X] $^+$. Iron reduction has also been found to be affected by Anion- π interactions. Namely, the loss of CH $_3$ O \cdot radical from the ion [B15C5 + Fe + NO $_3$ + CH $_3$ O] $^+$ proceeds more readily than from [NO $_2$ -B15C5 + Fe + NO $_3$ + CH $_3$ O] $^+$. (J Am Soc Mass Spectrom 2009, 20, 257–262) © 2009 American Society for Mass Spectrometry

A few years ago, Meyer et al. published an excellent review devoted to noncovalent interactions involving aromatic ring [1]. Among others, the authors discussed in details arene–arene interactions, hydrogen bonding to aromatic π systems, cation- π interactions, and the influence of counter ions on the cation- π interactions. The possibility that aromatic ring may also interact with the anion due to the Anion- π interactions has not been mentioned, which indicates that the anion- π interactions are not so common. Indeed, the chemistry of noncovalent Anion- π interactions is much less developed than that of the other types of π interactions. Most likely the reason is the electron-donating character of anions, which is expected to lead to repulsive interactions with aromatic π clouds. Anion- π interactions are energetically less favorable than their cation- π counterparts because the anions have greater van der Waals radii than cations and the binding energies strongly depend upon distance [2–6].

In the field of supramolecular chemistry, crown ethers (CE) belong to the most popular hosts since their inclusion complexes have found a vast number of practical applications [7]. The aromatic ring-containing crown ethers may have enhanced complexing properties due to the π -stacking interactions. It has been

found that cation- π interactions are of crucial importance for formation of complexes between dibenzo-24-crown-8 and tetramethylammonium cation [8]. Donor-acceptor π -stacking interactions have been established to significantly enhance the formation of mixed-ligand sandwich complexes formed by crown ethers [9]. Crown ethers having aromatic sidearms exhibited cation- π interactions between K $^+$ and a benzene ring [10].

Here we asked if the complexes of benzo-crown ethers with metal cation interact with the anion through the anion- π interactions and if this interaction can be observed by ESI-MS. Obviously, a benzo-crown ether should contain an aromatic ring poor in electrons, e.g., nitro-benzo-15-crown-5 (NO $_2$ -B15C5). To the best of our knowledge the anion- π interactions have not been observed yet by ESI-MS. Thus, the obtained results could be interesting for those mass spectrometrists involved in ESI-MS application in the field of supramolecular chemistry.

For the purpose of the present study, a vast number of metal cations and anions can be considered. Of course, the valency of the metal cation and the anion must be different; otherwise the complex would not be charged and would not be observed in the ESI mass spectra. As counter ions, we decided to use the three Cl $^-$, NO $_3^-$, and ClO $_4^-$. We also decided to use the cations that are easily reduced under ESI conditions, namely Cu $^{2+}$, Fe $^{3+}$, Hg $^{2+}$ [11]. One of the metal reduction mechanisms upon the ESI condition is the loss of a

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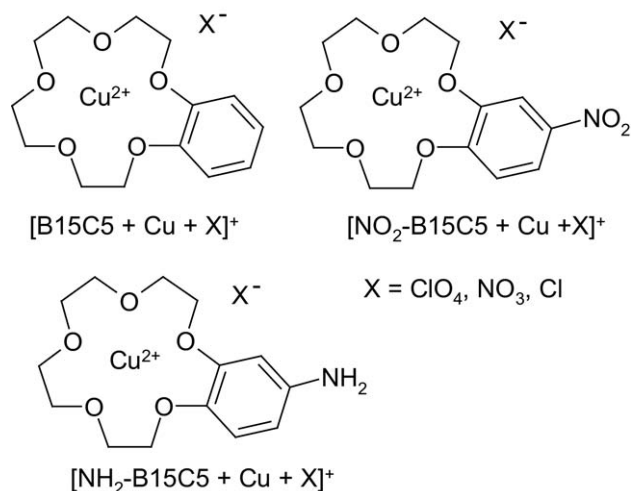
respective radical (applying a higher cone voltage, which leads to the so-called in-source fragmentation) from the counter ion containing species, e.g., $[L + Cu + X]^+ \rightarrow [L + Cu]^+ + X^-$ (L – neutral ligand molecule, X^- – counter ion) [12, 13]. In the presence of the anion– π interactions, e.g., between NO_2 -B15C5 and X^- , the loss of X^- (copper reduction) should proceed with a different efficiency than that of the loss of X^- in the absence of the anion– π interactions, e.g., for benzo-15-crown-5 (B15C5), which contains an electron-rich aromatic ring.

For complexation of the first-row transition-metal cation it is better to use the smaller ring crown ethers [14]. Thus, to analyze the complexes of Cu^{2+} and Fe^{3+} we used *nitro*-benzo-15-crown-5 (NO_2 -B15C5, because of the resonance effect of NO_2 group the aromatic ring is poor in electrons), benzo-15-crown-5 (B15C5) and *amino*-benzo-15-crown-5 (NH_2 -B15C5, because of the resonance effect of NH_2 group the aromatic ring is enriched in electrons). Copper complexes of crown ethers and counter ions used in the study are shown in Scheme 1.

As described below, the use of benzo-12-crown-4 and *nitro*-benzo-12-crown-4 resulted in formation of a respective radical cation (e.g., $[B12C4]^+$); thus the Anion– π interactions could not be observed. For mercury complexation we used the benzo-18-crown-6 and *nitro*-benzo-18-crown-6 but the formation of organo-metallic species prevented the observation of the anion– π interactions.

Experimental

The ESI mass spectra were obtained on a Waters/Micromass (Manchester, UK) ZQ2000 mass spectrometer (single quadrupole type instrument, Z-spray, software MassLynx ver. 3.5). The sample solutions were prepared in methanol, at crown ether concentration of 2×10^{-5} mol/dm³ and inorganic salt concentration of



Scheme 1. Copper complexes of crown ethers and counter ions used in the study.

5×10^{-5} mol/dm³ and mixed by ultrasonic bath. Excess of inorganic salt was necessary to obtain sufficient abundance of the ions of interest, e.g., $[NO_2\text{-B15C5} + Cu + Cl]^+$.

The sample solutions were infused into the ESI source using a Harvard pump; the flow rate was 80 μ L/min. The ESI source potentials were capillary 3 kV, lens 0.5 kV, extractor 4 V, and cone voltage 10–60 V. This parameter had the most profound effect on the mass spectra obtained. Increase in this parameter leads to the so called “in-source” fragmentation/dissociation but a too low cone voltage may cause sensitivity dropping. The source temperature was 120 °C and the desolvation temperature was 300 °C. Nitrogen was used as the nebulizing and desolvating gas at the flow rates of 100 and 300 L h⁻¹, respectively.

ESI mass spectra are shown in the m/z range of interest. In the lower m/z range there were the peaks of abundant ions corresponding to the complexes with sodium cation, e.g., $[B15C5 + Na]^+$, and the peaks in the higher m/z range corresponded to the ions of the sandwich type complexes, e.g., $[215C5 + K]^+$ (sodium and potassium are always present as impurities).

It is a general opinion that the CID MS/MS experiment is more appropriate to study the fragmentation of ions of interest than the CID “in-source” technique, especially if the fragmentation pathway is complicated. However, for such a simple process as $[L + Cu + X]^+ \rightarrow [L + Cu]^+ + X^-$, when ion abundances are of interest, CID “in-source” seems to be more appropriate. For example, ions $[NO_2\text{-B15C5} + Cu + Cl]^+$ and $[B15C5 + Cu + Cl]^+$ dissociate simultaneously, thus at exactly the same conditions. We do not have to worry about any pressure/temperature fluctuations in the instrument used. Such fluctuations surely affect the abundances of the fragment ions formed and if the abundance differences are small, any conclusions are disputable.

Benzo-crown ethers and amino-benzo-crown ether were obtained from Sigma-Aldrich and used without further purification. Nitro-benzo-crown ethers were synthesized by nitration of corresponding benzo compounds with nitric acid (60%) and sulfuric acid (98%) mixture (1:3, vol/vol) in 10 °C. After dilution with water, the products were collected by filtration and purified by crystallization from ethanol; yield about 70%.

Results and Discussion

Crown Ether– Cu^{2+} Complexes

Figure 1 shows the ESI mass spectra obtained for a methanol solution containing NO_2 -B15C5, B15C5 and $Cu(ClO_4)_2$, taken at the cone voltage 10 V (top) and 40 V (bottom) as examples.

At a higher voltage, the abundances of ions $[NO_2\text{-B15C5} + Cu]^+$ and $[B15C5 + Cu]^+$ increased as a result of ClO_4^- radical loss from ions $[NO_2\text{-B15C5} + Cu + ClO_4]^+$ and $[B15C5 + Cu + ClO_4]^+$, respectively. As can

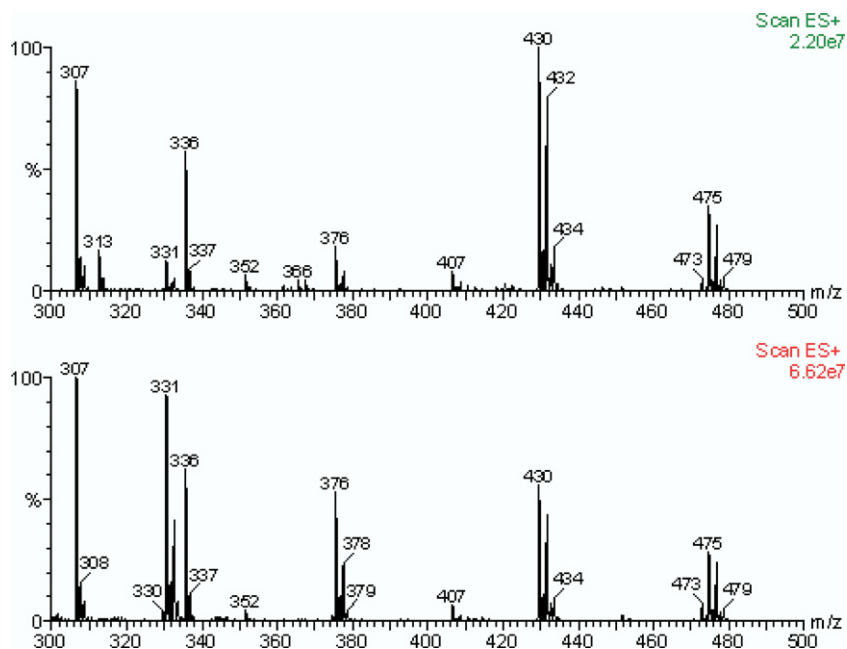


Figure 1. ESI mass spectra obtained for a methanol solution containing $\text{NO}_2\text{-B15C5}$, B15C5 , and $\text{Cu}(\text{ClO}_4)_2$, taken at the cone voltage 10 V (top) and 40 V (bottom). $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ m/z 475, $[\text{NO}_2\text{-B15C5} + \text{Cu}]^+$ m/z 376, $[\text{NO}_2\text{-B15C5} + \text{Na}]^+$ m/z 336, $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$ m/z 430, $[\text{B15C5} + \text{Cu}]^+$ m/z 331, $[\text{B15C5} + \text{K}]^+$ m/z 307.

be concluded from Figure 1, the loss of ClO_4^- radical occurs with higher efficiency for ion $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$. The relative abundance of ion $[\text{B15C5} + \text{Cu}]^+$ increased from 12% to 94% when the cone voltage was adjusted from 10 to 40 V, while the relative abundance of ion $[\text{NO}_2\text{-B15C5} + \text{Cu}]^+$ increased from 19% to 54%. It is reasonable to conclude that the anion- π interactions prevent the loss of ClO_4^- radical from ion $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$. Analogous results were obtained for the complexes containing other counter ions used (NO_3^- , Cl^-).

Much higher abundance of the ion $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$ than $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ at a low cone voltage may be caused by two reasons. The first is that because of the electron withdrawing effect of NO_2 group, the stability constant of $\text{NO}_2\text{-B15C5}$ complex with copper cation is lowered, and the second is that because of the interactions of NO_2 group with methanol via hydrogen bond formation in solution, the ionization efficiency (desolvation) of the $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ ion is lowered. The $[\text{NO}_2\text{-B15C5} + \text{Cu}]^+$ and $[\text{B15C5} + \text{Cu}]^+$ ions are detected at a low cone voltage, most probably as a result of electrolytic copper reduction. Slightly higher abundances of the former ion result from the lower complexation ability of $\text{NO}_2\text{-B15C5}$ toward copper cation, which facilitates copper reduction.

If it is true that the anion- π interactions prevent the decomposition of $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$, the cone voltage necessary to initiate the effective loss of ClO_4^- radical form $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ should be higher than that needed to initiate the loss of ClO_4^- radical form $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$, which was ob-

served, indeed. Figure 2 shows the breakdown plots of the abundances of the $[\text{B15C5} + \text{Cu}]^+$, $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$, $[\text{NO}_2\text{-B15C5} + \text{Cu}]^+$, $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ ions against the cone voltage. This is an effective

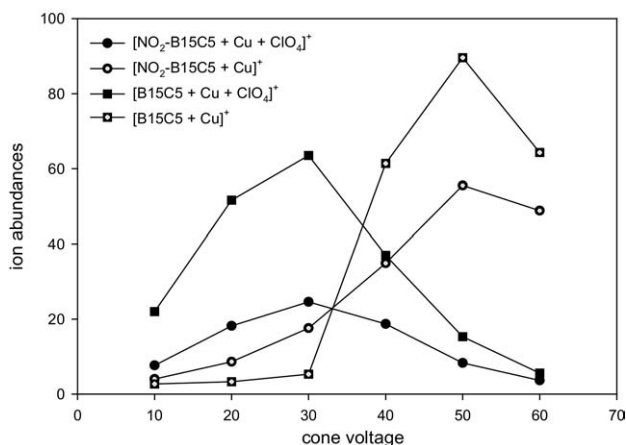


Figure 2. The abundances of $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$, $[\text{NO}_2\text{-B15C5} + \text{Cu}]^+$, $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$, $[\text{B15C5} + \text{Cu}]^+$ ions versus the cone voltage (V). The absolute ion abundances (in arbitrary units) taken from mass spectra recorded were divided by 106. The data were obtained from one methanol solution containing $\text{NO}_2\text{-B15C5}$ (2×10^{-5} mol/dm³), B15C5 (2×10^{-5} mol/dm³), and $\text{Cu}(\text{ClO}_4)_2$ (5×10^{-5} mol/dm³). Increase in the cone voltage from 30 to 40 V initiated the effective decomposition of $[\text{B15C5} + \text{Cu} + \text{ClO}_4]^+$ ion, whose abundance was decreased by 42%. Increase in the cone voltage from 30 to 40 V initiated only small decomposition of $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^+$ ion, whose abundance was decreased by 24%.

way of presentation of multiple ions obtained by the “in-source” CID [15].

The cone voltage increase from 10 to 30 V causes an increase in the $[M + Cu + ClO_4]^+$ ion abundances, (the sensitivity is increased since more ions reach the high vacuum region). Increase in the cone voltage from 30 to 40 V initiated the effective decomposition of $[B15C5 + Cu + ClO_4]^+$ ion, whose abundance was decreased by 42%. However, as seen in Figure 2, the increase in the cone voltage from 30 to 40 V initiated only small decomposition of $[NO_2-B15C5 + Cu + ClO_4]^+$ ion, whose abundance was decreased by 24%. In other words, the loss of ClO_4^- proceeds more readily for B15C5 complex than for $NO_2-B15C5$ complex. Analogous results were obtained for the complexes containing other counter ions used (NO_3^- , Cl^-). It is reasonable to conclude that the anion- π interactions prevent the loss of ClO_4^- from the $[NO_2-B15C5 + Cu + ClO_4]^+$ ions.

If it is true that there is attractive interaction between the anion and the aromatic ring in the $[NO_2-B15C5 + Cu + X]^+$ ion ($X^- = ClO_4^-, NO_3^-, Cl^-$), the repulsive interaction between the electron rich aromatic ring and the anion should also be observable. The loss of the counter ion from $NH_2-B15C5$ should proceed more readily than from B15C5. Figure 3 shows the breakdown plot of the abundances of $[B15C5 + Cu + ClO_4]^+$, $[B15C5 + Cu]^+$, $[NH_2-B15C5 + Cu + ClO_4]^+$, and $[NH_2-B15C5 + Cu]^+$ ions against the cone voltage.

Increase in the cone voltage from 30 to 40 V initiated the decomposition of $[B15C5 + Cu + ClO_4]^+$ ion, whose abundance was decreased by 29%. However, as seen in Figure 3, the decomposition of $[NH_2-B15C5 + Cu +$

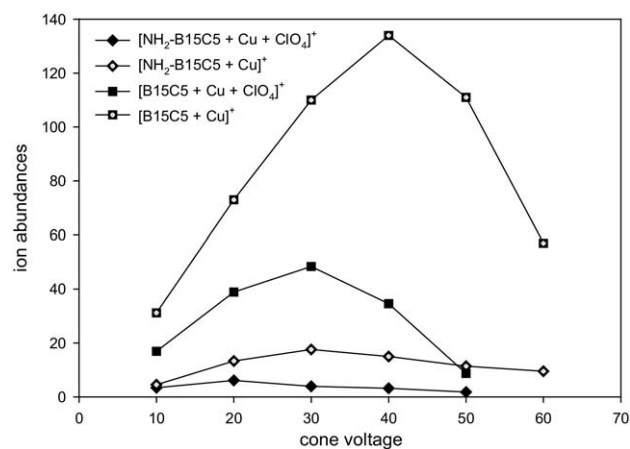


Figure 3. The abundances of $[NH_2-B15C5 + Cu + ClO_4]^+$, $[NH_2-B15C5 + Cu]^+$, $[B15C5 + Cu + ClO_4]^+$, $[B15C5 + Cu]^+$ ions versus the cone voltage (V). The absolute ion abundances (in arbitrary units) taken from mass spectra recorded were divided by 10^6 . The data were obtained from one methanol solution containing $NH_2-B15C5$ (2×10^{-5} mol/dm³), B15C5 (2×10^{-5} mol/dm³), and $Cu(ClO_4)_2$ (5×10^{-5} mol/dm³). Increase in the cone voltage from 30 to 40 V initiated the decomposition of $[B15C5 + Cu + ClO_4]^+$ ion, whose abundance was decreased by 29%. The decomposition of $[NH_2-B15C5 + Cu + ClO_4]^+$ ion was initiated already by the cone voltage increase from 20 V to 30 V (abundance was decreased by 36%).

$ClO_4]^+$ ion was initiated already by the cone voltage increase from 20 to 30 V (abundance was decreased by 36%). In other words, the loss of ClO_4^- proceeds more readily for $NH_2-B15C5$ complex than for B15C5 complex. Analogous results were obtained for the complexes containing other counter ions used (NO_3^- , Cl^-). The $NH_2-B15C5$ molecule contains the aromatic ring enriched in electrons, in comparison to the B15C5. Because of the anion- π repulsion, the loss of the ClO_4^- radical proceeds more readily for $[NH_2-B15C5 + Cu + ClO_4]^+$ ion than for B15C5.

It is worth explaining why the abundance of the $[NH_2-B15C5 + Cu + ClO_4]^+$ ion is so low. First, in the range of low masses, the $[NH_2-B15C5 + H]^+$ ion was observed. Thus, the protonation of $NH_2-B15C5$ molecule prevents the copper complex formation. Second, because of the interactions of the NH_2 group with methanol with a hydrogen bond formation in solution, the ionization efficiency (desolvation) of $[NH_2-B15C5 + Cu + ClO_4]^+$ ion is lowered.

More difficult is to rationalize why the presence of the basic compound $NH_2-B15C5$ in the solution analyzed leads to the high abundance of the copper(I) containing ion, e.g., $[B15C5 + Cu]^+$ already at the cone voltage 10 V (in other words, why the presence of the basic compound facilitates the electrolytic copper reduction). This is the subject of metal redox potentials in relation to pH and will not be discussed here.

It is interesting to check if the size of the crown ethers affects metal reduction at higher cone voltages. Thus, we used 12-crown-4 (12C4) and its respective derivatives. However, the aromatic derivatives of 12C4 were found to be inappropriate compounds for the study because the loss of X^- from $[B12C4 + Cu + X]^+$ was a minor process. For the derivatives containing an aromatic ring, e.g., benzo-12-crown-4 (B12C4), the formation of $[B12C4]^+$ ion (radical cation, formally molecular ion of benzo-12-crown-4) was found to be the main fragmentation pathway of $[B15C5 + Cu + ClO_4]^+$, competing with the ClO_4^- radical loss. The formation of respective radical cations (molecular ions) upon ESI conditions, as a result of the interactions of Cu^{2+} with aromatic systems has been already described [16–18]. Because of a smaller distance, the interactions between Cu^{2+} and the aromatic ring were very effective for B12C4 and hardly detectable for B15C5. Figure 4 shows the ESI mass spectra of a methanol solution containing 12C4, B12C4, and $Cu(ClO_4)_2$ obtained at the cone voltages 20 V (top) and 50 V (bottom).

For the low cone voltage, $[B12C4 + Cu + ClO_4]^+$ ion is characterized by higher abundance than that of $[12C4 + Cu + ClO_4]^+$ ion. At higher cone voltages, $[B12C4 + Cu + ClO_4]^+$ ion is characterized by lower abundance than $[12C4 + Cu + ClO_4]^+$. Lower abundance of the former ion is caused by its very efficient fragmentation involving the formation of $[B12C4]^+$ ion. The loss of ClO_4^- radical is a minor fragmentation pathway of $[B12C4 + Cu + ClO_4]^+$ ion. The $[B12C4 +$

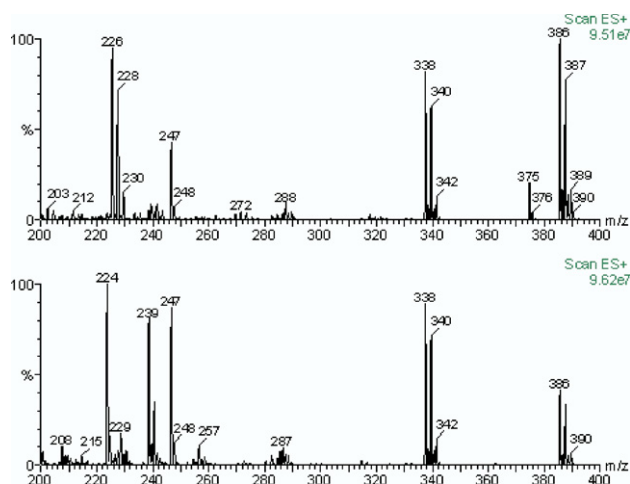


Figure 4. ESI mass spectra obtained for a methanol solution containing 12C4, B12C4 and $\text{Cu}(\text{ClO}_4)_2$ (cone voltage 20 V, top, cone voltage 50 V, bottom). $[\text{B12C4} + \text{Cu} + \text{ClO}_4]^+$ m/z 386, $[\text{B12C4} + \text{Cu}]^+$ m/z 287, $[\text{B12C4}]^+$ m/z 224, $[\text{B12C4} + \text{Na}]^+$ m/z 247, $[\text{12C4} + \text{Cu} + \text{ClO}_4]^+$ m/z 338, $[\text{12C4} + \text{Cu}]^+$ m/z 239.

$\text{Cu}]^+$ ion is characterized by low abundance in contrast to $[\text{12C4} + \text{Cu}]^+$ ion (Figure 4, bottom).

The use of benzo-18-crown-6 (B18C6) also yielded an abundant $[\text{B18C6}]^+$ ion similarly as described above for B12C4. The question is why the formation of copper(I) containing complex ($[\text{B15C5} + \text{Cu}]^+$ ion) from $[\text{B15C5} + \text{Cu} + \text{X}]^+$ ion is favored over the formation of $[\text{B15C5}]^+$ and for B12C4 and B18C6 we have the opposite situation. The answer was provided by the so-called best-fit concept. The radii of the cations Cu^{2+} and Cu^+ are 72 and 96 pm, respectively [19]. It is well known that Na^+ cation, which has the radius of 98 pm, fits very well into the cavity of 15-crown-5 [20]. Thus, the Cu^+ cation also forms stable complexes with 15C5 and its derivatives.

One can suggest that different efficiencies of the loss of X $^\cdot$ from $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{X}]^+$ and $[\text{B15C5} + \text{Cu} + \text{X}]^+$ ions are caused by the interactions of copper cation with aromatic rings. However, as described above, if such interactions exist, the respective radical cations (e.g., $[\text{B12C4}]^{\cdot+}$) are formed.

Crown Ether- Fe^{3+} Complexes

Figure 5 shows the ESI mass spectra obtained for a methanol solution containing $\text{NO}_2\text{-B15C5}$, B15C5 and $\text{Fe}(\text{NO}_3)_3$ at the cone voltage 10 V (top), 30 V (bottom).

The parent ions are $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ and $[\text{B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ (deprotonation of coordinated solvent molecule is a common way of charge reduction in the ESI conditions [11]. These ions lose the $\text{CH}_3\text{O}^\cdot$ radical (the loss of NO_3^\cdot radical has been observed at the cone voltage 50 V and higher). Analogous results were obtained for solutions containing $\text{NO}_2\text{-B15C5}$, B15C5, and $\text{Fe}(\text{ClO}_4)_3$. For the solution containing $\text{NO}_2\text{-B15C5}$, B15C5, and FeCl_3 the presence of $[\text{NO}_2\text{-15C5} + \text{Fe} + 2\text{Cl}]^+$ and $[\text{B15C5} +$

$\text{Fe} + 2\text{Cl}]^+$ ions was observed, and at the higher cone voltage the loss of Cl^\cdot radical proceeded.

As can be concluded from Figure 5, the decomposition of $[\text{B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ ion proceeds more readily than that of $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ ion. The relative abundance of ion $[\text{B15C5} + \text{Fe} + \text{NO}_3]^+$ increased from 18% to 100% when the cone voltage was adjusted from 10 to 30 V, while the relative abundance of ion $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3]^+$ increased from 12% to 56%. Thus (analogously as for the copper complexes), it is reasonable to conclude that the anion- π interactions prevent the loss of $\text{CH}_3\text{O}^\cdot$ from ion $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ (showing the breakdown plot of the abundances of iron containing ions against the cone voltage seems to be unnecessary).

The radii of the cations Fe^{3+} and Fe^{2+} are 67 and 82 pm, respectively [19]. It is well known that the Li^+ cation, which has a radius of 58 pm, fits very well into the cavity of 12C4, and the Na^+ cation, which has a radius of 98 pm, fits very well into the cavity of 15-crown-5 [20]. Thus, the best-fit concept cannot be valid for iron cations; fortunately, the radical cations (e.g., ion $[\text{B15C5}]^{\cdot+}$) have not been formed from iron containing ions.

Crown Ether- Hg^{2+} Complexes

The Hg^{2+} ion has a greater radius than Cu^{2+} and Fe^{3+} , thus to analyze its complexes we used 18-crown-6 derivatives. It is well known that the cation K^+ , which has a radius of 133 pm, fits very well into the cavity of 18-crown-6 [20]. Thus, the derivatives of 18C6 seem to be appropriate for formation of inclusion complexes with mercury cations. However, mercury reduction was not observed and the formation of organometallic species proceeded. At the higher cone voltages, abundant ions $[\text{NO}_2\text{-B18C6} - \text{H} + \text{Hg}]^+$ and $[\text{B18C6} - \text{H} + \text{Hg}]^+$

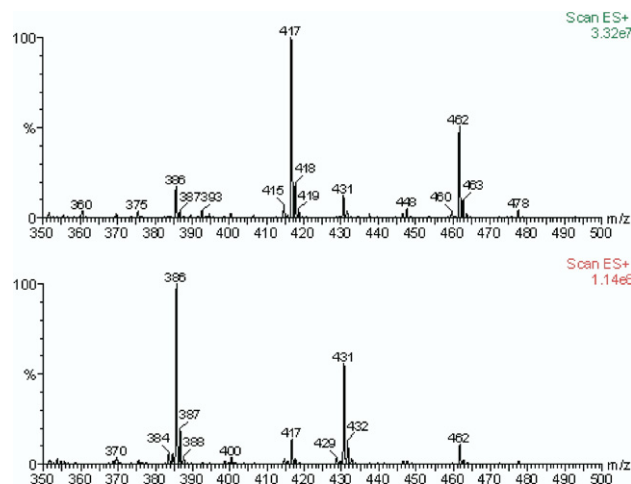


Figure 5. ESI mass spectra obtained for a methanol solution containing $\text{NO}_2\text{-B15C5}$, B15C5, and $\text{Fe}(\text{NO}_3)_3$ at the cone voltage 10 V (top), 30 V (bottom). $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ m/z 462, $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3]^+$ m/z 431, $[\text{B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ m/z 417, $[\text{B15C5} + \text{Fe} + \text{NO}_3]^+$ m/z 386.

were detected, but not the $[\text{NO}_2\text{-B18C6} + \text{Hg}]^+$ and $[\text{NO}_2\text{-B18C6} + \text{Hg}]^+$ ones. In other words, the loss of HClO_4 molecule took place but the loss of ClO_4^- radical did not. The $[\text{NO}_2\text{-B18C6} - \text{H} + \text{Hg}]^+$ and $[\text{B18C6} - \text{H} + \text{Hg}]^+$ ions should be regarded as organometallic species formed as a consequence of the C–H bond activation and will not be discussed here. The C–H bond activation is a common phenomenon in the ESI conditions [21–23], but it cannot be used in the study of the anion– π interactions. The presence/lack of NO_2 group on the aromatic ring surely affects the C–H bond activation, thus it cannot be concluded that the observed differences are caused by the anion– π interactions.

Conclusions

The loss of X^\cdot radical (copper reduction) occurs with lower efficiency for $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{X}]^+$ ions than for $[\text{B15C5} + \text{Cu} + \text{X}]^+$ ions (X^- – the counter ion). The cone voltage necessary to initiate the effective loss of X^\cdot radical form $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{X}]^+$ is higher than that to initiate the loss of X^\cdot radical from $[\text{B15C5} + \text{Cu} + \text{X}]^+$. It is reasonable to conclude that the anion– π interactions prevent the loss of X^\cdot from the $[\text{NO}_2\text{-B15C5} + \text{Cu} + \text{X}]^+$ ions. The presence of NO_2 group implies that the aromatic ring is poor in electrons and its interactions with anions are possible. For the ion containing an aromatic ring enriched in electrons, namely $[\text{NH}_2\text{-B15C5} + \text{Cu} + \text{ClO}_4]^{+}$, the opposite situation is observed. Because of the anion– π repulsion, the loss of X^\cdot radical proceeds more readily for $[\text{NH}_2\text{-B15C5} + \text{Cu} + \text{X}]^+$ than for $[\text{B15C5} + \text{Cu} + \text{X}]^+$ ion. Iron reduction was also found to be affected by the anion– π interactions. Namely, the loss of $\text{CH}_3\text{O}^\cdot$ radical from $[\text{B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ ion proceeds more readily than from $[\text{NO}_2\text{-B15C5} + \text{Fe} + \text{NO}_3 + \text{CH}_3\text{O}]^+$ ion. If interactions of copper cation with aromatic rings exist, the respective radical cations (e.g., $[\text{B12C4}]^{+}$ from $[\text{B15C5} + \text{Cu} + \text{X}]^+$) are formed.

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