



Short communication

Influence of alkali metal cations on mixed tetramer formed by guanosine and cytidine – GCGC



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ABSTRACT

By using electrospray ionization mass spectrometry, it was found that larger alkali metal cations (K^+ , Rb^+ , Cs^+) favor formation of mixed tetramer **GCGC**. This tetramer, cationized by these cations (ions $[2C+2G+K]^+$, $[2C+2G+Rb]^+$ and $[2C+2G+Cs]^+$), was more abundant than other tetramers cationized by these cations (e.g. $[2C+2G+K]^+ > [C+3G+K]^+$). The observed influence of K^+ , Rb^+ and Cs^+ on mixed **GCGC** tetramer is different from their influence on mixed dimer **GC**, since K^+ , Rb^+ and Cs^+ disfavor formation of mixed dimer **GC** (e.g. $[2C+Rb]^+ > [C+G+Rb]^+ < [2G+Rb]^+$). As demonstrated by CID MS/MS spectra, gas phase decomposition of cationized **GCGC** is dominated by loss of cytidine molecule.

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1. Introduction

The most common (well known) complex formed by guanine and cytosine is one of the Watson–Crick base pairs – **GC**. Other biologically important complex formed by guanine and cytosine is the mixed tetramer – **GCGC** [1–9]. Similarly as the well-known guanine tetramer **G4** [10] (called also **G**-quartet, **G**-quadruplex, **G**-tetrad), the tetramer **GCGC** formation is based on the respective hydrogen bonds. For **G4** formation the stabilization by alkali metal cation (sodium or potassium) is of crucial importance, as demonstrated by electrospray ionization mass spectrometry (ESI-MS) [11–15]. However, the influence of metal cation on **GCGC** formation has not been widely studied [16–18]. In this paper the influence of alkali metal cations on the formation of **GCGC** is studied by using ESI-MS. The effect of alkali metal cations on the dimer and trimer is also discussed for comparison. It is worth adding that mass spectrometric techniques have found a number of applications in the study of nucleic acids and nucleic acid constituents [19,20].

2. Experimental

Full scan ESI mass spectra and CID MS/MS spectra were taken on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK).

The sample solutions were prepared in methanol (the most common solvent for ESI) at guanosine (**G**), cytidine (**C**) and alkali metal concentrations 10^{-5} mol/dm³ (the concentrations refer to each ingredient, not to the sum). Guanine is hardly soluble in methanol; thus, it is reasonable to take respective nucleosides. Further in the text, letters **G** and **C** refer to the nucleosides (guanosine and cytidine), not to the nucleobases (guanine and cytosine). Respective chlorides (LiCl, KCl, RbCl, CsCl) were used as the source of alkali metal cations. Sodium chloride was not added since abundant sodium adducts were observed without adding sodium cation. It is difficult to control, or to remove, sodium cation at concentration level 10^{-5} mol/dm³. Potassium adducts were also observed without adding potassium cation; however, in order to increase the potassium adduct abundances, potassium cation has been added.

The sample solutions were infused into the ESI source by a syringe pump at a flow rate of 5 μ l/min. The electrospray voltage was 2.7 kV and the cone voltage was 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 800 l h⁻¹, respectively. Argon was used as a collision gas at the flow-rate 0.5 ml/min in the collision cell. Collision energy, the most important parameter for MS/MS experiments, is indicated in particular figure captions.

3. Results and discussion

Although the subject of this paper is the tetramer **GCGC**, at first the dimers **GC**, cationized by alkali metal cations, observed in ESI

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mass spectra will be briefly discussed. Fig. 1 shows the ESI mass spectra, in dimer m/z range, obtained for a solution containing cytidine (C) and guanosine (G).

Fig. 1a shows the ESI mass spectrum obtained for a solution with lithium cation added (Na and K were not added but their adducts are always detected). Signal of the Li^+ cationized cytidine dimer is higher than signal of the Li^+ cationized mixed dimer and the latter signal is higher than signal of the Li^+ cationized guanosine dimer ($[2\text{C}+\text{Li}]^+ > [\text{C}+\text{G}+\text{Li}]^+ > [2\text{G}+\text{Li}]^+$). Electro spray is a very soft ionization technique; thus, the signal intensities strongly depend on ion concentrations in solution. Obviously the intensities of the signals of the discussed dimers may be affected by a few factors, e.g. their decomposition, formation of dimer from trimer, desolvation energy. Fig. 1b shows the ESI mass spectrum obtained for a solution containing cytidine and guanosine. Sodium cation was not added but the signal of sodium adducts is intense enough. The signal intensities reflect the same order as for lithium adducts, namely $[2\text{C}+\text{Na}]^+ > [\text{C}+\text{G}+\text{Na}]^+ > [2\text{G}+\text{Na}]^+$. Fig. 1c shows the ESI mass spectrum obtained for a solution with potassium cation added (similarly as in sodium adducts, potassium adducts are always detected but when potassium cation is added potassium adducts are more abundant). Relative intensities of potassium adducts are not the same as for lithium and sodium adducts. The order of signal intensities is $[2\text{C}+\text{K}]^+ > [2\text{G}+\text{K}]^+ > [\text{C}+\text{G}+\text{K}]^+$; thus, mixed dimer has the lowest abundance. Analogical order of signal intensities has been observed for Rb^+ and Cs^+ cationized dimers, namely $[2\text{C}+\text{Rb}]^+ > [2\text{G}+\text{Rb}]^+ > [\text{C}+\text{G}+\text{Rb}]^+$ and $[2\text{C}+\text{Cs}]^+ > [2\text{G}+\text{Cs}]^+ > [\text{C}+\text{G}+\text{Cs}]^+$. Thus, the conclusion can be drawn that larger alkali metal cations disfavor the formation of mixed dimer **GC** (in spite the fact that hydrogen bonded dimer **GC** is one of the Watson–Crick base pairs).

Fig. 2 shows the ESI mass spectra, in trimer and tetramer m/z range, obtained for a solution containing cytidine (C) and guanosine (G).

Fig. 2a shows the ESI mass spectrum obtained for a solution with lithium cation added. Only two trimers have been detected, namely $[3\text{C}+\text{Li}]^+$ and $[2\text{C}+\text{G}+\text{Li}]^+$. There are also sodium adducts, among them the well-known **G4** tetramer, thus ion $[4\text{G}+\text{Na}]^+$. Fig. 2b shows the ESI mass spectrum obtained for a solution containing cytidine and guanosine. Signals of sodium adducts are characterized by high intensities. The abundances of the trimers decrease in the order $[3\text{C}+\text{Na}]^+ > [2\text{C}+\text{G}+\text{Na}]^+ > [\text{C}+2\text{G}+\text{Na}]^+$, while the abundances of tetramers decrease in the order $[4\text{G}+\text{Na}]^+ > [\text{C}+3\text{G}+\text{Na}]^+ > [2\text{C}+2\text{G}+\text{Na}]^+$. Thus, the expected conclusion can be drawn that for sodium adducts, cytidine is more prone than guanosine to form trimers, whereas guanosine is more prone than cytidine to form tetramers (sodium cation does not favor formation of mixed tetramer **GCGC**). Fig. 2c shows the ESI mass spectrum obtained for a solution with potassium cation added. The abundances of trimers decrease in the same order as those of sodium adducts, namely $[3\text{C}+\text{K}]^+ > [2\text{C}+\text{G}+\text{K}]^+ > [\text{C}+2\text{G}+\text{K}]^+$. However, the abundances of tetramers do not decrease in the same order as for sodium adducts. The most abundant tetramer is mixed one, namely the ion $[2\text{C}+2\text{G}+\text{K}]^+$. It indicates that potassium cation, in contrast to smaller sodium and lithium cation, favors formation of important mixed tetramer **GCGC**. Larger alkali metal cation Rb^+ and Cs^+ also favors formation of tetramer **GCGC**, as it is clearly seen in Fig. 2d and e (in relation to other tetramers, ions $[2\text{C}+2\text{G}+\text{Rb}]^+$ and $[2\text{C}+2\text{G}+\text{Cs}]^+$ are abundant). In other words formation of tetramer **GCGC** in the presence of larger alkali metal cations (K^+ , Rb^+ , Cs^+) is favored.

Fig. 2d and e also shows that Rb^+ and Cs^+ favor the formation of trimers **CG2** ($[\text{C}+2\text{G}+\text{Rb}]^+ > [2\text{C}+\text{G}+\text{Rb}]^+$ and $[\text{C}+2\text{G}+\text{Cs}]^+$ is the only cesium cationized trimer detected).

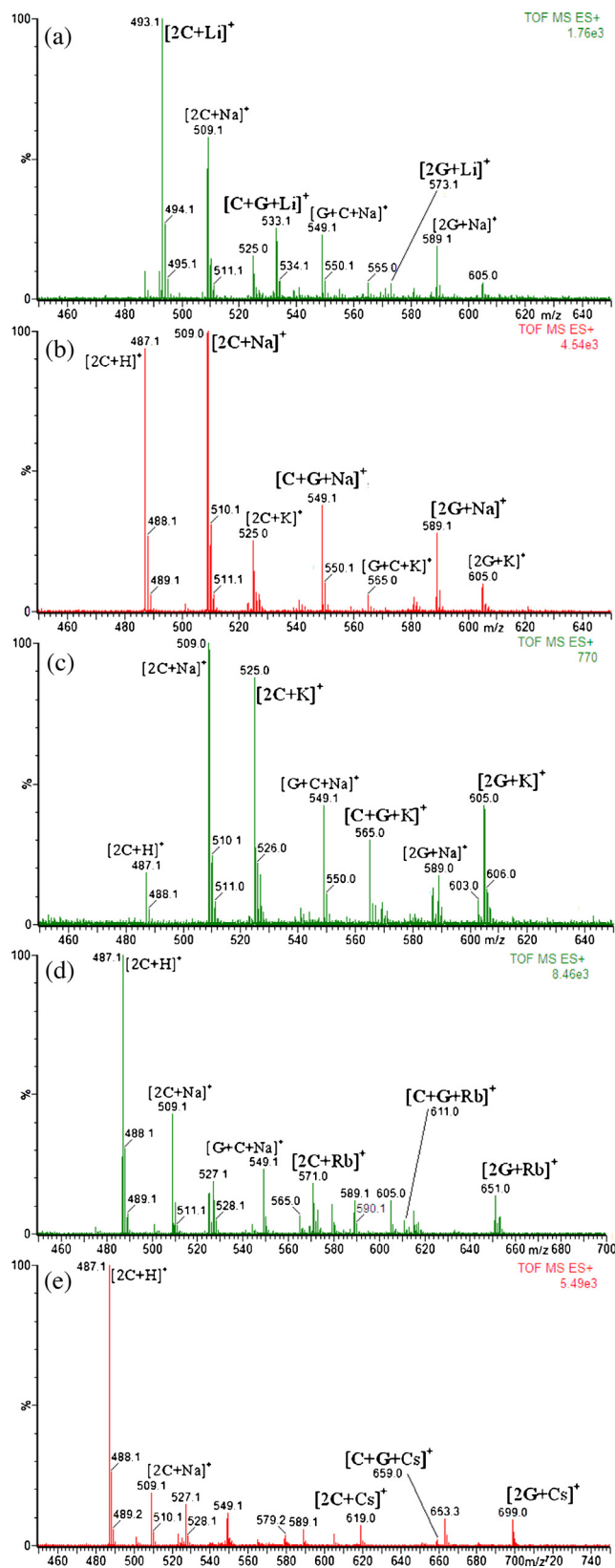


Fig. 1. Full scan ESI mass spectra, in dimer m/z range, obtained for solution containing cytidine (C) and guanosine (G). (a) Li^+ added, (c) K^+ added, (d) Rb^+ added, (e) Cs^+ added.

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