

Quintets of uracil and thymine: a novel structure of nucleobase self-assembly studied by electrospray ionization mass spectrometry

by Bo Qiu et al (2009)

Supporting material

Experimental Sections

Chemicals

HPLC grade methanol was purchased from Fisher Scientific (Pittsburgh, PA, USA). Uracil, 1-methyluracil, 3-methyluracil, 1,3-dimethyluracil, thymine, 5-ethyluracil, 5,6-dimethyluracil, and 4-thiouracil were obtained from Sigma-Aldrich (St. Louis, MO, USA). 6-Methyluracil was purchased from Tokyo Chemical Industry (Tokyo, Japan). 2-Thiouracil was obtained from J&K Chemical LTD (Beijing, China). Alkali metal salts (LiCl, NaCl, KCl, RbCl and CsCl) were purchased from Acros Organics (Morris Plains, NJ, USA).

ESI-MS

All experiments were performed in positive ion mode on a Thermo Finnigan LCQ Advantage MAX ion-trap mass spectrometer (San Jose, CA, USA) with a home-build open access ESI source.¹ The main experimental parameters used were as follows: spray voltage 5.5 kV, capillary voltage 8.0 V, tube lens offset 0.0 V, heated capillary temperature 150 °C, nebulizing gas pressure 0.4 MPa. The samples were dissolved in solution of methanol/water (1:1), and were introduced into the emitter at a flow rate of 2.5 μ L/min. To obtain collision energy dependent dissociation profiles, the non-covalent complexes were isolated in the ion trap and activated by gradually increasing collision energies (in 1% increment from 5% to 15% relative collision energies). The resonant excitation occurred at a q_z value of 0.25 for 30 ms. All MS data were processed using the instrument software (Xcalibur version 1.4 SR1).

Computational Method

To save calculation time, the preliminary optimization was carried out on the base of MM2 force field from Chem3D ultra 8.0.3. Then the non-covalent complexes, $[U_5 + Na]^+$ and $[U_5 + K]^+$, were fully optimized by using Gaussian 03W with DFT method at B3LYP/6-311 G(*d*, *p*) level.

Reference

1. B. Qiu, H. Luo, *J. Mass. Spectrom.*, published online on January 21, 2009.

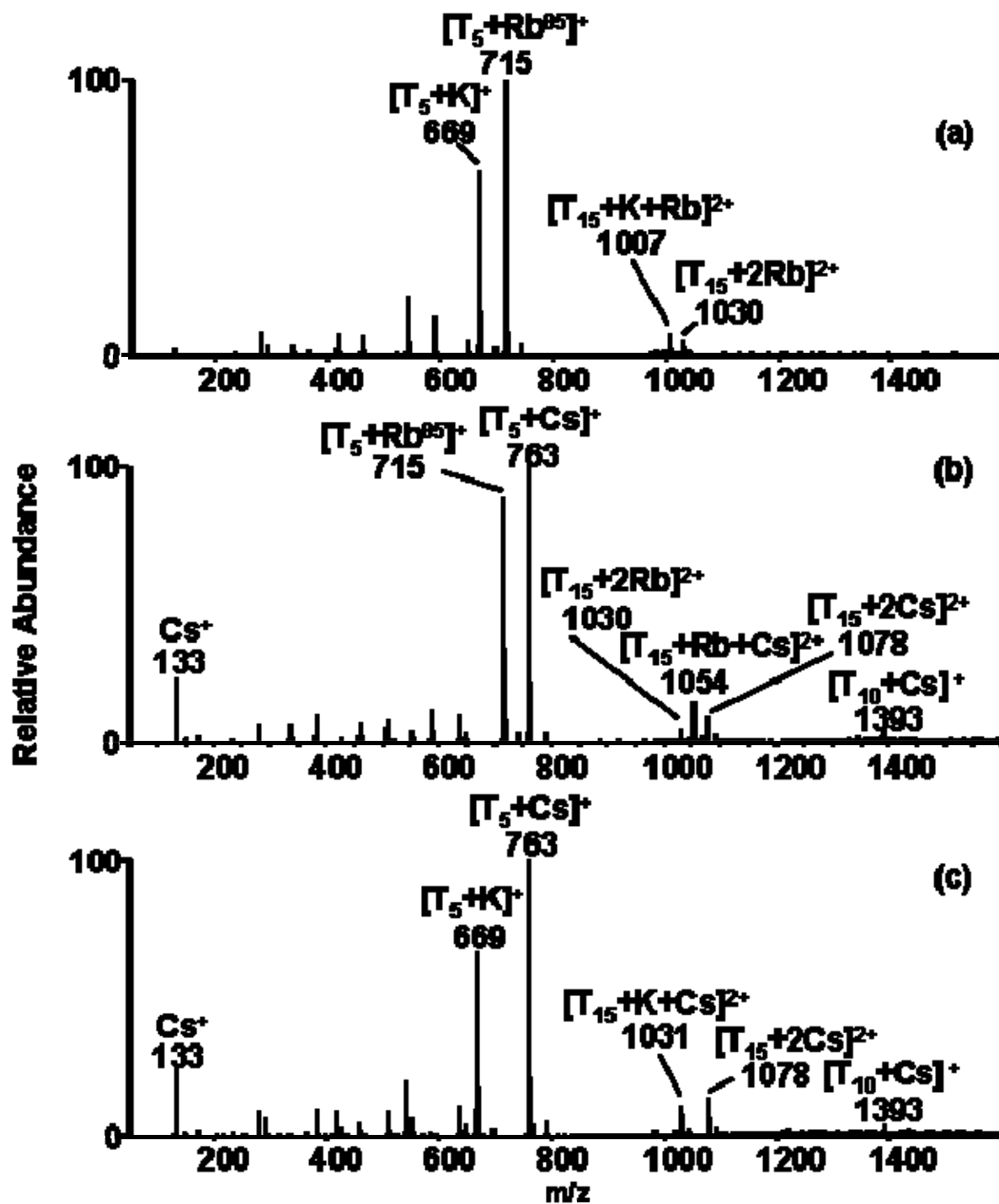


Fig. S1. ESI mass spectra of 6.0×10^{-4} M thymine mixed with 2.0×10^{-4} M KCl and 2.0×10^{-4} M RbCl (a); 2.0×10^{-4} M RbCl and 2.0×10^{-4} M CsCl (b); 2.0×10^{-4} M KCl and 2.0×10^{-4} M CsCl (c). The signal of $[T_5 + Rb^{87}]^+$ which is not labeled in the figures was also included in the total ion intensity of $[T_5 + Rb]^+$ for the comparison.

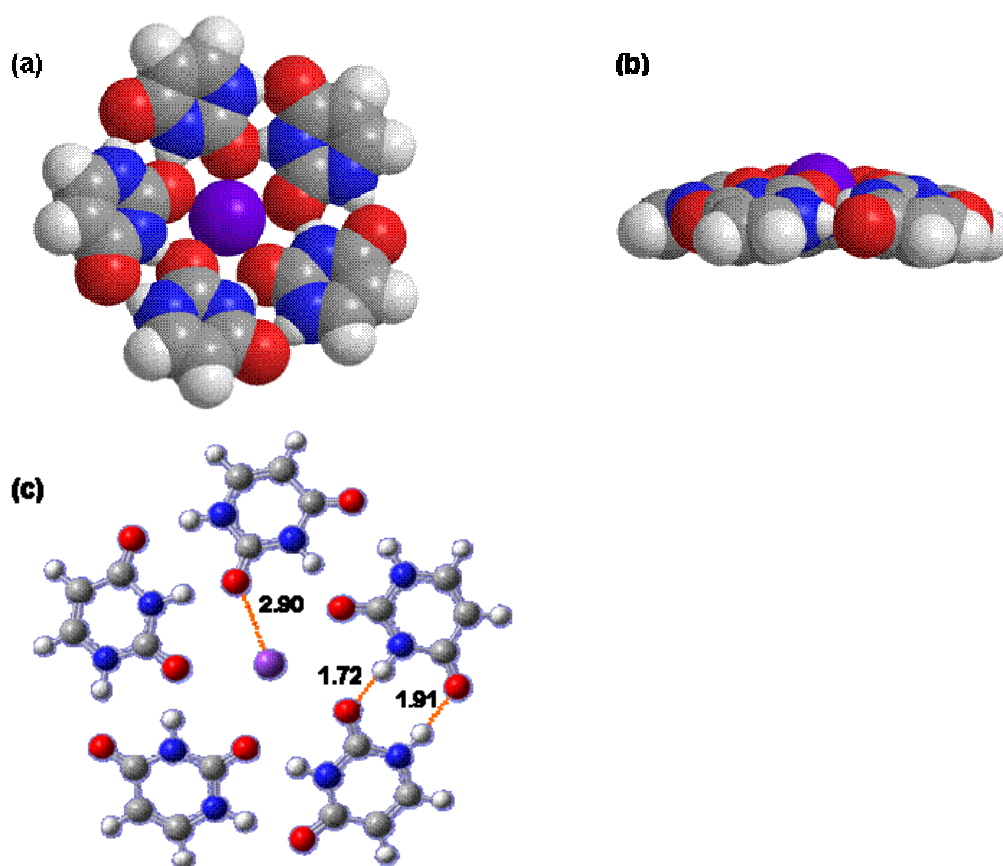


Fig. S2. The optimized structure of $[U_5 + K]^+$ in "space filling" mode (a) top view, (b) side view, and "ball and stick" mode (c). The bond length is in Å. Color representations for atoms are: red for O; blue for N; grey for C; white for H; purple for metal ion.

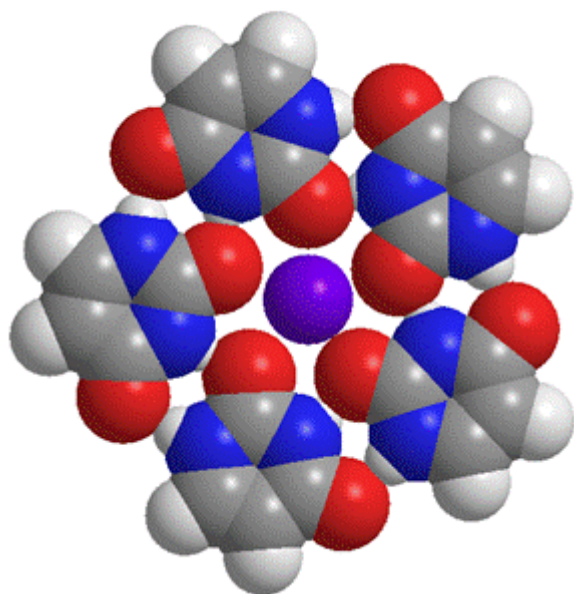


Fig. S3. The optimized structure of $[U_5 + Na]^+$ in “space filling” mode. Color representations for atoms are: red for O; blue for N; grey for C; white for H; purple for metal ion.