Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

Interaction of Cu^+ with cytosine and formation of *i*-motif-like C-M^+-C complexes: alkali versus coinage metals

Juehan Gao[1], Giel Berden[1], M. T. Rodgers[2], Jos Oomens[1,3]*

[1]Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands

[2]Department of Chemistry Wayne State University, Detroit, MI 48335 USA

[3]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

*Corresponding author: Phone: (+31) 24 3653950. E-mail: joso@science.ru.nl

SUPPORTING INFORMATION

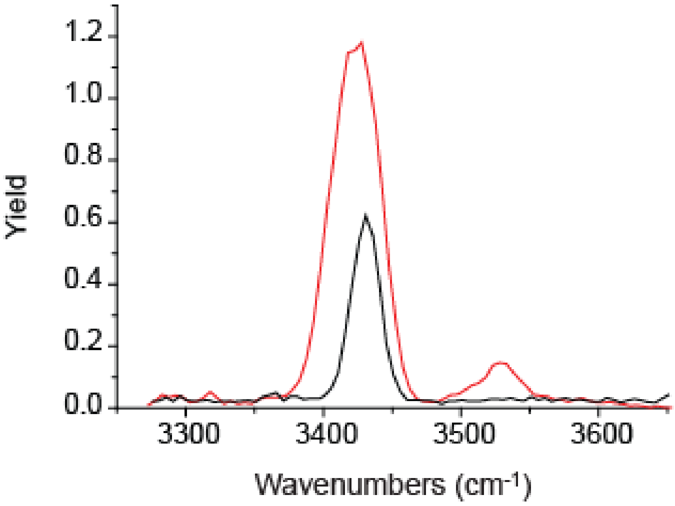

Figure S1: *Experimental IRMPD spectrum of Cu^+Cytosine between 3300 - 3700 cm^{-1} recorded with additional CO_2-laser irradiation (in red) and without additional irradiation (in black). The comparison shows that the main IR absorption band is broader and slightly (8 cm^{-1}) red-shifted when using the CO_2 laser as post-excitation after OPO irradiation. Use of the CO_2 laser allows us to observe the NH asymmetric stretching mode around 3528 cm^{-1}, which would otherwise have been missed.*

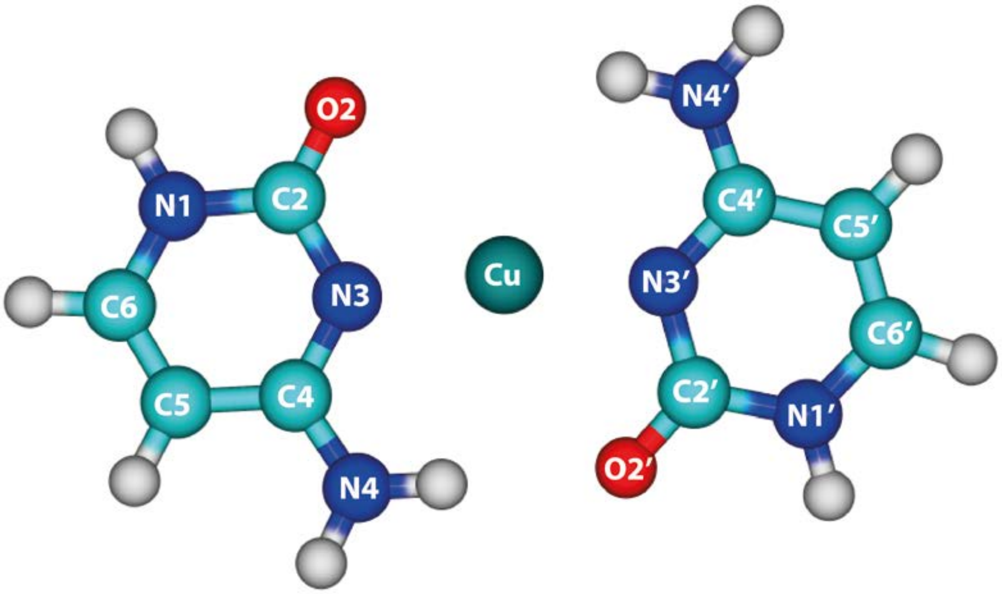

Figure S2: *Atom numbering used in this study (structure shown is* Cu^+ $C1_{N3}C1_{N3}$*).*

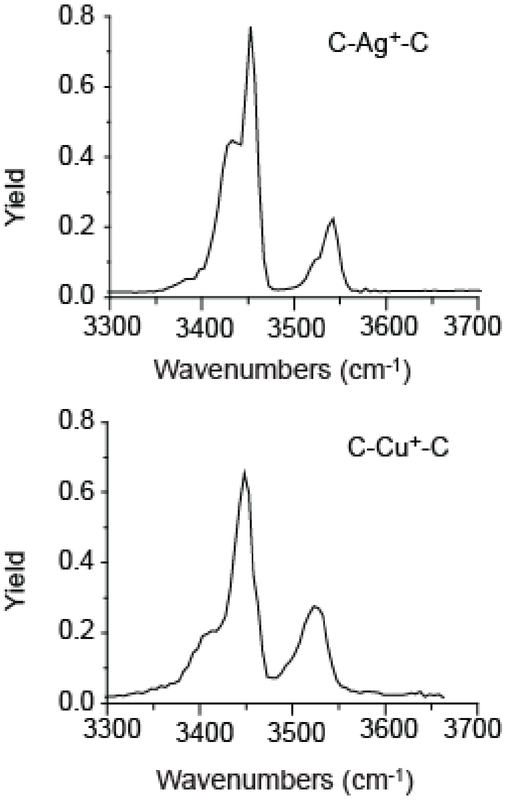

Figure S3: *Comparison of the experimental IRMPD spectra of* $C\text{-}Cu^+\text{-}C$ *and* $C\text{-}Ag^+\text{-}C$ *in the hydrogen-stretching region shows that in both cases no band is observed around 3330* cm^{-1}*, where the strong absorption due to the hydrogen-bonded NH-stretching mode is predicted (see Figure 3 in the main text). We speculate that strong anharmonic effects cause the non-observation and/or mis-calculation of this mode.*

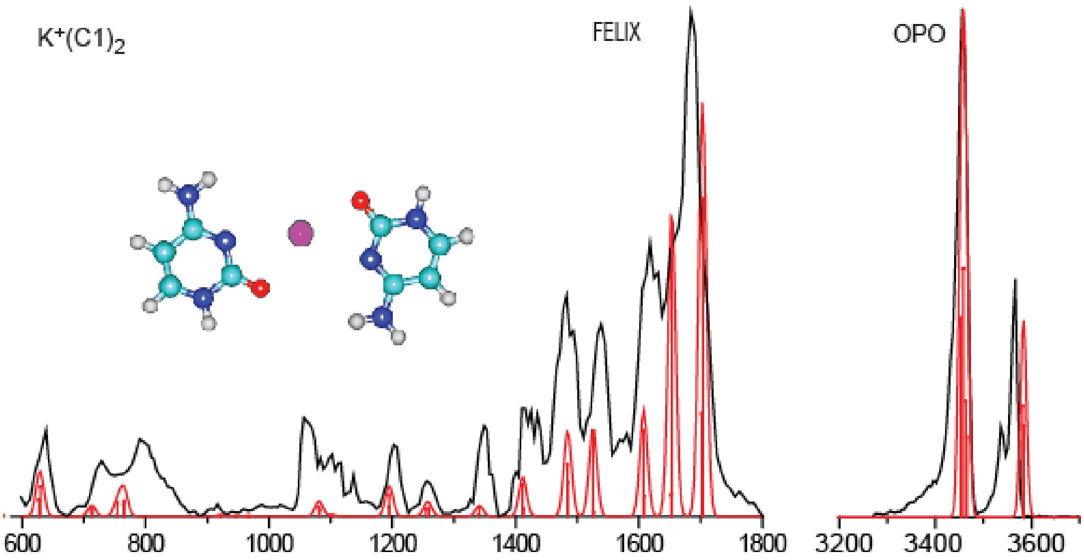

Figure S4: *Experimental IRMPD spectrum of C-K^+-C (black trace), compared with the computed spectrum for the $C1_{N3O}C1_{N3O}$ isomer of this complex (red trace).*

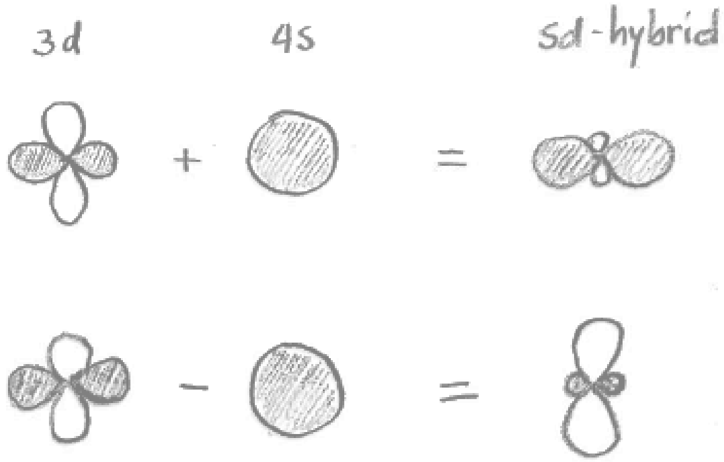

Figure S5: *Valence Bond picture of sd hybridization explaining n-donor ligand binding at 180^o. A filled 3d atomic orbital and the empty 4s orbital form linear combinations resulting in two sd-hybrid atomic orbitals, one being doubly occupied and hence repulsive, and one being empty and accepting electron density from n-donor ligands.*

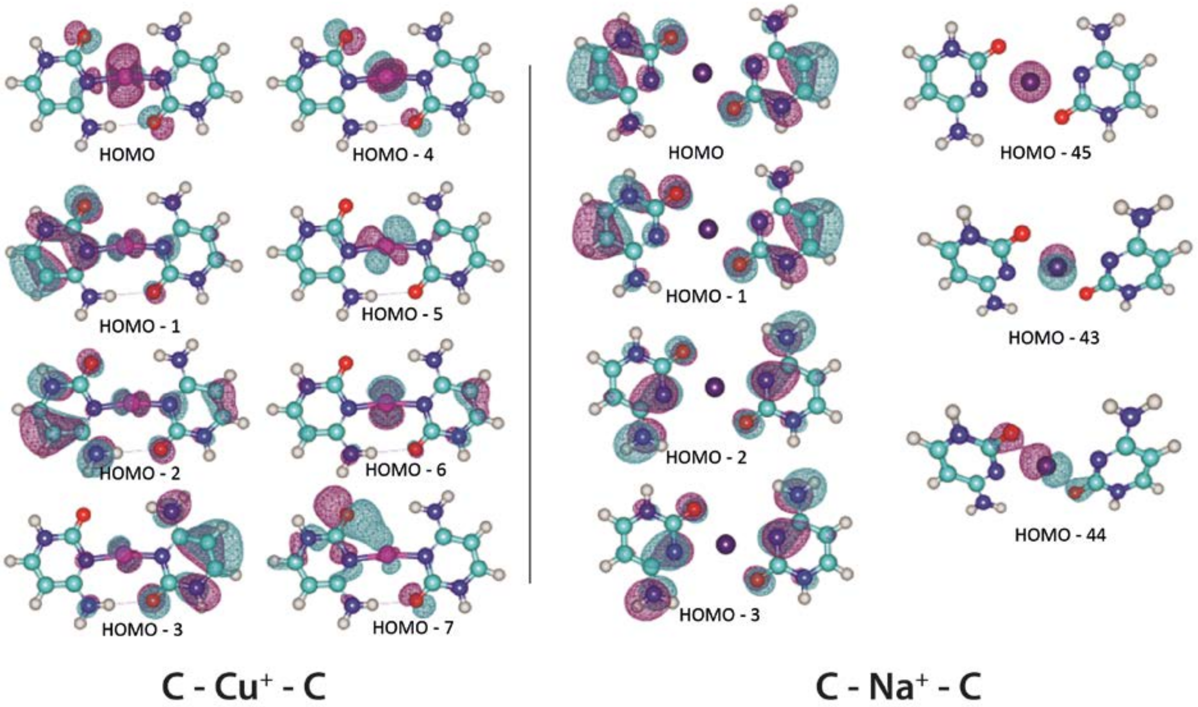

Figure S6: *Comparison of a selection of computed MO's for C-Cu$^+$-C (left) and C-Na$^+$-C (right), suggestive of a more covalent interaction of the cytosine nucleobases with Cu$^+$ versus a more electrostatic interaction with Na$^+$.*