Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

On the stability of $[(uracil)_2\text{-}Cu]^{2+}$ complexes in the gas phase. Different pathways for the formation of $[(uracil\text{-}H)(uracil)\text{-}Cu]^{+}$ monocations.

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Supporting Information

(A total of 5 pages)

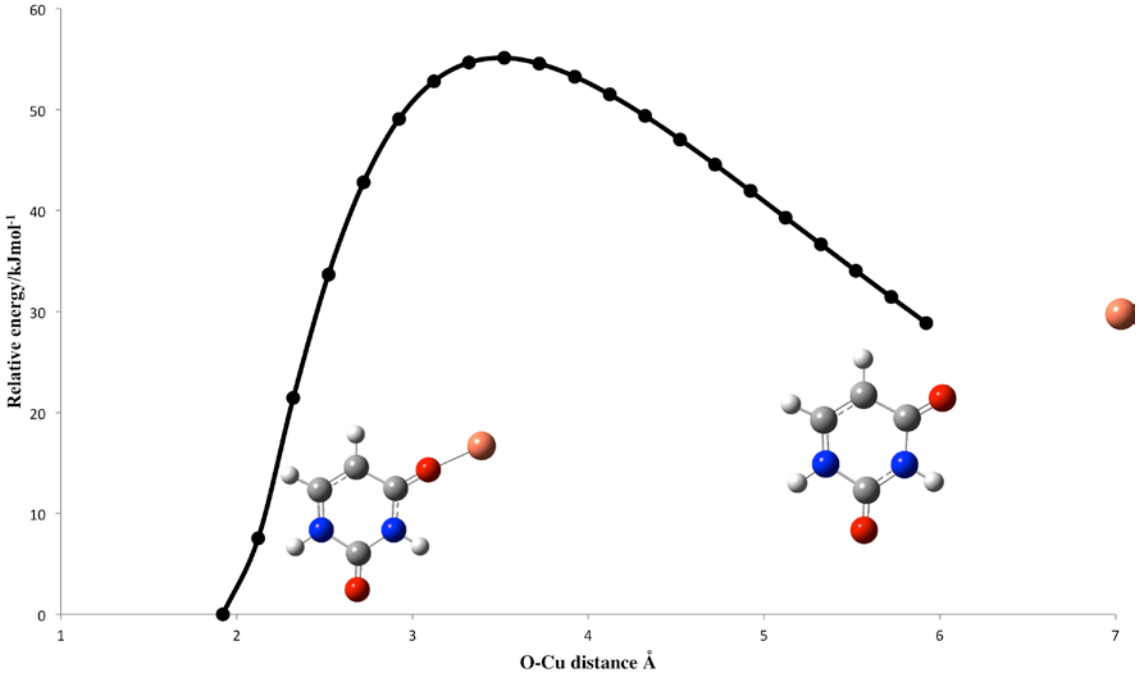

Figure S1. Calculated energy barrier corresponding to the $(uracil\text{-}Cu)^{2+} \rightarrow uracil^{+} + Cu^{+}$ dissociation.

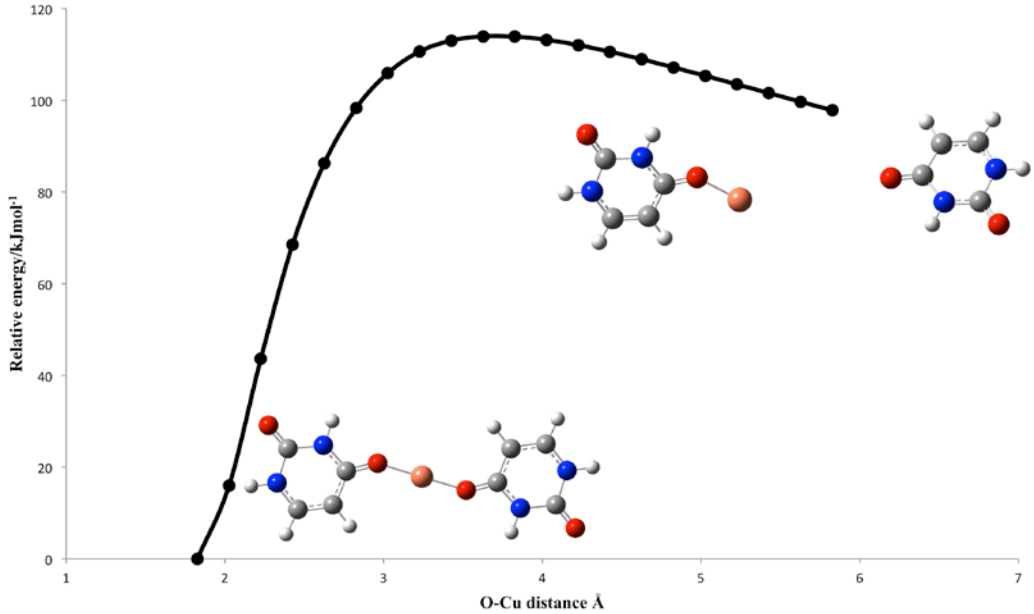

Figure S2. Calculated energy barrier corresponding to the $[(uracil)_2\text{-}Cu]^{2+} \rightarrow (uracil\text{-}Cu)^{+} + uracil^{+}$ dissociation.

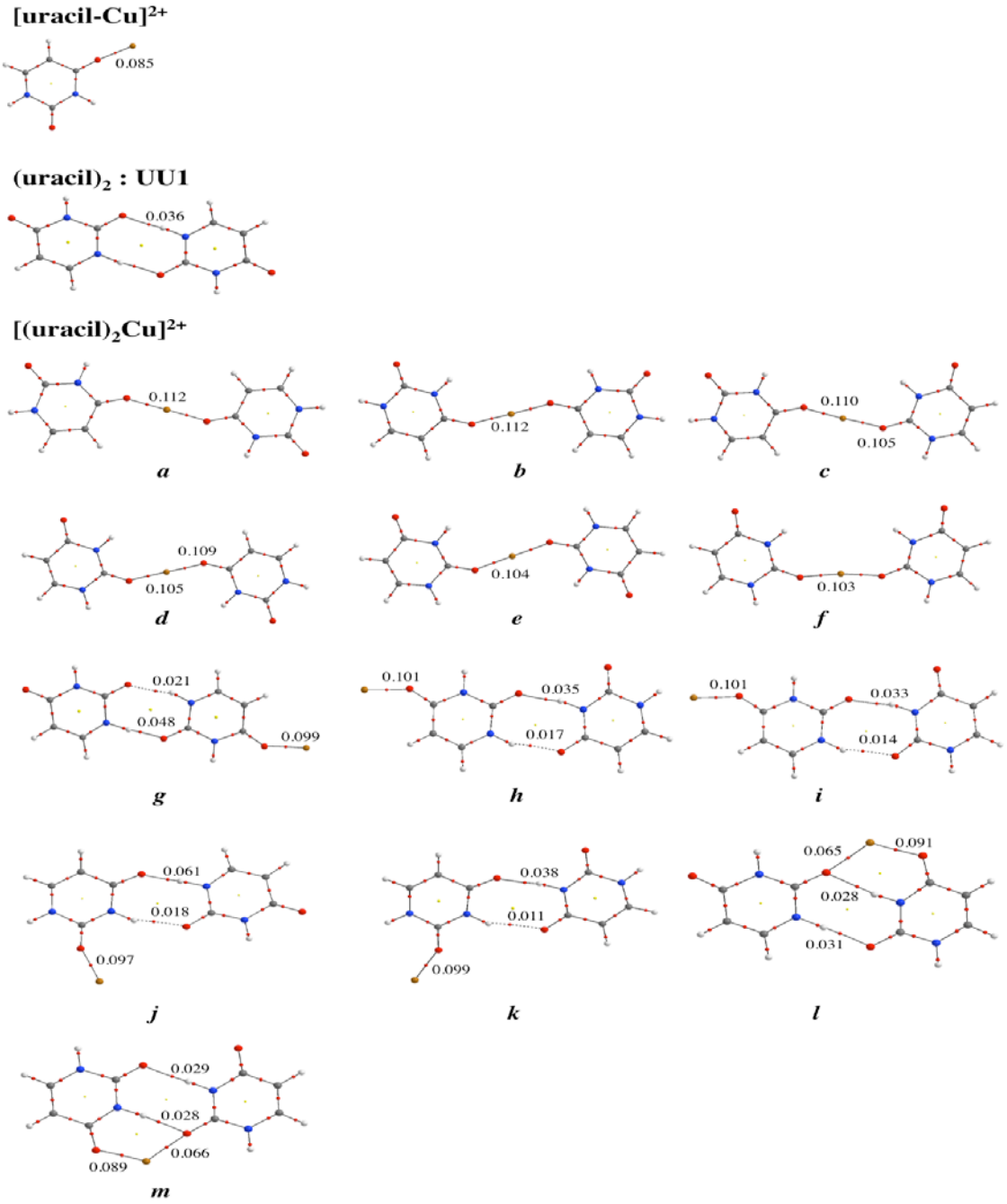

Figure S3. Molecular graphs for the most stable $[(uracil)_2Cu]^{2+}$, $[(uracil)Cu]^{2+}$complexes, and $(uracil)_2$. Red and yellow dots denote bond and ring critical points respectively. Electron densities are given in a.u.

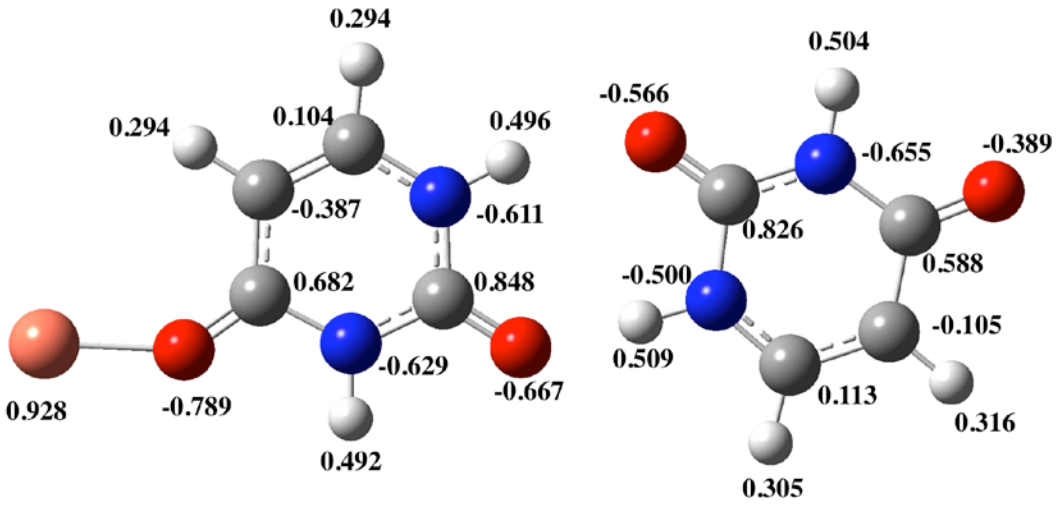

Figure S4. Natural net charges of the different atoms of complex ***g***. The spin density is located on the uracil unit which does not interact directly with the metal.

Table S1. Total energies (**E**), Zero point vibrational energies (**ZPE**), Thermal corrections (298.15 K and 1 atm) to the enthalpy (**TCE**), and to the free energy (**TCG**) for the local minima of $[(uracil)_2Cu]^{2+}$ and $[(uracil)(uracil\text{-}H)Cu]^{+}$ complexes and the transition states involved in the mechanisms shown in Figures 3, 4 and 7. All values are in hartrees.

Complexes	E	ZPE	TCE	TCG
$[(uracil)_2Cu]^{2+}$				
a	-2469.871	0.176	0.192	0.128
b	-2469.870	0.176	0.192	0.127
c	-2469.861	0.176	0.192	0.126
d	-2469.861	0.176	0.192	0.127
e	-2469.853	0.175	0.191	0.126
f	-2469.852	0.175	0.191	0.125
g	-2469.848	0.175	0.191	0.127
h	-2469.846	0.175	0.191	0.126
i	-2469.844	0.175	0.191	0.126
j	-2469.838	0.175	0.191	0.126
k	-2469.836	0.175	0.191	0.125
l	-2469.833	0.175	0.191	0.128
m	-2469.823	0.175	0.191	0.128
$[(uracil)(uracil\text{-}H)Cu]^{+}$				
(U-H)UCu(O2O4)a	-2469.637	0.165	0.180	0.120
(U-H)UCu(O4O4)b	-2469.648	0.165	0.180	0.121
(U-H)UCu(O2O4)b	-2469.642	0.165	0.180	0.120
(U-H)UCu(O2O2)b	-2469.642	0.165	0.180	0.121
Transition States				
TS1	-2469.801	0.171	0.187	0.122
TS1-MA	-2469.801	0.171	0.186	0.123

TS1-MB	-2469.791	0.171	0.186	0.122
TS2	-2469.812	0.173	0.188	0.126
TS2-MA	2469.805	0.172	0.187	0.124
TS2-MB	-2469.802	0.172	0.187	0.124
TS3	-2469.613	0.162	0.176	0.119
TS4	-2469.622	0.164	0.178	0.122
TS5	-2469.628	0.165	0.178	0.122

Table S2. Calculated intrinsic acidity (kJ mol^{-1}) of the N1H and N3H groups of complex ***a***.

	N1H	**N3H**
a	623.0	671.6