Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION FOR:

Metal Containing Cryptands as Hosts for Anions. Evaluation of Cu(I)•••X and π•••X interactions in Halide-Tricopper(I) Complexes through Relativistic DFT Calculations.

Miguel Ponce-Vargas and Alvaro Muñoz-Castro

Table S1. Selected calculated distances (Å) and angles (degrees) for the hypothetical **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes.

	1-Ne	**1**-Ar	**1**-Kr	**1**-Xe
Cu−Cu	4.418	4.399	4.362	4.434
Cu···Ng	2.542	2.538	2.519	2.570
N-Cu	1.828	1.832	1.838	1.833
N-N	3.202	3.180	3.178	3.197
C_6···Ng	3.091	3.056	3.077	3.095
< N-Cu-N	122.3°	120.3°	119.5°	121.2°

Table S2. Energy Decomposition Analysis for the hypothetical **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes.

	1-Ne		**1**-Ar		**1**-Kr		**1**-Xe	
ΔE_{orb}	-2.37	12.20%	-20.99	25.52%	-33.47	25.50%	-47.89	24.16%
ΔE_{elec}	-13.53	69.63%	-52.83	64.22%	-86.77	66.10%	-136.75	68.98%
ΔE_{disp}	-3.53	18.17%	-8.44	10.26%	-11.03	8.40%	-13.60	6.86%
ΔE_{Pauli}	25.18		90.48		137.95		205.73	
ΔE_{int}	5.75		8.22		6.68		7.49	

Table S3. Principal components of the electronic quadrupole tensor of the arms (**2**) and rings (**3**) moieties, for a representative copper and guests (Buckinghams).

	Cu				X			
	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}
Arms								
2	-0.294	-0.200	0.494	0.741	-	-	-	-
2-F	-0.551	-0.474	1.025	1.538	-0.066	-0.066	0.132	0.198
2-Cl	0.175	0.058	-0.233	-0.350	-0.050	-0.050	0.101	0.151
2-Br	-0.211	-0.055	0.266	0.399	-0.105	-0.105	0.211	0.316
2-I	-0.240	-0.080	0.321	0.481	0.739	0.739	-1.478	-2.216
Rings								
3-F	-	-	-	-	0.007	0.007	-0.015	-0.022
3-Cl	-	-	-	-	-0.023	-0.023	0.045	0.068
3-Br	-	-	-	-	-0.013	-0.013	0.027	0.040
3-I	-	-	-	-	-0.139	-0.139	0.278	0.417

Table S4. Principal components of the electronic quadrupole tensor of the studied systems, for a representative cooper and guests (Buckinghams), according to $\Theta_{11} > \Theta_{22} > \Theta_{33}$, depicting the more negative component as Θ_{33}.

	Cu				X			
	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}
1	-0.412	-0.244	0.656	0.984				
1-F	-0.482	-0.474	0.957	1.435	-0.087	-0.087	0.173	0.26
1-Cl	0.146	0.056	-0.203	-0.304	-0.108	-0.108	0.216	0.324
1-Br	-0.201	-0.056	0.257	0.386	-0.175	-0.175	0.350	0.525
1-I	-0.351	-0.047	0.398	0.597	0.588	0.588	-1.175	-1.763

Table S5. Comparison of the performance of several hybrid, GGA, and meta-GGA functionals in the calculation of the Cu(I) Dipole Moment Vectors of the studied systems (Debyes).

	1	**1**-F	**1**-Cl	**1**-Br	**1**-I
B1LYP	0.0966	0.1467	0.1545	0.0349	0.4406
B3LYP	0.0858	0.1602	0.1469	0.0304	0.4289
BP86	0.0088	0.2342	0.0813	0.0383	0.3946
PW91	0.0116	0.2262	0.0948	0.0330	0.4093
PBE	0.0078	0.2314	0.0911	0.0411	0.3501
PBE0	0.0078	0.2314	0.0911	0.0368	0.4043
M06-L	0.0934	0.1958	0.0783	0.0126	0.4032
TPSS	0.0062	0.2235	0.0948	0.0356	0.4002

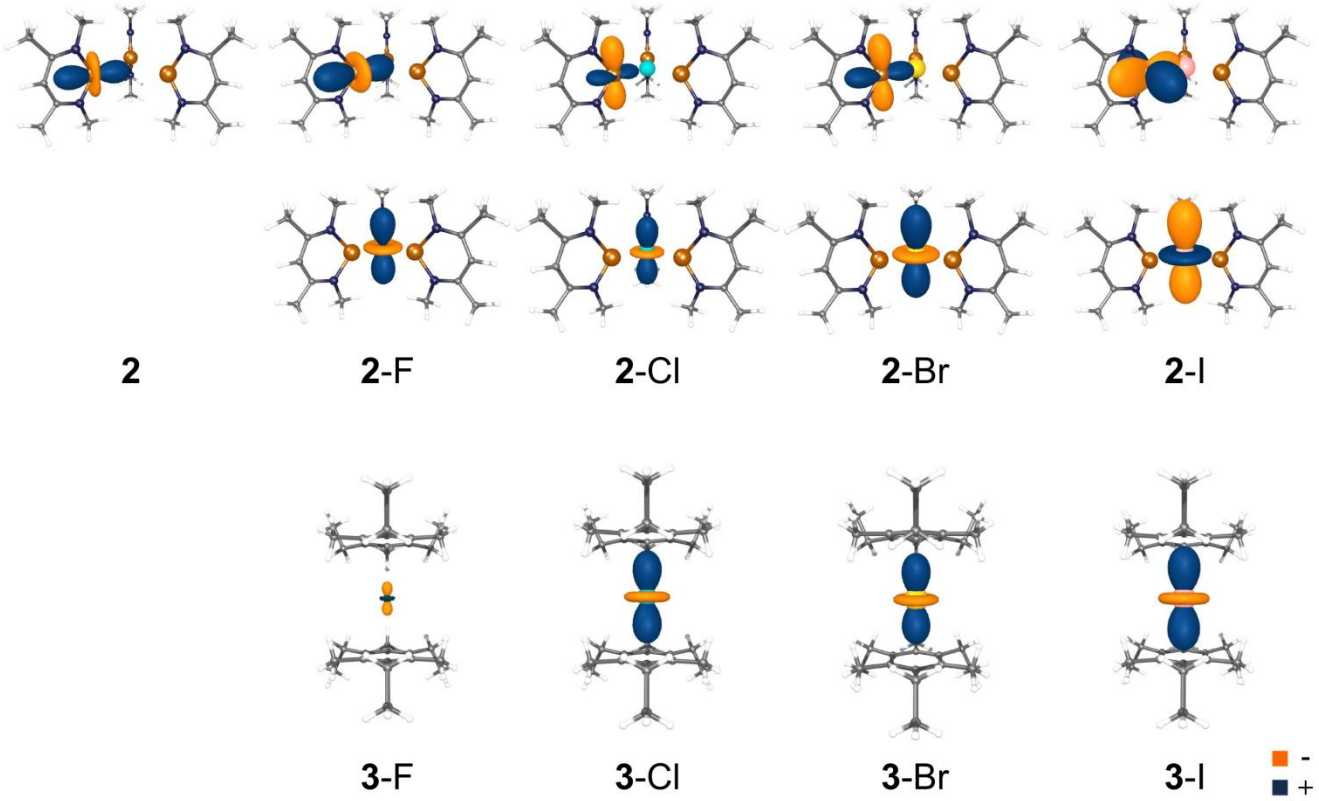

Figure S1. Graphical representation of copper and guests quadrupole moment tensors of the arms (**2**) and rings (**3**) moieties.