SUPPORTING INFORMATION FOR:

On the versatility of metallacycles in Host-Guest Chemistry. Interactions in Halide-centered hexanuclear copper (II) pyrazolate complexes.

Figure S1. Representation of the quadrupole moment tensor (Θ) for a representative Cu (II) center, in the hypothetical noble gases-centered pyrazolate complexes **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe.

Figure S2 Representation of the magnetic response, showing the bond critical points of the Cu_6-Cl interaction.

Table S1. Energy decomposition Analysis under the TPSS/ZORA level for **1**-Cl considering acetonitrile as solvent (kcal/mol).

Table S2. Selected calculated distances and angles of the **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes (Å).

Table S3. Energy Decomposition Analysis of the **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes (kcal/mol).

Table S4. Energy Decomposition Analysis under the PBE/ZORA level for some relevant studied systems (kcal/mol).

Table S5. Principal components of the electronic quadrupole tensors of a representative Cu (II) center and the guests, at the PBE/ZORA level for some relevant studied systems (Buckinghams).

Table S6. Comparison of the performance of several hybrid, GGA, and meta-GGA functionals in the calculation of the Electronic Quadrupole Tensors of the different noble-gas guests, denoting on the principal axis system (Buckinghams).

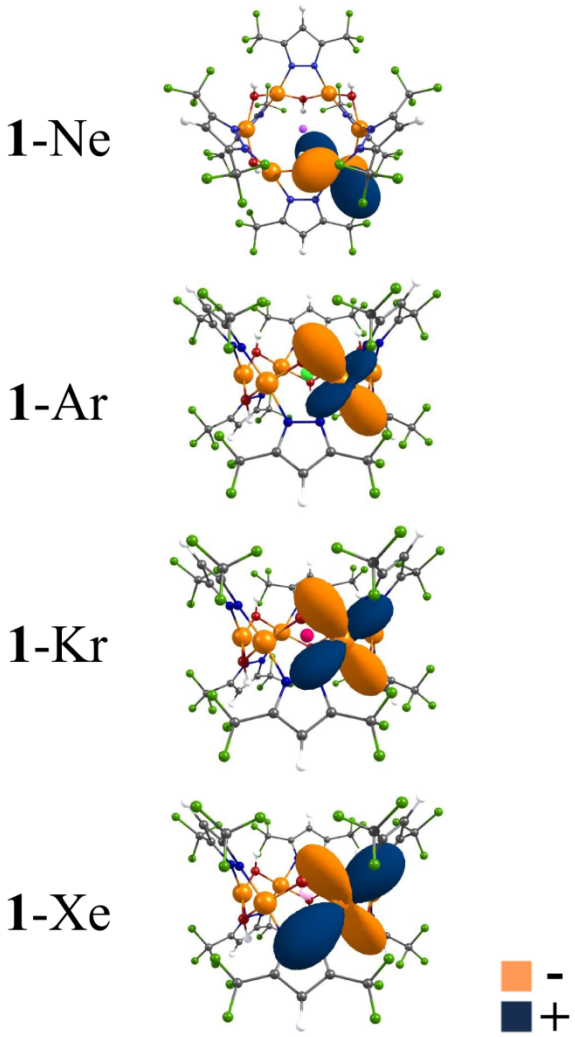

Figure S1. Representation of the quadrupole moment tensor (Θ) for a representative Cu (II) center, in the hypothetical noble gases-centered pyrazolate complexes **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe.

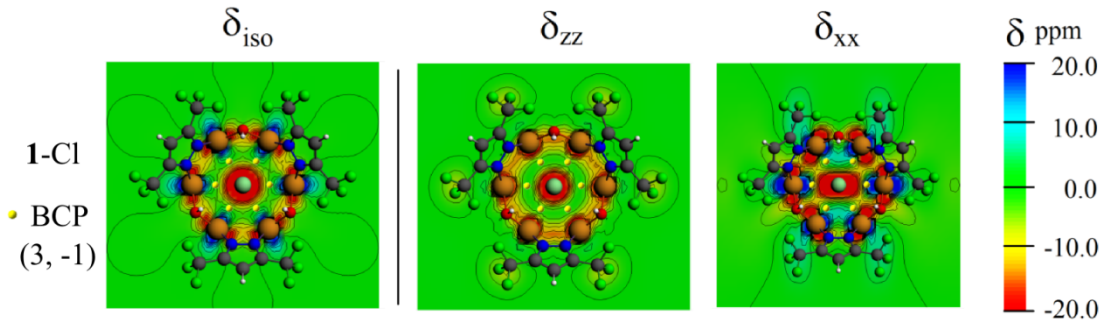

Figure S2. Representation of the magnetic response, showing the bond critical points of the Cu_6-Cl interaction.

Table S1. Energy decomposition Analysis under the TPSS/ZORA level for **1**-Cl considering acetonitrile as solvent (kcal/mol).

	1-Cl	
ΔE_{orb}	-34.15	25.72%
ΔE_{elec}	-91.09	68.60%
ΔE_{disp}	-7.54	5.68%
ΔE_{Pauli}	58.23	
ΔE_{int}	-74.55	

Table S2. Selected calculated distances and angles of the **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes (Å).

[*trans*-$Cu_6\{\mu$-3,5-$(CF_3)_2pz\}_6(\mu$-$OH)_6Ng$], Ng = Ar, Kr, Xe				
	1-Ne	**1**-Ar	**1**-Kr	**1**-Xe
Diam. Cu_6	6.405	6.441	6.447	6.489
Cu−Cu	3.203	3.220	3.224	3.245
Cu···(center of the cavity)	3.203	3.220	3.224	3.245
H···(center of the cavity)	3.619	3.646	3.666	3.694
(Cu_6 plane)−(Cu-N-N-Cu plane) angle	118	117	117	116
(Cu_6 plane)−(Cu-O-Cu plane) angle	114	116	116	117

Table S3. Energy Decomposition Analysis of the **1**-Ne, **1**-Ar, **1**-Kr and **1**-Xe complexes under the TPSS/ZORA level (kcal/mol).

	1-Ne	**1**-Ar	**1**-Kr	**1**-Xe
ΔE_{orb}	-0.15 2.19%	-3.54 15.0%	-5.87 16.0%	-11.24 18.4%
ΔE_{elec}	-2.89 42.19%	-11.70 49.7%	-20.82 56.7%	-38.07 62.3%
ΔE_{disp}	-3.81 55.62%	-8.30 35.3%	-10.03 27.3%	-11.80 19.3%
ΔE_{Pauli}	4.12	22.99	40.10	67.16
ΔE_{int}	-2.73	-0.55	3.38	6.05

Table S4. Energy Decomposition Analysis under the PBE/ZORA level for some relevant studied systems (kcal/mol).

	1-Cl	**1**-Br	**1**-I	**1**-Ar	**1**-Kr	**1**-Xe
ΔE_{orb}	-33.86 25.0%	-31.95 19.0%	-33.30 15.8%	-4.77 20.2%	-6.77 18.6%	-9.90 17.1%
ΔE_{elec}	-96.27 71.0%	-129.63 77.1%	-170.31 80.6%	-12.83 54.4%	-22.57 61.9%	-39.73 68.6%
ΔE_{disp}	-5.43 4.0%	-6.52 3.9%	-7.71 3.6%	-5.99 25.4%	-7.13 19.6%	-8.28 14.3%
ΔE_{Pauli}	59.46	98.65	154.30	21.94	36.82	64.51
ΔE_{int}	-76.10	-69.45	-57.02	-1.65	0.35	6.60

Table S5. Principal components of the electronic quadrupole tensors of a representative Cu (II) center and the guests, at the PBE/ZORA level for some relevant studied systems (Buckinghams).

	Cu				X			
	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{aniso}
1	0.241	0.053	-0.294	-0.441	-	-	-	-
1-Cl	0.395	-0.160	-0.235	-0.353	0.193	0.193	-0.385	-0.578
1-Br	0.421	-0.154	-0.267	-0.401	0.121	0.121	-0.242	-0.363
1-I	0.558	-0.147	-0.411	-0.617	1.357	1.357	-2.714	-4.071
1-Ar	0.227	0.076	-0.304	-0.456	0.025	0.025	-0.050	-0.075
1-Kr	0.287	0.006	-0.293	-0.440	0.044	0.044	-0.088	-0.132
1-Xe	0.435	-0.091	-0.344	-0.516	0.574	0.574	-1.149	-1.723

Table S6. Comparison of the performance of several hybrid, GGA, and meta-GGA functionals in the calculation of the Electronic Quadrupole Tensors of the different noble-gas guests, denoting on the principal axis system (Buckinghams).

[*trans*-$Cu_6\{\mu$-3,5-$(CF_3)_2pz\}_6(\mu$-$OH)_6Ng$], Ng = Ar, Kr, Xe									
	1-Ar			**1**-Kr			**1**-Xe		
	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{11}	Θ_{22}	Θ_{33}	Θ_{11}	Θ_{22}	Θ_{33}
B1LYP	0.0174	0.0174	-0.0349	0.0335	0.0335	-0.0669	0.5271	0.5271	-1.0543
B3LYP	0.0189	0.0189	-0.0378	0.0359	0.0359	-0.0718	0.5390	0.5390	-1.0780
O3LYP	0.0205	0.0205	-0.0410	0.0383	0.0361	-0.0744	0.5610	0.5637	-1.1247
BP86	0.0265	0.0265	-0.0529	0.0453	0.0453	-0.0906	0.5720	0.5720	-1.1441
PW91	0.0251	0.0251	-0.0503	0.0431	0.0431	-0.0861	0.5696	0.5696	-1.1392
PBE	0.0252	0.0252	-0.0504	0.0442	0.0442	-0.0885	0.574	0.574	-1.490
PBE0	0.0252	0.0252	-0.0504	0.0442	0.0442	-0.0885	0.5745	0.5745	-1.1490
M06L	0.0195	0.0195	-0.0389	0.0424	0.0424	-0.0847	0.4779	0.4779	-0.9557
TPSS	0.024	0.024	-0.049	0.041	0.041	-0.082	0.565	0.565	-1.130