PCCP

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Electronic Supplementary Information: Meta-stability through intermolecular interactions protecting the identity of atomic metal clusters: *Ab initio* evidences in $(Cu_5–Cu_5)_n$ $(n < 3)$ cases.†

Berta Fernández[a*] and María Pilar de Lara-Castells[b*]

Notes and references

1 J. Garrido-Aldea and M. P. de Lara-Castells, *Phys. Chem. Chem. Phys.*, 2022, **24**, 24810–24822.

2 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

3 E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2019, **150**, 154122.

[a] *Department of Physical Chemistry. University of Santiago de Compostela. E-15782. E-mail: berta.fernandez@usc.es*

[b] *Institute of Fundamental Physics (AbinitSim Unit), Madrid, Spain. E-mail: Pilar.deLara.Castells@csic.es*

Table 1 Cartesian coordinates (in Å) of the optimized structures corresponding to Figure 1 and Tables 1 and 2 of the main manuscript. CCSD/Def2-TZVP, Def2-TZVPP- and DF-CASSCF(10,10)/cc-pVTZ-PP-based results are shown for isolated Cu_5 and coupled Cu_5–Cu_5 clusters, repspectively. The term 'Cu_5-bp' corresponds to the bypiramidal Cu_5 3D structure.

Cu_5-planar, CCSD/Def2-TZVP	*X*	*Y*	*Z*
Cu	−1.257528	−1.283399	0.000251
Cu	1.257490	−1.283387	−0.000251
Cu	−2.442286	0.864920	−0.000126
Cu	2.442316	0.864881	0.000132
Cu	0.000007	0.836985	−0.000006
Cu_5-bp, CCSD/Def2-TZVP	*X*	*Y*	*Z*
Cu	0.000000	1.278654	−0.736969
Cu	0.000000	−1.278654	−0.736969
Cu	1.970676	0.000000	−0.000339
Cu	−1.970676	0.000000	−0.000339
Cu	0.000000	0.000000	1.474615
Cu_5-bp, CCSD/Def2-TZVPP	*X*	*Y*	*Z*
Cu	0.000000	1.274377	0.146646
Cu	−0.000000	−1.274377	0.146646
Cu	1.959735	0.000000	0.881618
Cu	−1.959735	0.000000	0.881618
Cu	−0.000000	0.000000	2.351058
Cluster 1	*X*	*Y*	*Z*
Cu	2.2342249950	1.9624549506	0.0748486461
Cu	−2.0522113999	1.7256038455	−0.0446353691
Cu	0.1866253320	0.1043525010	0.0310209444
Cu	0.0127164996	2.5884916673	1.3480108993
Cu	0.0885257269	2.5682349512	−1.3312257445
Cu	1.2872914643	4.4930744703	0.0289306592
Cu	−1.3884396321	4.3452774038	−0.0457116789
Cu	−0.1862194363	6.8911876914	−0.0309398804
Cu	−0.0303714799	5.1444105640	−2.1654420728
Cu	−0.1521430694	5.1769119548	2.1351435966
Cluster 2	*X*	*Y*	*Z*
Cu	0.3217539858	0.8219452327	−0.1683691674
Cu	0.2633470323	−1.1947873922	1.8857120104
Cu	1.8702256439	0.7961496484	2.0156452338
Cu	−2.2733079314	−0.6933003854	2.5708803119
Cu	−0.7285312045	1.4156244592	2.1563514749
Cu	0.8674637658	2.1287705439	4.1883800201
Cu	−0.5908200883	−2.1028916646	4.2404839504
Cu	1.4371509934	−0.5073392563	4.2983446981
Cu	−1.0859876011	0.4405338469	4.6812939562
Cu	−0.0812945956	−1.1047040327	6.6453895116
Cluster 3	*X*	*Y*	*Z*
Cu	−1.2603993699	−1.8010688900	3.4774873829
Cu	0.3723222660	0.2023087941	3.5504021997
Cu	1.9625231176	2.1773390667	4.0380151307
Cu	−0.6830104270	−0.9453763891	5.8520758426
Cu	0.9351330021	1.0518383319	6.1304864315
Cu	0.8986142499	−0.8676967392	8.1224721552
Cu	−1.0957595170	0.7690604045	7.9855838914
Cu	1.6186376548	−1.8244864743	10.4203837194
Cu	−2.3545719554	1.4428977943	10.1462616017
Cu	−0.3934890216	−0.2048158992	10.4909446449
Cluster 4	*X*	*Y*	*Z*
Cu	1.3090338597	0.1010288580	−0.7104059189
Cu	−1.2779098404	−0.1327426402	−0.7143503857
Cu	2.5221416757	0.0005717085	1.6517595204
Cu	−2.5093736208	0.0170265311	1.6343604434
Cu	0.0084130927	0.0143845348	1.6126054359
Cu	1.2190472968	0.7119902776	3.9448677111
Cu	−1.2179961557	−0.7041151841	3.9278337936
Cu	1.9328919118	1.6389686461	6.2710645008
Cu	−1.9691635367	−1.6417594734	6.2337019635
Cu	−0.0170846832	−0.0053532583	6.3626759357

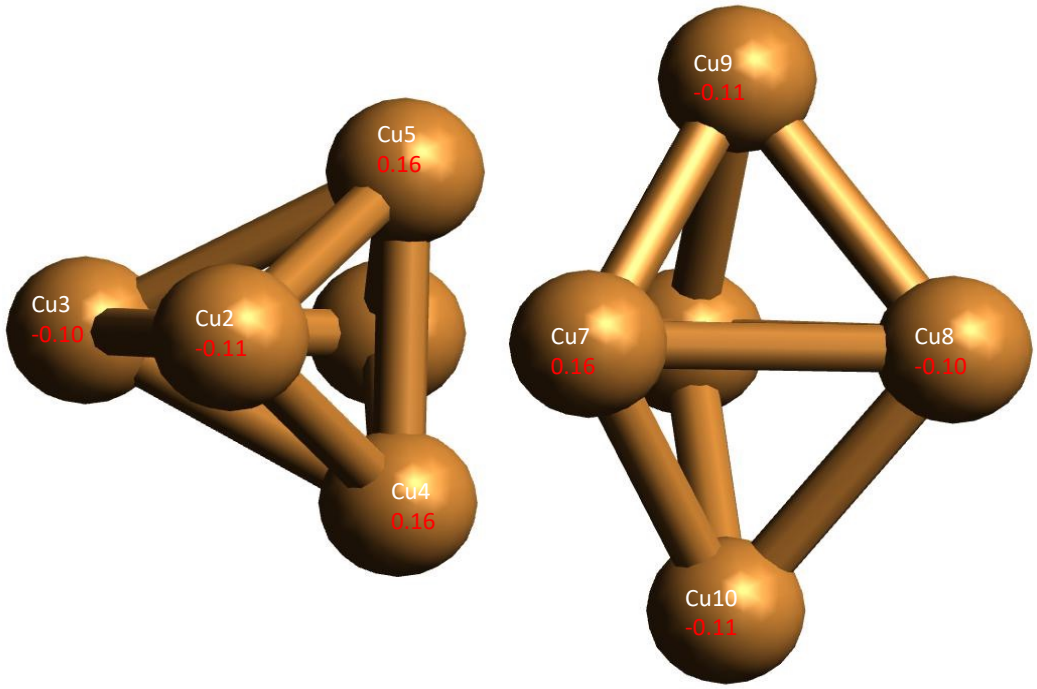

Fig. 1 Complex **1** structure obtained at DF-CASSCF(10,10)/cc-pVTZ-PP level showing the two Cu_5 subunits. The Mulliken charges (in a.u.) presented in Table 3 of the main manuscript are shown in red color.

Table 2 Values of Cu–Cu distances (in Å) for the structure shown in Figure 1. An active (10,10) space has been used for both DF-CASSC/cc-pVTZ-PP- and RS2C/cc-pVTZ-PP-based geometry optimizations. For comparison purposes, DFT-D4/Def2-TZVPP values from Ref. 1 are included. These DFT-D4 values were obtained by using the Perdew-Burke-Ernzerhof (PBE) density functional[2] aided with D4 Grimme's parametrization for the dispersion correction.[3] The average values for the Cu–Cu distances are 2.7, 2.5, and 2.4 Å for DF-CASSCF/cc-pVTZ-PP-, DFT-D4/Def2-TZVZPP-, and RS2C/cc-pVTZ-PP-based optimizations, respectively. Values between parenthesis and square brackets have been obtained for (isolated) Cu_5 through RS2C/cc-pVTZ-PP-based and CCSD/Def2-TZVPP-based optimizations, respectively. The magnitude of polarization effects in RS2C re-optimized Cu_5–Cu_5 structures is larger than without further re-optimization. However, the nature of the polarization effects is the same as the relative stability of different coupled Cu_5–Cu_5 isomers.

	DF-CASSCF	DFT-D4	RS2C	RS2C	CCSD
Cu3–Cu5	2.814	2.515	2.429	(2.418)	[2.549]
Cu5–Cu4	2.683	2.560	2.421	(2.418)	[2.549]
Cu3–Cu2	2.766	2.475	2.437	(2.418)	[2.549]
Cu2–Cu4	2.635	2.425	2.358	(2.349)	[2.450]
Cu7–Cu9	2.641	2.424	2.358	(2.349)	[2.450]
Cu6–Cu7	2.683	2.559	2.420	(2.418)	[2.546]
Cu6–Cu9	2.763	2.476	2.358	(2.349)	[2.450]
Cu7–Cu8	2.813	2.516	2.429	(2.418)	[2.546]