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A DFT investigation of the structure/electron count relationship in an electron-rich copper nanocluster with unprecedented Cu_{39} *superatomic* core

Bachir Zouchoune,^{*a,b} Mohamed Amine Zerizer^{a,b} and Jean-Yves Saillard^{*c}

- (a) Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Université Constantine (Mentouri), 25000 Constantine, Algeria
- (b) Laboratoire de Chimie appliquée et Technologie des Matériaux, Université Larbi Ben M'Hidi-Oum El Bouaghi, 04000 Oum El Bouaghi, Algeria
- (c) Univ Rennes, CNRS, ISCR-UMR 6226, 35000 Rennes, France

Abstract

This paper reports a DFT computational analysis of the richest in electron ever known thiolate-protected copper nanocluster that was recently reported by Liu, Huang and coworkers as being $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$. Our calculations suggest that this compound is most likely the closed-shell trication $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{3+}$ and that it is a 40-electron *superatom* with the $1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14} 2\text{P}^6$ configuration. This electron count is associated with an unprecedented multishell $[\text{Cu}_{39}]^- = \text{Cu}@\text{Cu}_{14}(\text{tetrakis hexahedron})@\text{Cu}_{24}(\text{truncated octahedron})$ *superatomic* core. This core is protected by 32 thiolate ligands and 36 Cu(I) metal centers which are coordinated to two or three sulfur lone pairs.

Introduction

Whereas the chemistry of atom-precise silver and gold clusters with M(I)/M(0) mixed valent character is nowadays largely developed, with a huge variety of structural examples ranging from a few to several hundreds of metal atoms [1-3], that of copper is much poorer, with less than twenty structurally characterized species [4-6]. This is likely related to the fact that the M(I)/M(0) reduction potential of Cu is much lower than that of Ag and Au, rendering (partly) reduced copper species less stable than their silver and gold relatives [7-9]. Consistently, most of the known mixed-valent Cu species have an average metal oxidation state much closer to +I than to 0 and most of them have a total number of 4s electrons (the so-called “free” electrons) of 2, which is the smallest closed-shell electron count for such mixed-valent species. Only very few copper nanoclusters having a number of “free” electrons equal or larger than 8 are known so far [8-14], and with the exception of the 8-electron $[\text{Cu}_{31}(\text{C}\equiv\text{CR})_{21}(\text{dppe})_3]^{2+}$ ($\text{R} = 4\text{-MeO-Ph}$; dppe = 1,2-bis(diphenylphosphino)ethane) [8] and the 18-electron isostructural family $[\text{Cu}_{50}(\text{CF}_3\text{CO}_2)_{12}(3,5\text{-diMe-PhS})_{18}(\text{PPh}_3)_4\text{H}_2]$ and $[\text{Cu}_{50}(\text{RCO}_2)_{10}(\text{SR}')_{20}(\text{PPh}_3)_6\text{H}_2]$ ($\text{R} = \text{CF}_3, \text{Ph}$; $\text{R}' = 4\text{-F-PhS}, \text{PhS}$) [14], their structure is unexpected, their electron count is not rationalized and, at least for some of them, they are lacking full characterization.

Within the family of noble metal mixed-valent clusters, the stability and structure of a given species can be rationalized within the concept of the *superatom* model [15-17], which is based on the spherical jellium approximation [18-20]. This approach consists in conceptually dividing the cluster into two parts, namely the compact M_n core of the molecule on one side and its peripheral protecting shell made of the ligands and (if any) supplementary outer metals (generally in their M(I) oxidation states) on the other side. Both parts should be considered in their actual group oxidation states, so that because most of the peripheral ligands are formally anionic, the metal core is generally formally cationic ($[\text{M}_n]^{x+}$). If the shape of this core is spherical enough, then the spherical jellium approximation allows describing $[\text{M}_n]^{x+}$ as a *superatom*, having an electronic structure related to that of a polyelectronic atom, with the filling of successive *superatomic* shells in the order $1\text{S} < 1\text{P} < 1\text{D} < 2\text{S} < 1\text{F} < 2\text{P} < 1\text{G} \dots$ (note that no relationship linking the $n > 0$ and $l \geq 0$ quantum numbers is required for S, P, D, F... *superatomic* orbitals). Closed-shell stability requires the so called “magic” electron counts of 2 (1S^2), 8 ($1\text{S}^2 1\text{P}^6$), 18 ($1\text{S}^2 1\text{P}^6 1\text{D}^{10}$), 20 ($1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2$), 34 ($1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14}$), ... $[\text{M}_n]^{x+}$ core which cannot be seen as spheroidal enough can be sometimes regarded as Jahn-Teller-distorted *superatoms* [21], or most often assemblies of *superatoms* (*supermolecules*), in a similar way as open-shell atoms can assemble to form stable molecules [22-25]. In such cases, their electron counts differ from the “magic” numbers mentioned above. Recently a very interesting and intriguing electron-rich copper nanocluster was reported by C. Liu, J. Huang and coworkers, namely $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$ (S-Adm = adamantanethiolate) [9]. Its structure and electron count being unexpected, below we propose their rationalization, based on a detailed analysis of its electronic structure computed at the density functional theory (DFT) level.

Computational details

Density functional theory (DFT) calculations were carried out by using the Amsterdam Density Functional (ADF) program suite developed by Baerends and co-workers [26-29], using the BP86 functional [30-33] and a Slater-type orbital basis sets of triple-zeta plus one polarization function quality (STO-TZP) [34]. The numerical integration procedure applied for the calculations was developed by te Velde *et al.* [29]. The frozen-core approximation was used to treat the core shells up to 1s for C, 2p for S and 3p for Cu. Full geometry optimizations were carried out using the analytical gradient method implemented by Versluis and Ziegler [35]. Vibrational frequency calculations [36-37] were performed on all the studied compounds to check that the optimized structures correspond to energy minima. The natural population-based analysis (NPA) [38] and The Wiberg bond indices (WBI) [39] were obtained from calculations implemented in the NBO 7.0 program [39, 40]. Representation of the molecular structures and molecular orbitals were represented by means of the ADF-GUI program [26].

Results and discussions

$[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$ was formed from the reaction of a solution containing $\text{Cu}(\text{NO}_3)_2$ and tetraoctylammoniumbromide with, firstly adamantanethiol, and subsequently NaBH_4 , according to a specifically designed reduction speed controlling method [9]. Its dicationic charge was determined from electrospray ionization mass spectrometry (ESI-MS) experiments through the attribution of the prominent signal on the spectrum to $[\text{Cu}_{70}(\text{S-Adm})_{29}(\text{CH}_3\text{OH})_{10}]^{2+}$, as resulting from the loss of $\text{Cu}_5(\text{S-Adm})_3$ from $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$ and combination with 10 solvent molecules [9]. No mention is made of the existence of counterion(s) in the description of the X-ray structure [9], meaning that, if any, they are likely highly disordered or that X-ray-undetectable hydride ligands are present on the cluster surface. On the other hand, both ESI-MS and ^1H NMR experiments show no evidence of hydrides. The +2 charge proposed by the authors implies an odd number of electrons, but the paper does not mention this fact and no EPR experiment could be performed to support the existence of (at least) one unpaired electron. Moreover, the ^1H NMR spectrum provided in the SI [9], does not seem to present any feature suggesting paramagnetism. Assuming this +2 charge and considering the monoanionic oxidation state of the thiolate ligands, the *superatomic* electron count is $75 - 32 - 2 = 41$. The closest “magic” electron count is 40 (*superatomic* configuration: $1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14} 2\text{P}^6$).

The structure of the cluster is unprecedented. It was originally described as a face-centered cubic Cu_{15} kernel encaged within a shell made of two identical $\text{Cu}_{30}(\text{S-Adm})_{16}$ semi-spherical units, each of them being viewed as composed of six Cu_5S distorted octahedra (of three kinds) connected by ten $\mu_3\text{-S}$ atoms [9]. Considering that the symmetry of the whole cluster can be idealized to T_h and that of its inner core to O_h , we propose a slightly different description which is sketched in Figure 1. The inner Cu_{15} hexacapped centered cube nicely approaches the ideality of a centered tetrakis hexahedron, a 14-vertex O_h Catalan solid with two types of edges whose length ratio is 0.75 (see also Figure S1 in the Supplementary data) [42]. The dual polyhedron of the tetrakis hexahedron is the truncated octahedron, a 24-vertex Archimedean solid of O_h symmetry, with 8 hexagonal and 6 square faces (Figure S1 in the Supplementary data) [42]. It turns out that the 24 faces of the Cu_{14} shell are capped by copper atoms nearly describing the shape of an ideal Cu_{24} truncated octahedron. The centers of the

hexagonal faces are occupied by the 8 vertices of the (hexacapped) cube, thus making the whole $\text{Cu@Cu}_{14}\text{@Cu}_{24}$ central part a rather compact Cu_{39} core of ideal O_h symmetry, which contrasts with its more peripheral counterpart. Only one half of the atoms belonging to the Cu_{24} shell are bonded (monocoordinated) to sulfur atoms.

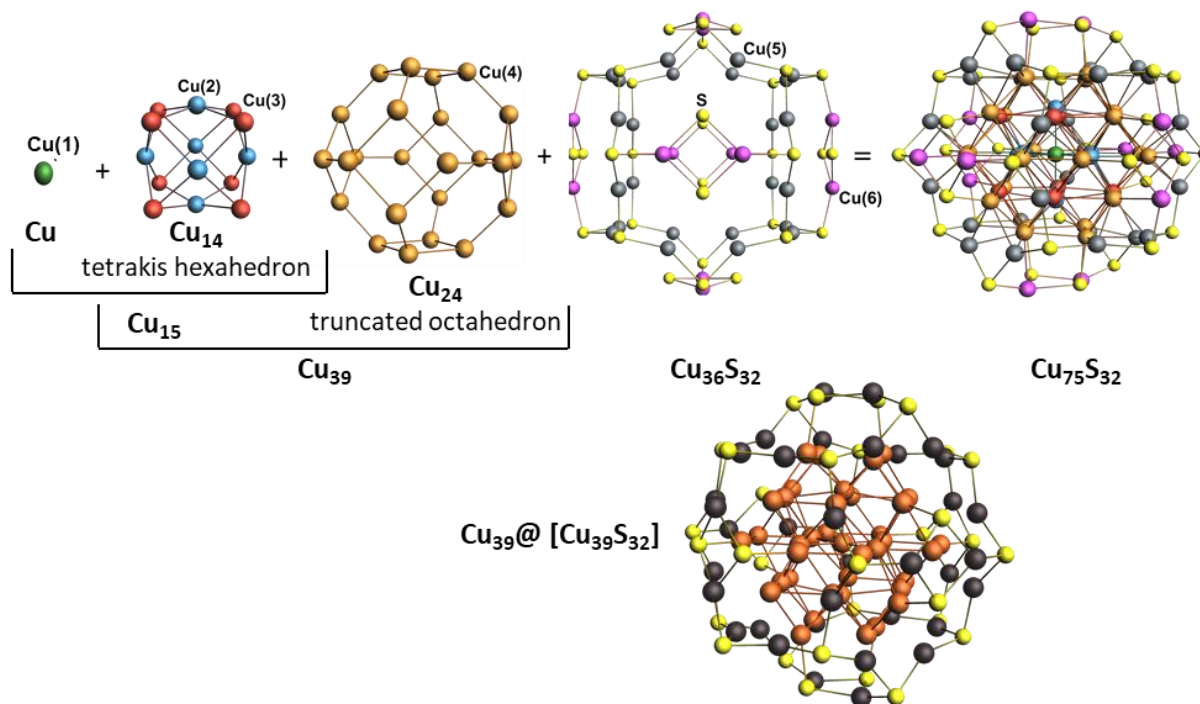


Figure 1. Top: Anatomy of the $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{n+}$ cluster in its idealized T_h symmetry, showing its $\text{Cu@Cu}_{14}\text{@Cu}_{24}\text{@[Cu}_{36}(\text{S-Adm})_{32}] \equiv \text{Cu}_{39}\text{@[Cu}_{36}(\text{S-Adm})_{32}]$ shell structure. Bottom: the core (Cu_{39})@shell $[\text{Cu}_{36}\text{@(S-Adm)}_{32}]$ structure with Cu(core) in orange, Cu(shell) in black and S in yellow. The adamantyl groups are omitted everywhere for clarity.

There are two types of peripheral metal atoms. 12 of them are in an approximate trigonal planar coordination mode with respect to sulfur and have one metallophilic contact with the truncated octahedron. The other 24 metals are in a distorted linear coordination mode with sulfur and have (at least) two metallophilic contacts with the truncated octahedron. Neglecting the metallophilic (non-covalent) contacts, one is tempted to consider the peripheral metals to be in their +I oxidation states, making locally stable 16- and 14-electron centers [15]. All the thiolates can be considered as in a μ_3 coordination mode [9], resulting in the existence of 96 Cu-S bonds, of which only 12 concern the Cu_{39} core. The dense S-Adm peripheral shell provides the metal atoms with efficient steric protection, ensuring kinetic stability to the cluster, at least as long as it does not lose any ligand.

Although there is some uncertainty in the proposed dicationic charge of $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$ [9], we assume that, the true charge should not be very different from +2. We thus looked, in a first step, for closed-shell situations (*i.e.*, an even number of electrons) secured by a significant HOMO-LUMO gap and corresponding to the following situations $[\text{Cu}_{75}(\text{SR})_{32}]^{n+}$ ($n = 1, 3, 5$). Full optimization of our $[\text{Cu}_{75}(\text{SH})_{32}]^{n+}$ model for these three cationic charges found open-shell situations for $n = 1$ and 5. In the case of $n = 3$, a significant HOMO-LUMO gap of 1.66 eV was found, suggesting a favored *superatomic* electron count of 40.

Considering the thiolates as formally anionic and assuming the 36 peripheral metals to be formally Cu^+ (see above), one is left with a $[\text{Cu}_{39}]^-$ core in the case of $n = 3$. A negative formal charge for a *superatomic* noble metal inner core is unusual. Indeed, reminding that in a M_n core the metal-metal bonding is ensured by the valence s orbitals and electrons, there are n MOs which are linear combinations of the metal s valence orbitals. Owing to the compactness and spheroidal shape of M_n , the number of bonding combinations is expected to be lower at equal to $n/2$, all the other combinations being antibonding. Then the favored number of electrons is expected to be most of the time lower than n , leading to a $[\text{M}_n]^{x+}$ cationic core. In the present case, and owing to the fact that the number of core metals is odd ($n = 39$), one can consider that the number of bonding combinations is maximum (~ 20), leading to an almost neutral 40-electron $[\text{Cu}_{39}]^-$ inner core. It is also possible that some of the (empty) valence p combinations tends to provide additional stabilization to the highest occupied valence s combinations.

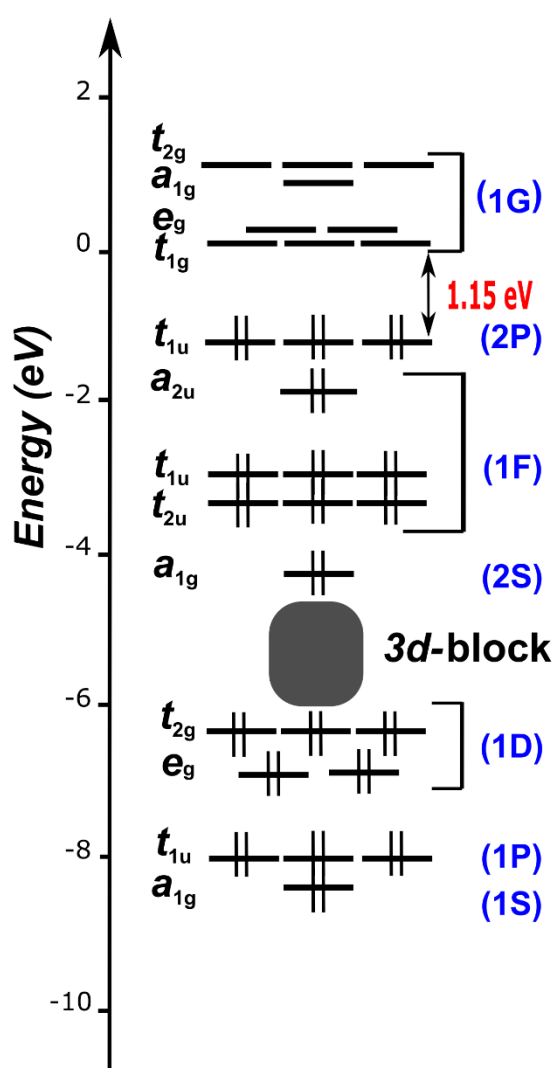


Figure 2. The Kohn-Sham orbital diagram of the *superatomic* core $[\text{Cu}_{39}]^-$ (O_h symmetry).

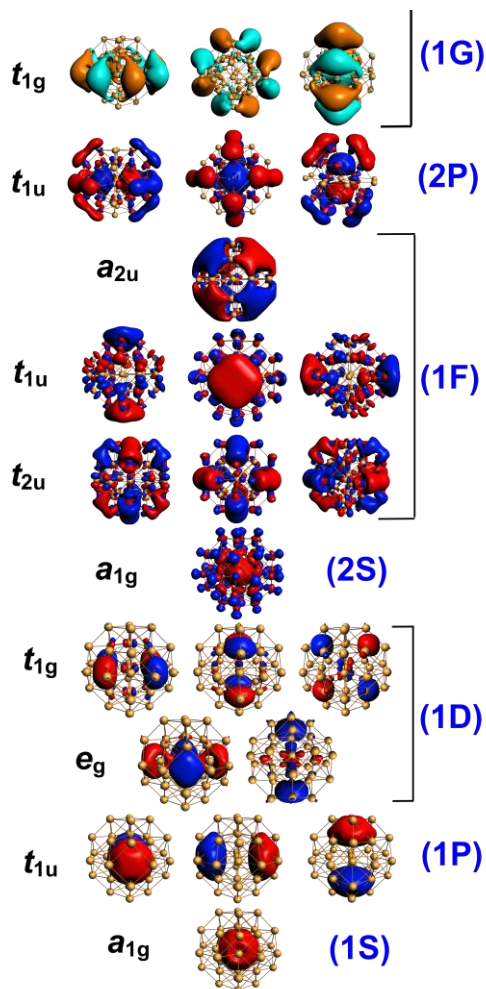


Figure 3. Representation of the $[\text{Cu}_{39}]^-$ superatomic orbitals (O_h symmetry).

The geometry of the $[\text{Cu}_{39}]^-$ core has been optimized. It has O_h symmetry and its Kohn-Sham orbital diagram is shown in Figure 2. Selected computed data are gathered in Table 1. It is possible to identify 20 orbitals of large $4s(\text{Cu})$ character which can be considered as the superatomic orbitals containing the 40 electrons (see Figure 2 and 3). Note that in the O_h symmetry, the D, F and G shells split in $(e_g + t_{2g})$, $(t_{1u} + t_{2u} + a_{2u})$ and $(t_{1g} + e_g + a_{1g} + t_{2g})$, respectively. The substantially bonding 1S, 1P and 1D levels are low-lying, situated below the 3d block, whereas the 2S, 1F and 2P levels are situated above 3d block and constitute the highest occupied ones. The LUMOs correspond to the vacant 1G superatomic orbitals. The HOMO-LUMO gap is large, in full agreement with the considered 40-electron count. We also looked for other possible electron numbers in optimizing various $[\text{Cu}_{39}]^{\pm q}$ ions.

Table 1. Relevant computed data $[\text{Cu}_{39}]^-$ and $[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$. The atom labels are defined in Figure 1. The atomic charges and configurations are from NPA calculations (see Computational Details). Average experimental bond distances [9] are reported in square brackets for comparison.

	$[\text{Cu}_{39}]^-$		$[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$			$[\text{Cu}_{39}]^-$		$[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$	
	Bond distance (Å)	WBI	Bond distance (Å)	WBI		Charge	Electronic configuration	Charge	Electronic configuration
Cu(1)-Cu(2)	2.285	0.118	2.291 [2.255]	0.122	Cu(1)	+0.35	$3d^{9.94}4s^{0.53}4p^{0.0}$	+0.33	$3d^{9.95}4s^{0.69}4p^{0.1}$
Cu(2)-Cu(3)	2.614	0.062	2.673 [2.629]	0.041	Cu(2)	-0.38	$3d^{9.93}4s^{1.31}4p^{0.0}$	-0.15	$3d^{9.93}4s^{1.15}4p^{0.1}$
Cu(2)-Cu(4)	2.438	0.071	2.384 [2.334]	0.063	Cu(3)	-0.03	$3d^{9.92}4s^{1.04}4p^{0.0}$	-0.02	$3d^{9.91}4s^{1.06}4p^{0.0}$
Cu(3)-Cu(4)	2.654	0.083	2.630 [2.664]	0.078	Cu(4)	+0.05	$3d^{9.94}4s^{0.98}4p^{0.0}$	-0.07	$3d^{9.92}4s^{0.87}4p^{0.1}$
$[\text{Cu}(4)\text{-Cu}(4)]_1$	2.758	0.124	2.571 [2.534]	0.065	Cu(5)			+0.63	$3d^{9.86}4s^{0.42}4p^{0.0}$
$[\text{Cu}(4)\text{-Cu}(4)]_2$	2.542	0.207	2.505 [2.480]	0.179	Cu(6)			+0.69	$3d^{9.87}4s^{0.40}4p^{0.0}$
Cu(4)-Cu(5)			2.565 [2.498]	0.065					
Cu(4)-Cu(6)			2.785 [2.701]	0.032					

The Kohn-Sham orbital diagram of $[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$ is shown in Figure 4 and relevant computed data are provided in Table 1. The optimized structure is of T_h symmetry and its metrical characteristic match reasonably well with their experimental counterparts. The computed spherical radii corresponding to the Cu(3), Cu(4), Cu(6) and S shells (3.23; 4.29, 6.71 and 6.75 Å) differ by less than 2% from their averaged experimental counterparts (3.29, 4.34, 6.74 and 6.83 Å) [9]. Unsurprisingly, the major variation in the Cu-Cu distances when going from $[\text{Cu}_{39}]^-$ to $[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$ affects the Cu(4) atoms, which are the core atoms in contact with the outer shell. Although mixing with ligand and peripheral metal orbitals tend to blurry them, it is still possible to identify the *superatomic* orbitals within the Kohn-Sham diagram. The 1S, 1P and 1D levels are still positioned below the 3d block, whereas the 1F, 2S and 2P levels lie above it in the same order than in $[\text{Cu}_{39}]^-$. The participation of the Cu_{39} core to the HOMO and LUMO is 54% and 63%, respectively, whereas that of the ligands are 18% and 14%, respectively. Thus, the 40-electron configuration $1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6$ is maintained in the full nanocluster. The natural charges are consistent with an oxidation state close to 0 for the metals in the Cu_{39} core. The positive charges ($\sim 0.6/0.7$) of the 36 peripheral metals are indicative of coordinated group 11 M(I) centers [42]. The Cu...Cu WBIs involving these atoms are small, indicative of metallophilic contacts. Then, it appears clearly that $[\text{Cu}_{75}(\text{SR})_{32}]^{3+}$ is a *superatom* made of a 40-electron $[\text{Cu}_{39}]^-$ compact core protected by a spherical outer shell consisting in the assembly of 36 Cu^+ ions and 32 SR^- ligands.

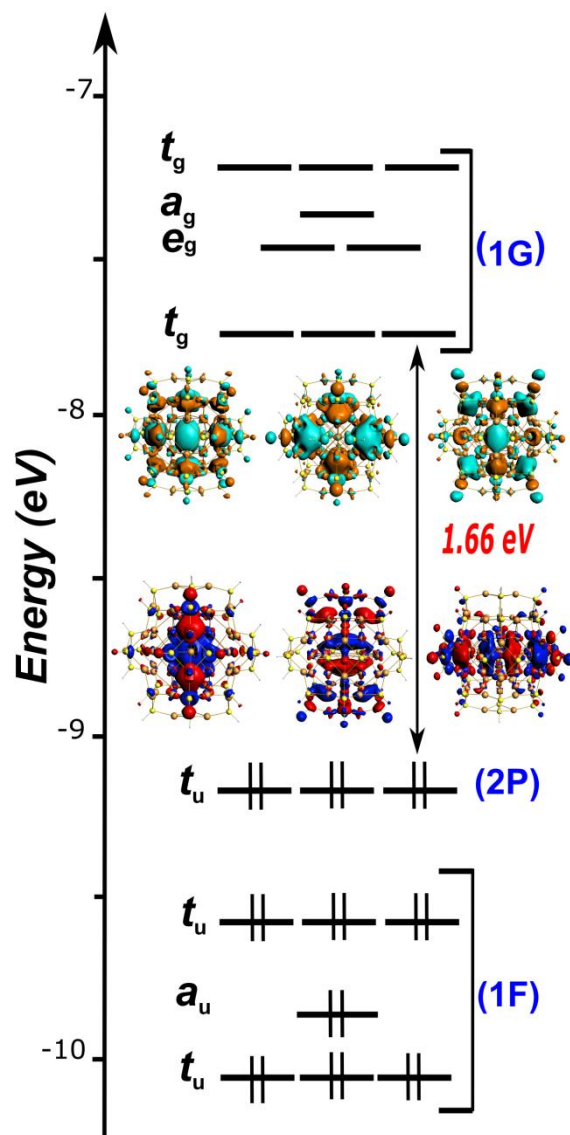


Figure 4. The Kohn-Sham frontier orbital diagram of $[\text{Cu}_{75}(\text{SH})_{32}]^{3+}$ (T_h symmetry).

The 2+ cationic charge proposed by C. Liu, J. Huang and coworkers for the $[\text{Cu}_{75}(\text{S-Adm})_{32}]$ nanocluster was assigned on the basis of mass spectrometry observations (see above). Mass spectrometry species can differ from their isolable counterparts and our results strongly suggest that the isolated species is a trication. Nevertheless, we also calculated the 41-electron bication in the T_h symmetry of the bication, assuming a doublet ground state. The most relevant results, which are given in Table S1 (see Supplementary data), are close to those obtained for the closed-shell bication, with optimized bond distances differing by less than 2% from those of the dication (average 1%), thus also in reasonable agreement with the experimental structure [9]. The unpaired electron is quite uniformly distributed over the whole Cu_{39} core, with minor contribution from the peripheral shell. It results that the spin density is very low everywhere (see Figure S2 in Supplementary data), its largest (by far) atom contributors being the Cu(2) metals, with a spin density of only 0.024).

Conclusion

Our calculations suggest strongly that the nanocluster reported as $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{2+}$ [9] is in fact likely to be the trication $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{3+}$. Indeed, there is no experimental evidence for the existence of an unpaired electron, which moreover would occupy a high-energy 1G orbital (Figure 3). On the other hand, $[\text{Cu}_{75}(\text{SR})_{32}]^{3+}$ is a stable 40-electron *superatom* with the $1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14} 2\text{P}^6$ configuration. To our knowledge, this “magic” electron count is unprecedented within the family of ligand-stabilized group 11 metal clusters, as well as the original shell nesting of the $[\text{M}_{39}]^-$ cluster core ($\text{M}@\text{M}_{14}$ (tetrakis hexahedron) $@\text{M}_{24}$ (truncated octahedron)). The negative formal charge of the latter is also unprecedented. $[\text{Cu}_{75}(\text{S-Adm})_{32}]^{3+}$ is the most electron-rich thiolate-protected atom-precise copper nanocluster known to date. Only a couple of NHC-protected copper species with larger electron counts (unfortunately lacking precise characterization) are known [13]. The original reduction speed controlling method used by C. Liu, J. Huang and coworkers for its synthesis [9] may be the key for its stabilization. At any rate, the existence of this outstanding compound let expecting that the synthesis of large and electron-rich chalcogenolate-protected copper nanoclusters is reachable.

Finally, it should be noted that the “magic” electron number of 34 (configuration $1\text{S}^2 1\text{P}^6 1\text{D}^{10} 2\text{S}^2 1\text{F}^{14}$) also provides closed-shell stability to the $\text{Cu}_{75}(\text{SH})_{32}$ framework, with a computed HOMO-LUMO gap of 1.94 eV. However, even if this electron count is perfectly OK from the strict point of view of the electronic structure, it implies a very large cationic charge for the cluster, *i.e.* $[\text{Cu}_{75}(\text{SR})_{32}]^{9+}$. Such a charge would require to be balanced by an equivalent number of hydrides on the cluster surface or the presence of many counterions, none of these species having been experimentally demonstrated to exist by C. Liu, J. Huang and coworkers [9]. This is why we strongly privilege the 40-electron count, corresponding to $[\text{Cu}_{75}(\text{SR})_{32}]^{3+}$.

CRedit authorship contribution statement

MAZ.: Methodology, investigation, formal analysis. **BZ and JYS:** Conceptualization, supervision, validation, writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/.....>

References

- [1] S. Li, X. Du, Z. Liu, Y. Li, Y. Shao, R. Jin, *Precis. Chem.* 1 (2023) 14–28.
<https://doi.org/10.1021/prechem.3c00008>
- [2] X. Zou, X. Kang, M. Zhu, *Chem. Soc. Rev.* 52, (2023) 5892–5967.
<https://doi.org/10.1039/D2CS00876A>
- [3] M. N. Pillay, W. E. van Zyl, C. W. Liu, *Nanoscale* 12 (2020) 24331–24348.
<https://doi.org/10.1039/D0NR05632D>
- [4] A. Baghdasaryan, T. Burgi, *Nanoscale* 13 (2021) 6283–6340.
<https://doi.org/10.1039/D0NR08489A>
- [5] L. L.-M. Zhang, W.-Y. Wong, *Aggregate* (2023) 4:e266.
<https://doi.org/10.1002/agt2.266>
- [6] B. Zouchoune, J.-Y. Saillard, *Molecules*, 29 (2024) 605.
<https://doi.org/10.3390/molecules29030605>
- [7] T.-A. D. Nguyen, Z. R. Jones, B. R. Goldsmith, W. R. Buratto, G. Wu, S. L. Scott, T. W. Hayton, *J. Am. Chem. Soc.* 137 (2015) 13319–13324.
<https://doi.org/10.1021/jacs.5b07574>
- [8] T. Jia, Z.-L. Guan, C. Zhang, X.-Z. Zhu, X.-Y. Chen, Q. Zhang, Y. Yang, D. Sun, *J. Am. Chem. Soc.* 145 (2023) 55–10363.
<https://doi.org/10.1021/jacs.3c02215>
- [9] J. Tang, C. Liu, C. Zhu, K. Sun, H. Wang, W. Yin, C. Xu, Y. Li, W. Wang, L. Wang, R. Wu, C. Liu, J. Huang, *Nanoscale* **2023**, 15, 2843–2848.
<https://doi.org/10.1039/D2NR05921E>
- [10] C. Borner, L. Anders, K. Brandhorst, C. Kleeberg, *Organometallics* 36 (2017) 4687–4690.
<https://doi.org/10.1021/acs.organomet.7b00775>
- [11] B.-L. Han, Z. Liu, L. Feng, Z. Wang, R. K. Gupta, C. M. Aikens, C.-H. Tung, D. Sun, *J. Am. Chem. Soc.* 142 (2020) 5834–5841.
<https://doi.org/10.1021/jacs.0c01053>
- [12] C. Kleeberg, C. Borner, *Organometallics* 37 (2018) 4136–4146.
<https://doi.org/10.1021/acs.organomet.8b00672>
- [13] W. Drescher, C. Borner, C. Kleeberg, *New J. Chem.* 45 (2021) 14957–14964.
<https://doi.org/10.1039/d0nj03166f>
- [14] J. Sun, X. Tang, Z.-H. Liu, Z. Xie, B. Yan, R. Yin, C. Chaolumen, J. Zhang, W. Fang, J. Wei, H. Shen. *ACS Mat. Lett.* 6 (2024), 281–289.
<https://doi.org/10.1021/acsmaterialslett.3c01305>
- [15] M. Walter, J. Akola, O. Lopez-Acevedo, P. Jazdzinsky, G. Calero, C. Ackerson, R. Whetten, H. Groenbeck, H. Hakkinen, *Proc. Natl. Acad. Sci. U. S. A.* 105 (2008) 9157–9162.
<https://doi.org/10.1073/pnas.0801001105>
- [16] H. Häkkinen, *Chem. Soc. Rev.* 37 (2008) 1847–1859.
<https://doi.org/10.1039/b717686b>
- [17] F. Gam, J. Wei, S. Kahlal, J.-Y. Saillard, J.-F. Halet, in: D. M. P. Mingos (Ed.), *50th Anniversary of Electron Counting Paradigms for Polyhedral Molecules: Bonding in Clusters, Intermetallics and Intermetallics. Structure and Bonding*, vol. 188. Springer, Cham, pp. 69–102.
https://doi.org/10.1007/430_2021_81
- [18] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, M. L. Cohen, *Phys. Rev. Lett.* 52 (1984) 2141–2143.
<https://doi.org/10.1103/PhysRevLett.52.2141>
- [19] D. M. P. Mingos, T. Slee, Z. Lin, *Chem. Rev.* 90 (1990) 383–402.

- <https://doi.org/10.1021/cr00100a003>
- [20] S. Khanna, P. Jena, *Phys. Rev. Lett.* 69 (1992) 1664–1667.
<https://doi.org/10.1103/PhysRevLett.69.1664>
- [21] M. A. Tofanelli, K. Salorinne, T. W. Ni, S. Malola, B. Newell, B. Phillips, H. Häkkinen, C. J. Ackerson, *Chem. Sci.* 7 (2016) 1882–1890.
<https://doi.org/10.1039/c5sc02134k>
- [22] L. Cheng, J. J. Yang, *Chem. Phys.* 138 (2013) 141101.
<https://doi.org/10.1063/1.4801860>
- [23] D. M. P. Mingos, *Dalton Trans.* 44 (2015) 6680–6694.
<https://doi.org/10.1039/C5DT00253B>
- [24] A. Munõz-Castro, *Chem. Commun.* 55 (2019) 7307–7310.
<https://doi.org/10.1039/C9CC02970B>
- [25] F. Gam, C. W. Liu, S. Kahlal, J.-Y. Saillard, *Nanoscale* 12 (2020) 20308–20316.
<https://doi.org/10.1039/D0NR05179A>
- [26] ADF2016, SCM; Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands.
<http://www.scm.com>
- [27] G. te Velde, E. J. Baerends, *J. Comput. Phys.* 99 (1992) 84–98.
[https://doi.org/10.1016/0021-9991\(92\)90277-6](https://doi.org/10.1016/0021-9991(92)90277-6)
- [28] C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* 99 (1998) 391–403.
<https://doi.org/10.1007/s002140050353>
- [29] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Fonseca Guerra, S. J. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* 22 (2001) 931–967.
<https://doi.org/10.1002/jcc.1056>
- [30] A. D. Becke, *J. Chem. Phys.* 84 (1986) 4524–4529.
<https://doi.org/10.1063/1.450025>
- [31] A. D. Becke, *Phys. Rev. A*, 38 (1988) 3098–3100.
<https://doi.org/10.1103/PhysRevA.38.3098>
- [32] J. P. Perdew, *Phys. Rev. B*, 33 (1986) 8822–8824.
<https://doi.org/10.1103/PhysRevB.33.8822>
- [33] J. P. Perdew, *Phys. Rev. B* 34 (1986) 7406–7406.
<https://doi.org/10.1103/PhysRevB.34.7406>
- [34] E. van Lenthe, E. J. Baerends, *J. Comput. Chem.* 24 (2003) 1142–1156.
<https://doi.org/10.1002/jcc.10255>
- [35] L. Versluis, T. Ziegler, *J. Chem. Phys.* 88 (1988) 322–329.
<https://doi.org/10.1063/1.454603>
- [36] L. Fan, T. Ziegler, *J. Chem. Phys.* 96 (1992) 6937–6941.
<https://doi.org/10.1021/j100196a016>
- [37] L. Fan, T. Ziegler, *J. Chem. Phys.* 96 (1992) 9005–9012.
<https://doi.org/10.1063/1.462258>
- [38] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* 83 (1984) 735–746.
<https://doi.org/10.1063/1.449486>
- [39] K. B. Wiberg, 24 (1968) 1083–1096.
[https://doi.org/10.1016/0040-4020\(68\)88057-3](https://doi.org/10.1016/0040-4020(68)88057-3)
- [40] F. Weinhold, C. R. Landis, *Valency and Bonding: a Natural Bond Order Donor Acceptor Perspective*, Cambridge University Press, U. K., 2005.
- [41] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, P. Morales, C. M. Karafiloglou, C. R. Landis, F. Weinhold, *NBO 7.0.; Theoretical Chemistry Institute, University of Wisconsin, Madison* (2018).

<https://nbo6.chem.wisc.edu>

[42] A. Holden, *Shapes, Space, and Symmetry*. Columbia University Press New York 1971.

[42] R. S. Dhayal, J.-H. Liao, Y.-C. Liu, M.-H. Chiang, S. Kahlal, J.-Y. Saillard, C. W. Liu, *Angew. Chem. Int. Ed.* 54 (2015) 3702–3706.

<https://doi.org/10.1002/anie.201410332>