LETTER

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Focus Article

On the stability of noble-metal nanoclusters protected with thiolate ligands

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PACS 61.46.Bc – Structure of clusters (e.g., metcars; not fragments of crystals; free or loosely aggregated or loosely attached to a substrate)
PACS 68.43.Hn – Structure of assemblies of adsorbates (two- and three-dimensional clustering)

Abstract – Noble metal nanoclusters (NCs) protected with thiolate ligands have been of interest because of their long-term stability that makes them suitable as building blocks for diverse assembled systems with emergent and improved functions. Despite the advances in synthesis and characterization, the mechanisms that contribute to their stability are still poorly understood. In this article, we review the different criteria that have been used to explain the experimental stability of NCs with a well-defined number of atoms that are protected with thiolate ligands. We discuss why these criteria are not enough to explain the stability. We conclude that there are other physical factors that should be included when explaining the stability of these systems and could be important for the discovery of new noble-metal NCs.

Introduction. – Some of the main challenges in nanoscience and nanotechnology are the reproducibility and uniformity of the properties of nanostructures. These are crucial for the advancement of this field from a fundamental point of view and for future applications. The study of noble-metal nanoparticles passivated with thiolate ligands has rapidly grown over the last two decades, during which fabrication and characterization techniques have evolved to achieve control over samples. Synthesis methods have allowed to obtain nanoparticles with a precise number of atoms, which ensures the uniformity and reproducibility of their physical properties. These nanoparticles are good candidates to be used as building blocks to construct more complex nanostructures, where the synergetic combination of the components permits the fabrication of nanostructures with novel properties that would impact fields like catalysis, solar energy, medicine, environmental sciences, pharmacology, among others [1–6].

Noble-metal nanoparticles of sizes smaller than 2 nm offer an opportunity to understand their synthesis and stability. Brust and Schffrin showed a two-phase reduction of a metal salt (AuCl₄⁻) in the presence of thiolate ligands (alkanethiol) [7], obtaining the first thiol-derived gold nanoparticles with sizes between 1 and 3 nm. Thiolate ligands prevent metal nanoparticles agglomeration and make them stable [7,8]. Since then, synthesis techniques of subnanometer nanoparticles or nanoclusters (NCs) have evolved to precisely control the number of atoms. These methods include interfacial and solid-state techniques, sputtering by charged particles or photons, templates, etc. [9]. Characterization techniques have also improved and techniques to characterize organic and inorganic molecules can be employed on NCs. Mass spectrometries (MS) like electrospray ionization (ESI MS) and matrix-assisted laser desorption/ionization (MALDI MS) have been successfully employed to characterize atomically precise NCs [9–15]. UV/vis optical absorption, ¹H NMR and IR techniques complement the characterization [16,17]. Recently, precise knowledge of the atomic structure of thiolate NCs has been achieved with X-ray crystallography,
where the same techniques used to crystallize proteins have been successfully applied [15,18,19]. In 2007, Jadzinsky et al. opened the way to the X-ray determination of a particle of 102 gold atoms and 44 p-mercaptobenzoic acids (p–MBAs), resulting in the first unambiguous atomic structure of Au$_{102}$(p–MBA)$_{44}$ [18].

A large number of atomically precise ligand-protected NCs, [M$_n$(SR)$_m$]$_x^y$, where M is the metallic atom, SR the thiolate group, m the number of ligands, and x the overall charge, have been fabricated using gold (M = Au), but also silver (M = Ag). Many of the processes to synthesize Au NCs are not successful for Ag, but the same techniques used to crystallize proteins acids (p–MBAs), resulting in the first unambiguous atomic structure of Au$_{102}$(p–MBA)$_{44}$ [18].

The abundance of some [M$_n$(SR)$_m$]$^y$ NCs have been explained adapting this superatom rule [18,21,31]. Now, magic numbers correspond to the number of electrons not engaged in bonding with ligands and are given by [22]

$$N^* = n \times \nu_A - m - x,$$

where $n$ is the number of metal atoms, $\nu_A$ is its valence (Ag = 5s$^1$ and Au = 6s$^1$, i.e., $\nu_A = 1$); $m$ is the number of ligands and $x$ the overall charge of the NCs. For example, the [Au$_{25}$(SR)$_{18}$]$^-\text{NC}$ counts $N^* = 25 \times 1 - 18 - (-1) = 8$, a magic number. But $N^*$ does not depend on the chemical composition of the ligand, thus any thiolate molecule can be used to stabilize the NCs as long as it satisfies this rule.

The [Au$_{25}$(SR)$_{18}$]$^-\text{NC}$ has been experimentally obtained using different ligands (SR) [32–37]. However, most magic NCs have been synthesized using only one kind of ligand [18,21,22,38–40]. A question arises: Is the radical an important factor to obtain [M$_n$(SR)$_m$]$^y$ NCs? Experimentally few [M$_n$(SR)$_m$]$^y$ NCs with different SR have been obtained and theoretically the influence of different ligands has not been systematically analyzed. For example, Wu et al. [41] showed that [Au$_{25}$(SR)$_{18}$]$^-\text{NC}$s with different R groups adopt the same two-shell structure. Jung et al. theoretically found that thiolate Au$_{25}$, Au$_{38}$, and Au$_{102}$ NCs are insensitive to the radical [42]. Using first-principles calculations, Aikens [43] demonstrated that the size of aliphatic ligand plays a minor role on the optical spectrum of [Au$_{25}$(SR)$_{18}$]$^-\text{NC}$s. Nevertheless, the role of the ligand on other less explored NCs is uncertain.

The overall charge, $x$, is important to assure the fulfillment of the superatom rule. The [Ag$_{30}$(p–MBA)$_{30}$]$^4^-\text{NC}$ is charged ($x = -4$), which guarantees a closed shell with $N^* = 18$ [22]. There are non-charged NCs ($x = 0$) that do not satisfy the superatom rule, but they are experimentally observed, like Au$_{20}$(SR)$_{16}$, Au$_{30}$(SR)$_{24}$ and Au$_{44}$(SR)$_{25}$ NCs with $N^* = 4, 12$ and 16, respectively [38,44,45]. Additionally, NCs can change their charge state depending on the experimental conditions. For example, [Au$_{25}$(SC$_4$H$_{13}$)$_{18}$]$^x$ shows $x = +2, +1$ and 0 in the first 30 min of exposure to a reducing agent, but after 3 hours it becomes $x = -1$ and does not change after 10 hours. The charge state of this NC can be tuned by changing oxidation and reduction times when using Ce(SO$_4$)$_2$ and NaBH$_4$ agents [36]. By using X-ray diffraction on [Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$]$^x$, it was shown that $x$ can be converted from $x = -1$ to $x = 0$ by air oxidation [36].

The magic numbers and the superatom rule have been important in explaining the stability of thiolate noble-metal NCs [31,46], but the existence of NCs which do not fulfill this rule is a fact [36,38,44,45]. Thus, additional properties have been considered, like the effectiveness of the geometry of the core and ligands, the core...
stability against dissociation and the existence of large HOMO-LUMO gaps [24].

Atomic structures. – Discussions about thiolate NCs include also geometrical factors. Thiolate NCs have been described as a metallic core capped with an external layer composed with ligands and metal atoms that form $-\text{SR} - [M-\text{SR}]_y$ oligomers. This capping layer has been proposed as an additional condition to explain the NCs stability [25,47]. The stability of $[\text{M}_{25}(\text{SR})_{18}]^−$, with $M = \text{Au}$ or $M = \text{Ag}$, has been attributed to a combination of a closed electron shell and a symmetric atomic structure [25]. This NC is composed by an icosahedral metal core, $\text{M}_{13}$ (fig. 1(a)). In a second layer there are twelve additional M atoms. Then, twelve S atoms each one attached to one internal M core atom and to one external M atom are observed (fig. 1(b)). The remaining six S atoms are each one attached to two external M atoms (fig. 1(c)). Thus, the NC is described as a metallic core capped with an external layer composed with ligands and metal atoms that form $[\text{Ag}_{44}(\text{SR})_{30}]^{4−}$ and $[\text{Au}_{44}(\text{SR})_{28}]^0$ NCs.

NCs with 44 metal atoms are totally different when $M$ is Ag or Au. Even when both NCs have the same number of M atoms, it has been experimentally determined that the number of ligands is $n = 30$ for Ag [21,22] and $n = 28$ for Au [38,39,48]. Thus, according to eq. (1) to close the electronic shell a charge of $x = −4$ is needed for Ag, while for Au it should be $x = −2$. But only the neutral case has not been observed experimentally. There are important differences between $[\text{Ag}_{44}(\text{SR})_{30}]^{4−}$ and $[\text{Au}_{44}(\text{SR})_{28}]^0$ NCs. Let us emphasize that the Ag NC fulfills the superatom rule, while the Au one does not. The Ag core is more symmetric than the Au case and capping units are defined different, as we discuss below.

In the case of Ag, the first layer of 12 Ag atoms forming a hollow icosahedron that is inside of a second layer of 20 Ag atoms forming a dodecahedron, see fig. 2(a). Eight of these 20 atoms are at the vertices of a cube, see fig. 2(b). In a third layer there are two Ag atoms placed in each face of the cube, adding twelve more for a total of $n = 12 + 20 + 12 = 44$ Ag atoms. Each face of the cube is passivated with four ligands where S atoms are bonded to one Ag in the second layer and one Ag in the third layer, see fig. 2(c), for a total of 24 ligands. Next, there are six ligands each one attached to the two Ag atoms in the third layer. Figure 2(e). Thus, we can define six capping units, one for each face of the cube, composed by the two silver atoms and 5 ligands as shown in fig. 2(c), Ag$_2$(SR)$_5$, with a metallic core shown in fig. 2(a). But capping units can be defined also including the Ag atoms in the second layer that are attached to ligands, like in the case of M$_{25}$(SR)$_{18}$. Now, the capping units are Ag$_4$(SR)$_5$ oligomers shown in fig. 2(d) and the metallic core has 20 atoms, Ag$_{20}$, shown in fig. 2(b). Finally, a charge $x = −4$ that closes the electronic shell is needed, $[\text{Ag}_{44}(\text{SR})_{30}]^{4+}$. Since the overall atomic structure, electronic closure and HOMO-LUMO gap are independent of the choice of capping units representation, both descriptions are valid.

The atomic structure and number of ligands are different for the NC with 44 Au atoms [39]. With only 28 ligands a charge $x = −2$ would be required to close the electronic shell. Yong Pei et al. [38] calculated a very small HOMO-LUMO gap of 0.3 eV with $x = −2$. However, they also predicted that the neutral case Au$_{44}(\text{SR})_{28}$ shows a significant larger optical gap of about 1.5 eV in agreement with the experiment [39]. The synthesis of the neutral Au$_{44}(\text{SPh}−\text{t−Bu})_{28}$ and its ESI-MS and optical characterization confirmed the calculations [48], confirming that it does not fulfill the superatom rule. The stability of this NC is attributed to its HOMO-LUMO gap.

Let us describe its atomic structure. Figure 3 shows the atomic model of Au$_{44}(\text{SR})_{28}$ that is composed by an
 elongated metallic core Au26 shown in fig. 3(a). A second layer of ten Au atoms and a third layer with eight Au atoms are observed, defining Au36 and Au44. There are three kinds of capping units shown in fig. 3(b) [49]. We identify four Au26(SR)1 capping units where S atoms are attached to Au atoms in the second layer, other four Au26(SR)2 capping units with Au atoms in the second layer, see left- and right-hand sides in the central part of fig. 3(b). Figure 3(c) shows the overall NC.

The definition of the capping units is ambiguous. For the case of [Ag44(SR)30]4−, Desireddy and collaborators [21] differentiated between the two capping units Ag2(SR)5 and Ag4(SR)5 shown in fig. 2(c) and (d), respectively. They calculated the density of states (DOS) of a highly charged metallic core, Ag3214+, which showed a great similarity to that of [Ag44(SR)30]4−. They mentioned that the Ag2(SR)5 capping unit is better defined than Ag4(SR)5, because the Ag atoms in Ag2(SR)5 are at larger distances from the nearest atoms of the Ag32 core (> 3.1 Å), indicating a weak capping-to-core interaction. On the contrary, the Ag4(SR)5 case results in a strong capping-to-core coupling, because of the shorter distance between the two Ag atoms mounted in a Ag30 core (~2.83 Å). However, they did not study the stability of these capping units and whether they are considered as independent entities to prove their arguments. Furthermore, when an Ag3214+ core is defined, each Ag2(SR)5 capping unit should be highly charged also (x = −3) to fulfill the superatom rule [21]. As we show below, the optimization of such Ag3214+ core and [Ag2(SR)5]3− capping units separately shows that are not stable geometries.

**Stability of cores and capping units.** We studied the [Ag44(SR)30]4− NC, as well as the stability of the Ag2(SR)5 and Ag4(SR)5 capping units and their metallic cores: Ag2(SR)5 with a Ag321− core, Ag4(SR)5 with Ag204− and [Ag4(SR)5]1− with Ag202+. Calculations were performed within the density functional theory (DFT) as implemented in SIESTA [50], within the general-gradient approximation and Perdew-Burke-Ernzerhof exchange-correlation functional [51], with scalar-relativistic norm-conserving pseudopotentials [52] and a double-C polarized basis set of numerical atomic orbitals. Unconstrained atomic relaxations were achieved for forces smaller than 0.01 eV/Å. These parameters have proved to be optimum for these NCs [53]. Initial atomic positions were taken from X-ray measurements [21,22]. To study the stability of the capping units individually, four of the five ligands need to be saturated with H atoms, Ag44(SR)5H4, shown in fig. 4 and Ag2(SR)5H4.

Table 1 shows the geometrical data of each capping unit with SR = SH, SCH3 and SC6H5 ligands, as well as the experimental X-ray data and the corresponding DFT optimized structures of [Ag44(SR)30]4−, according to labels in fig. 4. The distances among Ag atoms in the third layer, |Ag1 – Ag2|, for the optimized [Ag44(SR)30]4− NC are between 2.96 Å and 2.99 Å for all the ligands, in very good agreement with the experimental value of 2.996 Å [21]. In general, the optimized distances and angles, |L(Ag3 – S5 – Ag2)|, for all ligands are in good agreement with experimental data, as seen in the second and last columns in table 1.

When capping units are optimized, |Ag1 – Ag2| is between 2.77 Å and 2.99 Å, at most 0.12 Å shorter as compared to the whole NC. For the distances between Ag atoms in the second layer, |Ag3 – Ag4|, we found that the [Ag4(SR)3H4]1− capping unit shows the most similar value to X-ray data, independently of the ligand. On the other hand, the capping unit [Ag2(SR)5H4]3− with R = −H and a core Ag3214+, proposed by Desireddy and collaborators [21], shows a |Ag1 – Ag2| distance of 4.78 Å and |L(Ag1 – S5 – Ag2) = 136°, which are out the range of the experimental and theoretical values. While considering SR = SCH3 and SC6H5 ligands, the highly charged capping unit is completely distorted and eventually forming other compounds. In conclusion, the Ag2(SR)5H4 capping unit loses its stability when a high negative charge is imposed.

Table 1 also shows |Ag – S| distances between different atoms and the angle (ζ) between the third-layer Ag atoms and the S attached to them, |L(Ag1 – S5 – Ag2)|, shown in fig. 4. The smaller deviations from the experimental
Table 2: $\Delta E_{1/2}$ in eV per ligand according to eqs. (2) and (3) when SR = SH, SCH$_3$, and SC$_6$H$_5$ ligands are considered.

<table>
<thead>
<tr>
<th>Ligands</th>
<th>$\Delta E_{1/2}$</th>
<th>$\Delta E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH</td>
<td>2.014</td>
<td>1.953</td>
</tr>
<tr>
<td>SCH$_3$</td>
<td>-1.903</td>
<td>-1.924</td>
</tr>
<tr>
<td>SC$_6$H$_5$</td>
<td>-2.140</td>
<td>-2.038</td>
</tr>
</tbody>
</table>

In table 2, $\Delta E_{1/2}$ per ligand are listed when using SH, SCH$_3$, and SC$_6$H$_5$. Although there are differences between $\Delta E_{1/2}$ obtained in each case, the same trend is observed for both capping units. $\Delta E_{1/2}$ of capping units with the phenyl group (SC$_6$H$_5$) is energetically more favored than when only a hydrogen atom is considered, while the less favorable case is when the SCH$_3$ ligands are considered. Also, the largest differences are $\Delta E_{1}$, i.e., those of the uncharged capping units. Therefore, the most probable stable core and capping units are Ag$_{20}^{4-}$ and Ag$_{4}(SC_6H_5)_5$, respectively.

Figure 5 shows the calculated DOS of [Ag$_{44}$(SR)$_{30}$]$^{4-}$ when using SH, SCH$_3$, SC$_6$H$_5$, and p-MBA ligands with homolumo gaps of 0.94, 0.86, 0.84, and 0.81 eV respectively. The calculated homolumo gap with p-MBA ligands is in close agreement with previous calculations of 0.78 eV [21]. In fig. 5 we observed a similar behavior of
DOS close to the Fermi level ($E_F$) for all ligands. However, below −1 eV and above 1 eV the DOS shows differences that are related to the different ligands. A big difference in DOS is observed for SC that are related to the different ligands. A big difference is observed for SC that are related to the different ligands. A big difference is observed for SC that are related to the different ligands. A big difference is observed for SC that are related to the different ligands.

**Energy balance and electrostatic interactions.**

Trying to understand the stability beyond the capping units and the superatom rule, Taylor et al. introduced a thermodynamic model [27]. This model is based on a balance between the core cohesive energy and the shell-to-core binding energy that seems to drive NC stabilization. The calculations of the shell-to-core and core energies depend on what is considered as shell and core in each particular case. They considered as core-metal atoms those with a natural bond orbital charge smaller than a charge threshold of 0.2 $e$. Hence, metal atoms coordinated to two S atoms were assigned to the shell, while the rest were assigned to the core. However, the 0.2 $e$ charge condition is not based on any physical property and it seems quite arbitrary. Also, we have showed that different capping units can be defined for the same NC. This fact was not considered in such analysis. Furthermore, we have showed that a given core and their corresponding capping units can be defined with different charges, as proposed by Desirieddy et al. [21], with highly charged entities. Both charge and geometrical structure of the NCs are important in order to understand how to define the core and shell, and thus the so-called thermodynamic energies [27].

Another interesting case is the synthesized [Ag$_{55}$(MoO$_4$)$_6$(C≡CtBu)$_{14}$(CH$_3$COO)$_{18}$]$_{18}^+$ NC with a Ag-center multishell structure [26]. This NC does not satisfy the superatom rule. To explain its stability, the authors employed a semi-empirical method to analyze the Mulliken charges. They found an alternate change between plus and minus signs from the inside to the outside NC, indicating the presence of strong electrostatic forces. These electrostatic forces are suggested to be the main reason of its stability, but no further studies were performed. They also reported a very large optical gap of about 3.8 eV. However, a more detailed analysis should be performed, for example, to change the ligands and look the charges and its influence in the NC stability, to develop a model where the electrostatic forces show the structural stability and to study the gap size as a function of the ligand type.

**Concluding remarks.** — The experimental and theoretical study of NCs with a precise number of atoms represents a unique opportunity to understand their synthesis process and fundamental properties. In this article we have discussed the available criteria to explain the stability of noble-metal NCs with a precise number of atoms protected with thiolate ligands. These criteria are based on partial arguments of the atomic structure, electronic and energetic properties. Although these criteria have been useful to understand the stability of some NCs, they are not sufficient to explain all the experimental evidence.

One of these criteria is based on the electronic closure of the shell of metal atoms and ligands within a so-called superatom rule. This rule does not discriminate between different thiolate ligands, but we have shown that the ligand plays an important role in its stability and most of the NCs have been fabricated using one kind of ligand. Additionally, there are several experimental examples of NCs that do not satisfy this rule, but they are stable, like Au$_{44}$(SR)$_{28}$ and [Ag$_{55}$(MoO$_4$)$_6$(C≡CtBu)$_{14}$(CH$_3$COO)$_{18}$]$_{18}^+$, among others.

It has been proposed to divide NCs in metallic cores and capping units to find some geometrical or energy balance between such structures. However, we have shown that the definition of these entities can be done in different ways. Again, this criterion does not take into account the composition of the ligands. Also, there is an idea to look at the electrostatic interactions at the different atomic layers that composed the NC. However, it has not been shown how these electrostatic forces can make the whole structure more or less stable.

Another criteria is the presence of a large HOMO-LUMO gap. However, we have found that [Ag$_{44}$(SR)$_{30}$]$_{14}^−$ using SR = SH, SCH$_3$, SC$_2$H$_5$, and p-MBA ligands have very similar gaps. This NC satisfies the superatom rule.
But there is not experimental evidence of the synthesis of this NC using the first three ligands. Therefore, the ligand should play an important role in the stabilization of the NC beyond the electronic shell closure and the existence of a HOMO-LUMO gap, which has not been been explored yet. For example, we found that above and below the Fermi level there are important differences in the DOS when using different ligands, which might influence the stability of the NC.

Despite the significant advances in the synthesis and characterization, we conclude that the mechanisms that conduct to the stability of NCs are still poorly understood. There are several factors that have not been studied, among them the role played by the different ligands in the electronic structure and their influence on the NC stability, the possible charge compensation of the ligands to the metallic core, and other elements that could unambiguously help to elucidate the formation and prediction of new NCs.

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