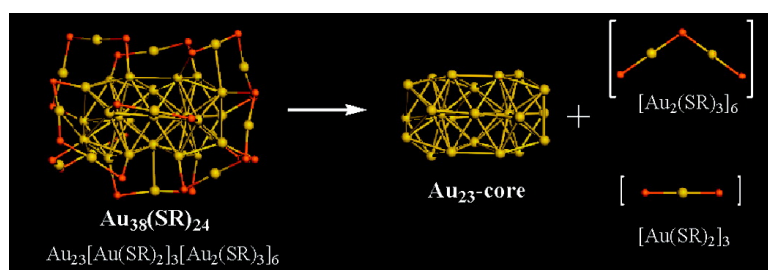


Structural Prediction of Thiolate-Protected Au: A Face-Fused Bi-icosahedral Au Core

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Structural Prediction of Thiolate-Protected Au₃₈: A Face-Fused Bi-icosahedral Au Core

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The synthesis and characterization of thiolate-group (RS[−]) protected gold nanoparticles (AuNP) have attracted extensive interest because of the unique physicochemical properties and promising applications of AuNPs in catalysis, optical sensors, etc.^{1,2} The recently revealed novel bonding between RS[−] and AuNP^{3,4} provided new insights into the interaction between the gold surface and the thiolate group.⁵

The properties of a thiolate-protected AuNP are controlled by both the ligands and the Au core.^{1,2} However, determination of the atomic structure of thiolate-protected AuNP represents a great challenge for both experiment and theory. Recently, a major breakthrough was made by Jadzinsky et al., who reported a total structure determination of thiolate-protected AuNP, Au₁₀₂(*p*-MBA)₄₄ (*p*MBA = *p*-mercaptobenzoic acid, SC₇O₂H₅).³ Another major advance was made with the determination of the atomic structure of the “magic-number” cluster [Au₂₅(SR)₁₈][−] (i.e., a cluster with high stability and selectivity) through three independent experimental^{6a,c} and theoretical studies.^{6b} These previous works have consistently shown that the Au core within a thiolate-protected AuNP is covered by certain number of “staple” motifs, including the simple −RS−Au−RS− [i.e., Au(SR)₂] and extended −RS−Au−RS−Au−RS− [i.e., Au₂(SR)₃]. It is also remarkable that the Au cores resolved thus far are all highly symmetric (near-*I_h* and near-*D_{5h}* symmetry for Au₁₃ and Au₇₉ in [Au₂₅(SCH₂CH₂Ph)₁₈][−] and Au₁₀₂(*p*-MBA)₄₄, respectively).^{3,4,6} It is known that, for bare Au clusters with size <40, few clusters show highly symmetric structures.⁷ For example, the icosahedral isomer of an Au₁₃ cluster has been confirmed to be a relatively high-energy structure from both theoretical⁸ and experimental studies.⁹

In this Communication, we report a theoretical prediction of a unique bi-icosahedral Au₂₃ core structure for another magic-number thiolate-protected gold cluster, Au₃₈(SR)₂₄. This study is motivated by the recent finding that the Au₁₃ core in [Au₂₅(SR)₁₈][−] exhibits high icosahedral symmetry.⁶ We note that, despite extensive experimental studies of the Au₃₈(SR)₂₄ cluster, its atomic structure is still not fully resolved.¹⁰ The structure of Au₃₈(SR)₂₄ reported in an earlier experimental study^{10a} was later reassigned¹¹ as that of the magic-number cluster [Au₂₅(SR)₁₈][−]. Recently, the structural composition of Au₃₈(SR)₂₄ was assigned as an Au:SR cluster with a core mass of 8 kDa.^{10h,i} The latter has a modest optical gap (ca. 0.9 eV)^{10h} and exhibits high stability; it can undergo ligand-exchange reactions while maintaining its core structure intact.^{10d} Several structural models for Au₃₈(SR)₂₄ have been proposed theoretically, with the Au core is either symmetric or disordered.¹² A state-of-the-art model was recently suggested by Jiang et al., who predicted a disordered and compact Au core, fully protected by mixed Au(SR)₂ and Au₂(SR)₃ motifs.^{12d}

Our study of the most viable structure for the Au₃₈(SR)₂₄ cluster is based on the pristine “divide and protect” scheme,^{12b} together with a set of structural rules derived from recent experimental

studies of thiolate-protected AuNPs.^{3,6} The basic idea in our construction of candidate structures for the thiolate-protected AuNP is to divide a thiolate-protected AuNP into groups as [Au]_{*a+a'*}[Au(SR)₂]_{*b*}[Au₂(SR)₃]_{*c*}, where *a*, *a'*, *b*, and *c* are integers. [Au]_{*a+a'*} represents the interior Au core which satisfies the condition that the number of core “surface” Au atom (*a'*) equals the sum of end points of the exterior motifs (*2b + 2c*); that is, each core surface Au atom is protected by one end point of the staple motif. This necessary condition is based on previous experimental studies of two magic-number clusters, Au₁₀₂(SR)₄₄ and [Au₂₅(SR)₁₈][−], the structures of which have been resolved as [Au]₃₉₊₄₀[Au(SR)₂]₁₉[Au₂(SR)₃]₂ and [Au]₁₊₁₂[Au₂(SR)₃]₆, respectively.^{3,6} Hence, for Au₃₈(SR)₂₄, the parameters *a*, *a'*, *b*, and *c* must satisfy *a + a' + b + 2c = 38*, *2b + 3c = 24*, and *a' = 2b + 2c*. We then specify five possible group divisions of *a*, *a'*, *b*, and *c*: (i) [Au]₂₊₂₄[Au(SR)₂]₁₂, (ii) [Au]₃₊₂₂[Au(SR)₂]₉[Au₂(SR)₃]₂, (iii) [Au]₄₊₂₀[Au(SR)₂]₆[Au₂(SR)₃]₄, (iv) [Au]₅₊₁₈[Au(SR)₂]₃[Au₂(SR)₃]₆, and (v) [Au]₆₊₁₆[Au₂(SR)₃]₈. A set of initial [Au]_{*a+a'*} (*a + a' = 22–26*) core structures are built and then covered by certain numbers of simple and extended staple motifs. Here, −CH₃ is chosen as the R group to minimize computational costs. The density functional theory computation is performed using DMol3 package,¹³ and the computation details are given in the Supporting Information.^{14,15}

Seven representative low-energy isomer structures, **Is1–Is7**, classified by group divisions (i)–(v), are shown in Figure S1. Among them, the top six lowest-energy isomer structures, **Is1–Is6**, are all lower in energy than the lowest-energy structure recently derived based on density functional simulated-annealing optimization.^{12d} The lowest-energy isomer, **Is1**, whose group division is (iv), exhibits exceptional stability. Not only is **Is1** 1.34 eV lower in energy than the second lowest-energy isomer, **Is2** [group division (iii)], but also, surprisingly, it is 3.36 eV lower in energy than the lowest-energy structure (with the same group division as **Is2**) proposed by Jiang et al.^{12d} Notably, isomer **Is1** has a sizable HOMO–LUMO gap (0.89 eV), a large adiabatic ionization potential (5.07 eV), and a modest adiabatic affinity (2.27 eV). The exceptional stability of the **Is1** is further affirmed by using a global-minimum search method¹⁶ (which involves a Monte Carlo run with **Is1** as the initial structure for 30 steps). The Monte Carlo run accounts for some temperature effects, which have been shown to be particularly important in the dominant structures of metal clusters.¹⁷

It is tempting to make a structural connection between the bi-icosahedral Au₂₃ core of **Is1** and the recently resolved thiolate-protected Au₂₅(SR)₁₈[−] magic-number cluster whose Au₁₃ core exhibits near-*I_h* symmetry. By removing the exterior staple motifs, it can be seen that the Au₂₃ core in **Is1** is composed of two slightly distorted icosahedral Au₁₃ clusters with a shared triangle Au–Au–Au face (Figures 1 and 2a). This bi-icosahedral Au₂₃ core has symmetry *C*₂ at 0.2 Å tolerance or *D*₃ at 0.3 Å tolerance. Note that the large

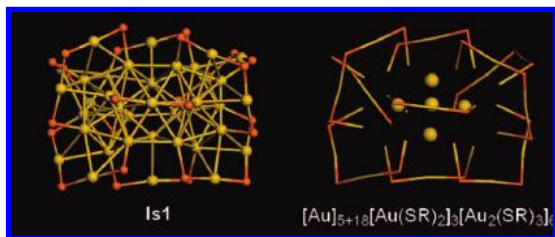


Figure 1. Structural views of the predicted lowest-energy isomer of $\text{Au}_{38}(\text{SR})_{24}$, **Is1**. The methyl groups are removed for clarity.

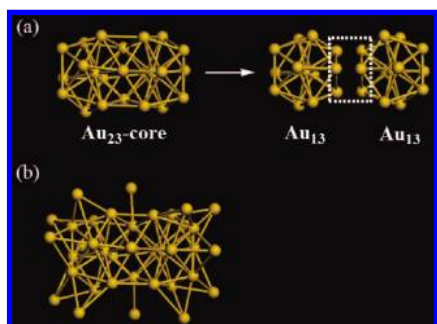


Figure 2. (a) Au_{23} core structure of the lowest-energy isomer of $\text{Au}_{38}(\text{SR})_{24}$, **Is1**. (b) The Au_{23} core plus the 15 exterior staple motifs containing Au atoms.

curvature of the icosahedral Au_{13} core fits very nicely with the $-\text{RS}-\text{Au}-\text{RS}-\text{Au}-\text{RS}-$ staple motif and forms semi-ring $\text{Au}(-\text{RS}-\text{Au}-\text{RS}-\text{Au}-\text{RS}-)\text{Au}$ protections (with average $\angle\text{S}-\text{Au}-\text{S} \approx 172.8^\circ$).⁶ In **Is1**, the six $\text{Au}_2(\text{SR})_3$ extended motifs are evenly distributed on two icosahedral “ Au_{13} ” subunits, bridged by three $\text{Au}(\text{SR})_2$ simple motifs. The $\text{S}-\text{Au}-\text{S}$ angles in optimized $\text{Au}_2(\text{SR})_3$ and $\text{Au}(\text{SR})_2$ motifs have average values of 173.5° and 172.0° , respectively, indicating very good structural compatibility with the Au_{23} core. Moreover, the ratio of $\text{Au}_2(\text{SR})_3$ to $\text{Au}(\text{SR})_2$ in **Is1** is 6:3, a manifestation of the gradual transition from a small thiolate-protected gold cluster (where the extended $\text{Au}_2(\text{SR})_3$ motifs dominate)⁶ to a large thiolate-protected AuNP (where the $\text{Au}(\text{SR})_2$ motifs are prevalent).³

Electronic shell models have been invoked to explain the high stability and selectivity of certain ligand-protected gold clusters,^{3,6b,18} such as $[\text{Au}_{25}(\text{SR})_{18}]^-$ and $\text{Au}_{102}(\text{SR})_{44}$, the Au cores of which were proposed to have 8 and 58 valence electrons, respectively, based on the assumption that each staple motif can effectively localize one $\text{Au}(6s)$ electron.^{3,6b} In thiolate-protected AuNP, the staple motif $\text{Au}_2(\text{SR})_3$ or $\text{Au}(\text{SR})_2$ can be viewed as a ligand bonding to the Au core. However, both the extended motif $\text{Au}_2(\text{SR})_3$ and the simple motif $\text{Au}(\text{SR})_2$ have odd numbers of total electrons, which tend to pair with another electron from the Au core to form a closed-shell structure. As such, each $\text{Au}_2(\text{SR})_3$ or $\text{Au}(\text{SR})_2$ motif may localize one electron from the Au core, and the localized electrons are no longer part of the total number of nonlocalized electrons accounted for by the spherical jellium model.¹⁹ The structural composition of a thiolate-protected $\text{Au}_m(\text{SR})_n$ can also be written as $[\text{Au}]_{a+a'}[\text{Au}(\text{SR})_2]_b[\text{Au}_2(\text{SR})_3]_c$, with the a, a', b, c satisfying eqs 1 and 2:

$$a + a' = m - b - 2c \quad (1)$$

$$2b + 3c = n \quad (2)$$

The effective total number of valence electrons for the Au core may be given by the number of core atoms (each Au atom contributes one $6s$ electron) minus the number of exterior staple

motifs, i.e., $a + a' - b - c = m - 2b - 3c = m - n$ (considering eqs 1 and 2). It is known that 8 and 58 are both magic numbers (to close electronic shells) for compact alkali metal clusters.¹⁹ Here, the net number of valence electrons for $\text{Au}_{38}(\text{SR})_{24}$ is 14, which is not a magic number according to the spherical jellium model. On the other hand, the net number of 14 valence electrons suggests that the Au core of **Is1** may be highly nonspherical and, as such, its electronic shell structure may be explained by the nonspherical shell model.²⁰ Indeed, it has been found that the alkali-metal cluster Na_{13}^- (with 14 valence electrons) has isoenergetic global minima of both oblate and prolate shapes.²¹

The UV-vis optical absorption spectrum and X-ray diffraction (XRD) pattern of **Is1** are computed (see Supporting Information) and compared with the experimental ones^{10h,i} (Figure 3). A comparison of the spectra of **Is1**, **Is2**, and the experimental spectrum is presented in Figure S2. Tsunoyama et al. showed that $\text{Au}_{38}(\text{SR})_{24}$ exhibits ~ 0.9 eV optical absorption edge and a major absorption peak near 2.0 eV.^{10h} As shown in Figure 3a, the computed optical absorption spectrum of **Is1** is in good agreement with the experimental spectrum. The extrapolated optical band-edge for **Is1** is 0.89 eV, in excellent agreement with the measured value (~ 0.9 eV).^{10h} Moreover, the flat absorption peak at 1.69 eV (peak *c* in Figure 3a) and the major peak at 1.98 eV (peak *d* in Figure 3a) for **Is1** are also in excellent agreement with the experimental peaks at 1.65 and ~ 2.0 eV, respectively.^{10h} In contrast, very small HOMO-LUMO gaps (< 0.1 eV) are found for the cation ($q = 1$, HOMO-LUMO gap = 0.06 eV) and anion ($q = -1$, HOMO-LUMO gap = 0.05 eV) charge states of **Is1**, confirming a close match between the neutral state of **Is1** and the experiment.

The computed Kohn-Sham (KS) molecular orbital (MO) energy levels of **Is1** and atomic orbital components in each KS MO are shown in Figure 3b. We note that **Is1** shows distributions of KS MO bands very similar to those reported for $[\text{Au}_{25}(\text{SR})_{18}]^-$.^{6c} As shown in Figure 3b, the HOMO and a set of unoccupied orbitals LUMO-LUMO+5, are mainly composed of the $\text{Au}(6sp)$ orbital, denoted as the *sp*-band. The set of HOMO-6-HOMO-1 are *d*-band due to the significant contribution of the $\text{Au}(5d)$ atomic orbital. The four major absorption peaks (*a-d*) in Figure 3a are assigned to the different excitation modes shown in Figure 3b. We note also that the HOMO, LUMO, and other orbitals, including HOMO-1-HOMO-3 and LUMO-1,-2, etc., are almost exclusively composed of atomic orbitals of the Au atoms in the bi-icosahedral core, suggesting that the absorption peaks *a-d* are mainly due to the electronic structure of the bi-icosahedral core. This good agreement between the theoretical and experimental optical spectra and the number of major absorption peaks (*a-d*) and their locations lends further support to the predicted bi-icosahedral Au core structure in $\text{Au}_{38}(\text{SR})_{24}$.

The simulated XRD pattern of **Is1** is shown in Figure 3c. It can be seen that major diffraction peaks in the experimental XRD pattern¹⁰ⁱ are well reproduced.

In conclusion, a face-fused bi-icosahedral Au_{23} structure is predicted as the Au core of the magic-number $\text{Au}_{38}(\text{SR})_{24}$ cluster. This prediction is supported by good agreement between experimental and simulated UV-vis spectra as well as the XRD pattern. Given that the icosahedral Au_{13} core and the vertex-fused bi-icosahedral Au_{25} core have been recently confirmed by experiments on the $[\text{Au}_{25}(\text{SR})_{18}]^-$ and $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_n\text{H}_{2n+1})_5\text{Cl}_2]^{2+}$ clusters, respectively,^{6,22} we expect that this prediction on the Au core structure for $\text{Au}_{38}(\text{SR})_{24}$ will stimulate future experimental and theoretical interests.

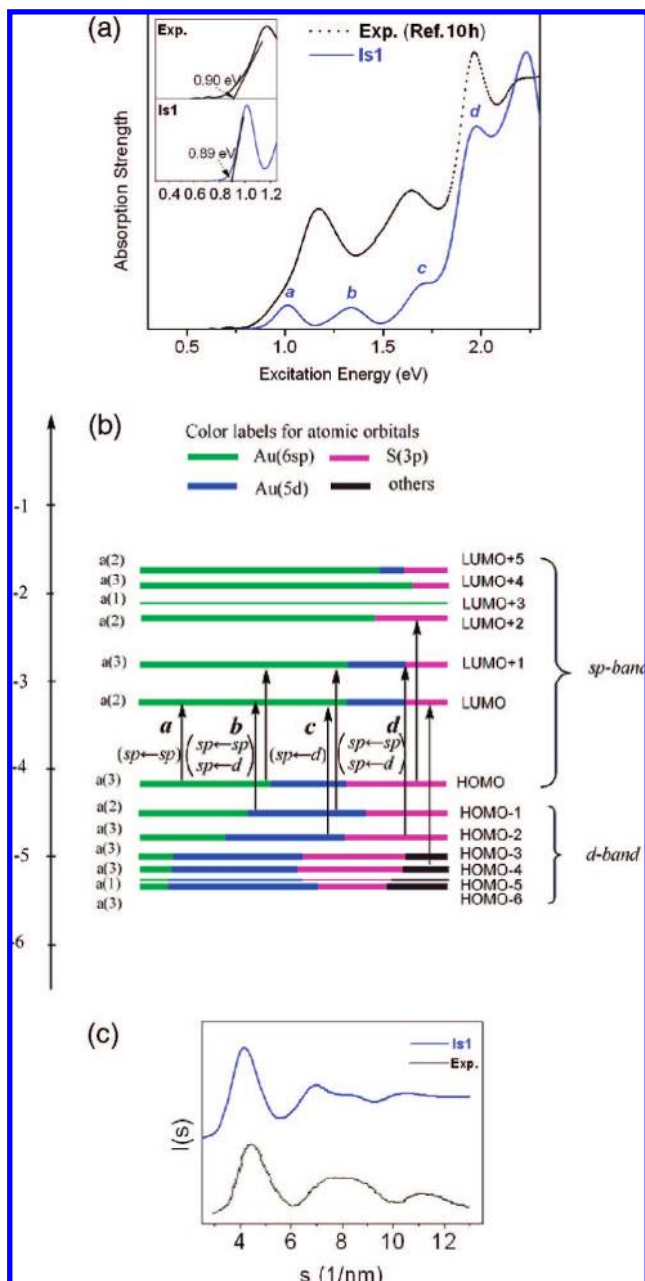


Figure 3. (a) Comparison of theoretical optical absorption spectrum of **Is1** with measured spectrum (ref 10h). The insets highlight the optical edge. (b) Kohn–Sham orbital energy level diagram for **Is1**. Peaks *a*, *b*, *c*, *d* in (a) are assigned to various excitation modes. The energies are in units of eV. Various colors are used to mark relative contributions (line length with color labels) of different atomic orbitals: green, Au(6sp); blue, Au(5d); and yellow, S(3p). Other smaller contributions are displayed in gray (each with <1% contribution). The orbital degeneracy for each KS orbital is shown in parentheses. For the purpose of comparison, (b) is drawn in the same fashion as in ref 6c. (c) Simulated XRD pattern of **Is1**, and measured XRD pattern (ref 10i).

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Supporting Information Available: Computational details, isomer structures **Is1–Is7**, computed optical spectra of **Is1** and **Is2**, and coordinates of **Is1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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