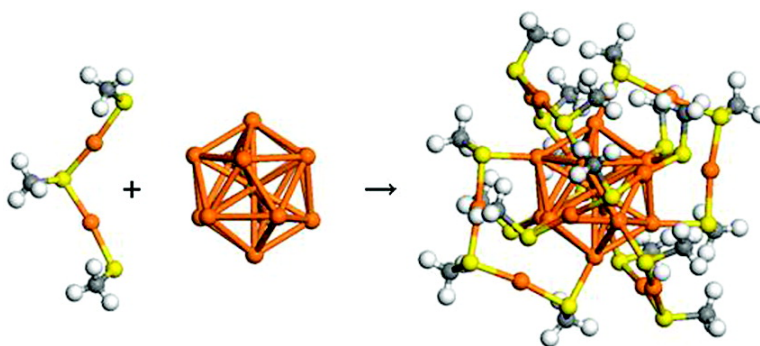


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On the Structure of Thiolate-Protected Au₂₅

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Ligand protection provides a convenient route to prepare robust nanosized metal particles. A prototypical example is thio-group-(RS-) protected gold nanoparticles (AuNPs)¹ which show a remarkable stability and exhibit distinct optical, electronic, electrochemical, and biolabeling properties. Although RS-protected AuNPs commonly are synthesized with a broad size distribution, certain metal cores (e.g., 5, 8, and 14 kDa) show enhanced stability.² The smallest of these was first isolated with glutathione (GS-) and its composition was (mis-) identified mass spectrometrically as Au₂₈(GS)₁₆.³ Later, its properties were mistakenly associated with the composition Au₃₈(RS)₂₄,⁴ for which several theoretical investigations have appeared.⁵ However, recent high-resolution mass spectrometry firmly established its composition as [Au₂₅(RS)₁₈]^q,⁶ where $q = \pm 1$ are its most common charge states.⁴

Understanding of the physicochemical properties of Au₂₅(RS)₁₈, including its extraordinarily stability,^{6c} requires knowledge of the structure. In general, determination of the atomic structure at the nanoscale is a challenge,⁷ and the recent total structural determination of Au₁₀₂(*p*-MBA)₄₄ (where *p*-MBA is *para*-mercapto benzoic acid, SC₇O₂H₅) is a breakthrough.⁸ The compound consists of a metal core capped by gold-thiolate units, a bonding motif which represents a version of the “divide and protect” scheme first proposed for Au₃₈(RS)₂₄.^{5d}

In the present communication, the Density Functional Theory (DFT) is used to explore the structure of [Au₂₅(RS)₁₈]^q ($q = -1, 0, +1$) for which an experimental determination remains elusive. The proposed structure is based on a compact icosahedral Au₁₃ core protected by six [(RS)₃Au₂] complexes. The structure bears similarities to the experimentally resolved Au₁₀₂(*p*-MBA)₄₄ and is clearly energetically preferred over a previous suggestion.^{6e,9} An enhanced stability of the anion is found to originate from an eight-electron shell closure of delocalized Au(6s) electrons. The calculated XRD pattern and optical absorption spectra are in good agreement with experimental data.

DFT is used in an implementation where the Kohn–Sham orbitals are expanded in Gaussian basis functions.¹⁰ The exchange and correlation functional is approximated with the spin-polarized Perdew–Burke–Ernzerhof (PBE) formula,¹¹ and scalar-relativistic pseudopotentials are used for the interaction between the valence electrons and the atomic cores.¹² The optical spectra are evaluated by use of the linear-response time-dependent DFT (TD-DFT) formalism implemented within the real space grid projector augmented wave formalism.¹⁴ Details are given in the Supporting Information.

Au₂₅(RS)₁₈ has been experimentally investigated with different RS groups such as glutathione and hexyl thiolate.^{6e} It has been,

however, theoretically demonstrated¹⁴ that structural and energetic properties depend weakly on the length of the alkyl group, and here the investigation is restricted to the smallest possible R, namely methyl thiolate (MeS).

Structural models of three optimized isomers are shown in Figure 1 together with relative total energies for the three considered charge states; $q = -1, 0, \text{ and } +1$. (Au₂₅(RS)₁₈ has been experimentally prepared with these values of q .^{6e}) Independently of q , the ground state (**1**) can be described as Au₁₃[(MeS)₃Au₂]₆, i.e., an icosahedral Au₁₃ core protected by six MeS–Au–MeS–Au–MeS complexes. The core is related to the phosphine protected undecagold (Au₁₁) which has the structure of an incomplete icosahedron.¹⁵ Each of the 12 surface atoms (of the core) is bound directly to one MeS group. However, MeS should not be regarded as the actual ligand; rather it is (MeS)₃Au₂ that constitutes the protective unit. The complexes are anchored to the metal core in a bidentate fashion via terminal S–Au bonds. This motif provides a compact structure with an efficiently shielded metal core. The structural ground state is energetically clearly separated from the meta-stable isomers. Isomers **2** and **3** are based on a near-planar Au₇ core with either three (MeSAu)₆ cyclic oligomers (**2**) or two (MeSAu)₃ and one (MeSAu)₁₂ cyclic oligomers (**3**). **3** is relaxed from the structure proposed in ref 9. **2** is slightly more stable than **3** in all charge states. This is rationalized by the fact that the strain in cyclic gold-thiolate oligomers is relieved only after (MeSAu)₄.¹⁴

Common for **1–3** is the existence of Au atoms in two oxidation states. In the complex (or oligomers) Au is close to Au¹⁺, whereas Au is metallic in the core. However, it should be realized that **1** is a considerably more robust isomer than **2** or **3**. The binding energy of each (MeS)₃Au₂ complex to the Au₁₃ core is 3.5 eV, whereas it is only 1.6 eV per (MeSAu)₆ oligomer in **2**.

The X-ray diffraction (XRD) pattern of the 5 kDa compound has experimentally been recorded from powder samples,^{3,9} and here it is compared to theoretical diffraction patterns for **1–3** as anions. (Details are given in the Supporting Information.) The experimental result is characterized by major peaks at $s = 2, 4, 7$ and 8.5 nm^{-1} (where s is the diffraction vector length). This sequence is reproduced only by **1**. Consistent with the observation that [Au₂₅(RS)₁₈]^q is robust with $q = -1, 0, +1$,^{6c} bond lengths depend weakly on q . Irrespective of q , the mean Au–Au distance for **1** is 3.0 Å and 3.3 Å for atoms within the core and between atoms in the core and the complexes, respectively. The mean Au–S distance is 2.45 (2.36) Å for S bonded to a Au atom in the core (complex), and the mean S–C distance is 1.84 Å.

The high stability of **1** is, moreover, manifested in electronic properties such as electronic affinity (EA) and ionization potential (IP), Table 1. In particular, both EA and IP are clearly higher for **1** than for **2** or **3**. Charge analysis of **1** as a cation (anion) uncovers that the deficit (excess) charge is accommodated both by the Au₁₃

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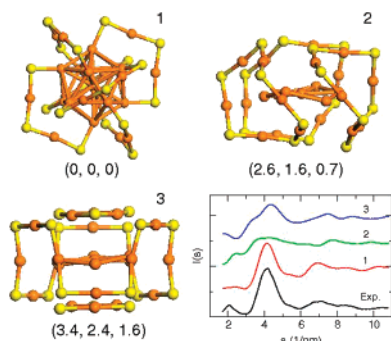


Figure 1. Optimized anionic structures (the Me groups are omitted for clarity) with corresponding XRD patterns. The experimental XRD pattern is adapted from ref 9. Relative total energies are given in eV for the three charge states (−1, 0, +1). Color code: Orange (Au) and yellow (S).

Table 1. Electronic Properties^a

isomer	AEA	AIP	$\Delta(-)$	$\Delta(0)$	$\Delta(+)$
1	3.0	5.0	1.2	0.1	0.6
2	1.9	4.1	0.2	0.1	1.1
3	2.0	4.1	0.2	0.1	1.0

^a Adiabatic electronic affinity (AEA) and adiabatic ionization potential (AIP). $\Delta(-,0,+)$ is the HL separation for the anionic, neutral, and cation charge states, respectively. All energies are in eV.

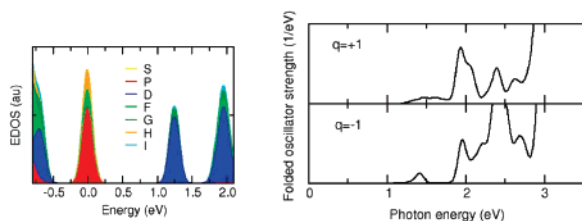


Figure 2. EDOS projected onto spherical harmonics (left, HOMO at 0). Optical spectra of **1** in cationic and anionic charge states (right).

core and the complexes. All reported isomers have distinct HOMO–LUMO (HL) separations as cations, whereas it is only **1** that shows an appreciable gap as an anion.

Given the high stability of **1**, the electronic density of states (EDOS) for $\text{Au}_{25}(\text{RS})_{18}^{1-}$ was investigated in detail near the HL gap, Figure 2. The HOMO level is 3-fold degenerate whereas the LUMO is 2-fold degenerate. The character of the electronic states in the Au_{13} core was analyzed by projection onto spherical harmonics placed at the center of the cluster (see Supporting Information). This analysis reveals that the HOMO is mainly of *P*-character, whereas the LUMO has *D*-symmetry. These results indicate that the electronic structure of the core can be understood within a model for delocalized $\text{Au}(6s)$ electrons in a spherical background potential.¹⁶ For such a potential, an electronic shell structure $1S^21P^61D^{10}...$ is obtained. The core of **1** as an anion has 14 valence electrons, yet the EDOS reveals a shell closing at eight electrons ($1S^21P^6$). This is explained by the fact that the complexes localize one $\text{Au}(6s)$ electron each via the formation of strongly polar covalent bonds. Each complex can effectively be regarded as $[(\text{MeS})_3\text{Au}_2]^-$ bound to (effectively) icosahedral Au_{13}^{5+} . Note that an enhanced stability of ligand-protected icosahedral Au_{13} compounds through an eight-electron shell closing was early predicted^{17a,b} and later realized as $[\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2](\text{PF}_6)_3$.^{17c} In fact, **1** (**2,3**) are examples of spherical (toroidal) ligand-protected Au clusters with closed electronic shells at $1S^21P^6$ ($1S^21P^4$).^{17b}

Experimental reports^{6e} have appeared on the optical properties of $\text{Au}_{25}(\text{RS})_{18}$, and the calculated optical absorption spectra of **1** are reported in Figure 2. The experimental absorption spectra for

$\text{Au}_{25}(\text{RS})_{18}$ with R being either glutathione or hexyl are identical, as are the spectra for the anionic and neutral compounds.^{6e} The calculated spectrum of **1** in the anionic state shows a large optical gap of 1.3 eV, and the separation between the first and second feature is 0.5 eV. Qualitatively, this matches the experimental spectrum, Figure 2a in ref 6e. Although the HL gap for **1** as a cation is reduced to 0.6 eV, the optical gap is similar to the anion case. This is rationalized by the fact that the dipole selection rules forbid transitions inside an electronic shell. However, change of the cluster charge state fills the separation between the first two features, which is also in agreement with the experimental observations.^{6e}

In summary, on the basis of first principles calculations the structure of $\text{Au}_{25}(\text{RS})_{18}$ is found to be a compact Au_{13} core protected by six $[(\text{MeS})_3\text{Au}_2]$ complexes. The high stability is obtained by fulfilling (i) structural robustness and for the anion (ii) an electronic eight-electron shell of delocalized $\text{Au}(6s)$ electrons.

Acknowledgment. During submission of this work, we learned that our prediction is experimentally confirmed.¹⁸ We thank Prof. R. Murray for communicating this result. We thank Prof. K. Nobusada for providing initial coordinates for **3**. The calculations were performed at CSC (Espoo), NIC (FZ Jülich), and C3SE (Göteborg). Support from the Swedish Research Council and the Academy of Finland is acknowledged.

Supporting Information Available: Details of the theoretical procedure and structural characterization of **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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