

Correspondence: On the bonding in ligand-protected gold clusters

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Ligand-protected gold nanoparticles (AuNPs) have attracted scientific interest ever since Michael Faraday synthesized and studied optical properties of gold colloids¹. The systems are widely used in sensing applications and represent examples in which electronic properties can be tuned by size and shape. For a long time, a detailed atomistic understanding of thiolate-protected AuNPs was missing due to experimental difficulties in synthesizing mono-dispersed AuNPs with high purity. However, following the complete determination of Au₁₀₂(RS)₄₄ in 2007², a range of structures have been reported. A common motif in these geometries is a metal core protected by (RS)_nAu_m units. Interestingly, this is the same motif as for self-assembled monolayers of thiolates on Au (111), which have (RS)₂Au₁ as protecting units^{3,4}.

In a recent communication, Gao and co-workers⁵ suggest a scheme to rationalize the structures of ligand-protected AuNP. The authors adopt the language of nuclear physics and postulate two types of elementary building blocks (particles), namely Au₃⁺ and Au₄²⁺. The trimer (equilateral triangle) and tetramer (tetrahedron) are both two-electron closed-shell systems and are in ref. ⁵ associated with protons and tetraquarks, respectively.

Despite the fact that known ligand-protected AuNP can be decomposed according to the flexible scheme in ref. ⁵, the model is questionable with respect to the description of the electronic structure. Electronic properties of gold are determined mainly by delocalized 6s valence electrons. For bare gas-phase clusters, this is demonstrated by pronounced electronic shell closings that coincide with filled electronic shells for a spherical potential⁶. Moreover, bare and ligand-protected gold clusters develop localized plasmons⁷, which is an optical signature of delocalized valence electrons and the basis for sensing applications.

The fundamental unit for gold in the condensed phase is the gold atom, and assigning a physical meaning to charged Au₃ and Au₄ in the AuNP is problematic. The coalescence of gold clusters induces bond re-hybridization, which makes the electronic configurations and properties of the initial constituents unimportant for the understanding of the final product. To make this clear, the case of Au₂₅(RS)₁₈⁻ is taken as a simple example. The structure consists of an icosahedral core protected by six Au₂(RS)₃ complexes^{8–10}, (Fig. 1). In ref. ⁵, the core is decomposed into two

triangular and two tetrahedral units, where corner sharing between two units yields the thirteen-atom core. The optimized structure does not support this division. The average Au–Au distance in the core is 2.95 Å with a small s.d. 0.09 Å. If the structure was to be understood as fused Au₃⁺ and Au₄²⁺ units, the inter-unit distances would be larger than the intra-unit distances, in similarity with molecular crystals.

The structure of Au₂₅(RS)₁₈⁻ is instead rationalized by electronic re-hybridization, where the gold atom is the basic building block. The Au₂(RS)₃ complexes are formally anions, which results in a closed eight-electronic shell for the core of Au₂₅(RS)₁₈⁻⁹. The electronic configuration within the spherical jellium model is 1S²1P⁶, where the orbitals are delocalized over the entire cluster. The 1S orbital is shown in Fig. 1. This orbital is not linked to the 1S states of Au₃⁺ or Au₄²⁺ (also shown in the figure) but instead to linear combinations of atomic 6s-orbitals with a substantial weight on the central atom.

In ref. ⁵ it is suggested that the stability of the metal core in ligand-protected AuNP should be related to the closed-shell character and stability of Au₃⁺ and Au₄²⁺. However, highly charged metal clusters are generally unstable with respect to fragmentation. This holds, e.g., for the low energy Au₆²⁺ isomer discussed in ref. ⁵, which is unstable with respect to fragmentation into two Au₃⁺ units by 1.4 eV. Moreover, Au₄²⁺ is unstable with respect to fragmentation into two Au₂⁺ units by 0.2 eV. The stability of ligand-protected AuNP is consequently difficult to rationalize using Au₃⁺ and Au₄²⁺ as building blocks and without considering the bonds to the ligands.

The underlying reason why some sizes of ligand-protected AuNP are possible to crystallize and structurally characterize, while other sizes are difficult to characterize in this way is not yet known. The crystallization is often sensitive to the experimental conditions, which stresses kinetic effects. The facile formation and enhanced stability of some sizes is presumably a balance between electronic and structural factors. Closed electronic shells result in enhanced stability but do not appear to be an absolute condition. Common for all ligand-protected AuNPs are, however, delocalized valence electrons that are confined by the potential generated by the metal cores of the particles. Models that aim to link stability with structure should preferably account for this fundamental property.

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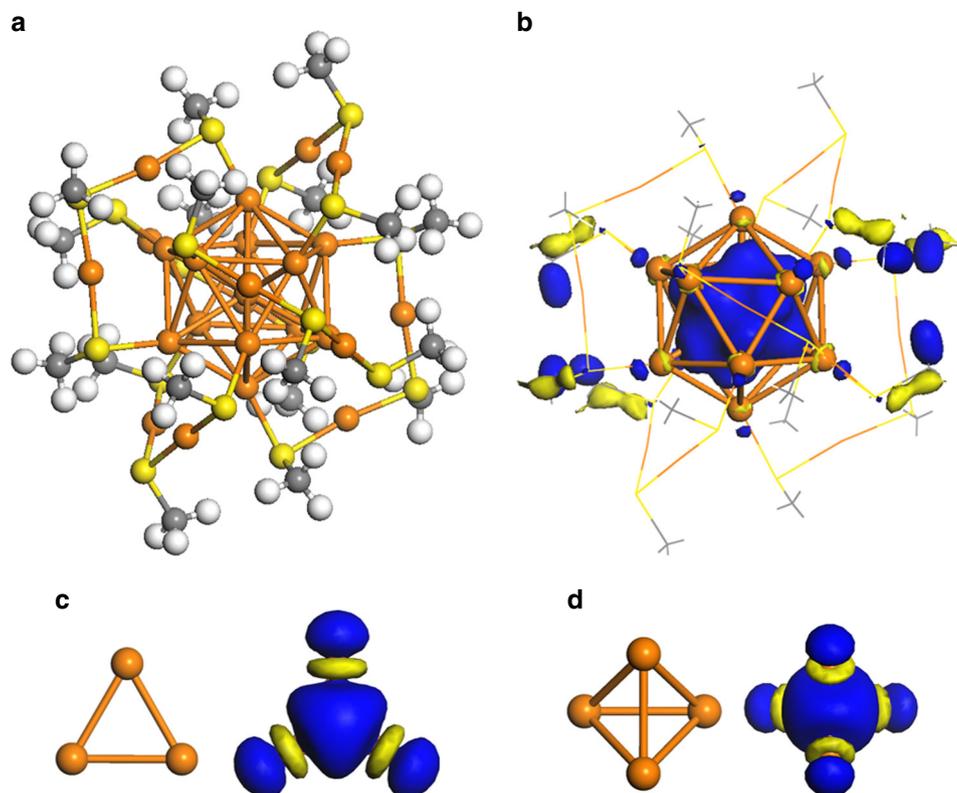


Fig. 1 Structural models and selected Kohn-Sham orbitals. **a** Structural model of $\text{Au}_{25}(\text{RS})_{18}^-$ with R being CH_3 . **b** The 1S orbital of $\text{Au}_{25}(\text{RS})_{18}^-$. The protecting complexes are for clarity shown as lines. **c** The structure and 1S orbital of Au_3^+ . **d** The structure and 1S orbital of Au_4^{2+} . Atomic color code: Au (orange), S (yellow), C (gray) and H (white)

Methods

Density functional theory is used in an implementation with local basis functions and the gradient corrected exchange-correlation functional according to Perdew, Burke, and Ernzerhof (PBE)¹¹. The Kohn–Sham orbitals are expanded with atomic numerical basis functions that are stored on radial grids centered at the atoms¹². A double numerical basis set with polarization functions (dnp) is used for all atoms with a real-space cutoff of 5.0 Å. A semi-core pseudo potential with relativistic corrections¹³ is employed for Au to describe the interaction between the valence electrons (19 electrons) and the nuclei together with the inner-shell electrons.

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Author contributions

H.G. performed the research and wrote the paper.

Additional information

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