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An Atomically Precise Bimetallic Au₁₉Cu₃₀ Nanocluster with an Icosidodecahedral Cu₃₀ Shell and an Alkynyl-Cu Interface

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Supporting Information Placeholder

ABSTRACT: Bimetallic nanoclusters Au₁₉Cu₃₀ with chemical composition of $[Au_{19}Cu_{30}(C=CR)_{22}(Ph_{3}P)_{6}Cl_{2}](NO_{3})_{3}$ (where RC=C is from 3-ethynylthiophene (H₃C₄S-3-C≡CH) or ethynylbenzene (PhC≡CH)) has been synthesized. Single X-ray structural analysis reveals that $Au_{19}Cu_{30}$ has a multishelled core structure of Au@Au₁₂@Cu₃₀@Au₆, comprising a centered icosahedral Au₁₃ (Au@Au₁₂) surrounded by an icosidodecahedral Cu₃₀ shell and an outmost shell of a chair-like hexagonal Au₆. The alkynyl carbon is bound to the hollow sites on the Au₁₉Cu₃₀ nanocluster surface, which is a novel interfacial binding mode in alkynyl-protected alloy nanoclusters. The Cu₃₀ icosidodecahedron is unprecedented and Au₁₉Cu₃₀ represents the first alkynyl-protected Au-Cu alloy nanocluster.

Ligand-protected gold nanoclusters have experienced great advances in the past decade.¹⁻²⁴ To further tune their structures and properties, alloy nanoclusters have been synthesized from the mixing of the second or third metal elements.²⁵⁻³⁴ Ligand choice is important in dictating the compositions and properties of nanoclusters. Recently, alkynyl ligands have been used in the preparation of gold^{21,35-38} and gold-silver nanoclusters and aklynyl protected Au-Ag bimetallic nanocluster such as Au₂₄Ag₂₀, Au₃₄Ag₂₈ and Au₈₀Ag₃₀ have been successfully crystallized and yielded to structural determination.³⁹⁻⁴¹ However, aklynyl-protected Au-Cu bimetallic nanocluster has not been reported so far. Although Au and Ag are of very similar atomic radii, the atomic radius of Cu is significantly smaller than Au. This Au-Cu size disparity may lead to new structures of metal kernel and interface that are very different from the recently discovered aklynyl-protected Au-Ag nanoclusters.

Herein, we report the synthesis and total structure determination of two isostructural $Au_{19}Cu_{30}$ bimetallic nanoclusters in the formula of $[Au_{19}Cu_{30}(C\equiv CR)_{22}(Ph_3P)_6Cl_2](NO_3)_3$ (R = H₃C₄S, 1; R = Ph, 2). The 49-metal-atom kernel has a Russian doll structure Au@Au₁₂@Cu₃₀@Au₆, in which the Cu₃₀ shell has a shape of icosidodecahedron. New bonding modes of alkynyls are found in $Au_{19}Cu_{30}$, suggesting the interfacial structure between alkynyls and copper may be different from alkynyl-gold. It is worth noting that $Au_{19}Cu_{30}$ has twenty-two free electrons, which is a rare case in ligandprotected gold nanoclusters.

The preparation of **1** involved the direct reduction of a mixture containing H_3C_4S -3-C=CAuPPh₃, Cu(NO₃)₂ and Ph₃PAuCl by NaBH₄ in dichloromethane. Cluster **2** was prepared in a slightly modified method via the reduction of PhC=CAuPPh₃, Cu(NO₃)₂ and CuCl by NaBH₄ in dichloromethane. Details of synthesis are provided in the supporting information. Transmission electron microscopic (TEM) analyses revealed that the as-prepared **Au**₁₉Cu₃₀ nanoclusters have roughly uniform size (Figure S1a).



Figure 1. Mass spectra of the $Au_{19}Cu_{30}$ clusters. Inset: The measured (black trace) and simulated (red trace) isotopic patterns. (a) $[Au_{19}Cu_{30}(C\equiv C-3-SC_4H_3)_{22}(Ph_3P)_6Cl_2]^{3+}$; (b) $[Au_{19}Cu_{30}(C\equiv CPh)_{22}(Ph_3P)_6Cl_2]^{3+}$.

Chemical compositions were determined by electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) in positive mode (Figure 1). The clean spectra show tri-cation at m/z = 3216.84 (theory: 3216.87 for 1) and 3172.51 (theory: 3172.53 for 2), corresponding to the molecular ions $[Au_{19}Cu_{30}(C=C-3-SC_4H_3)_{22}(Ph_3P)_6Cl_2]^{3+}$ and $[Au_{19}Cu_{30}(C=CPh)_{22}(Ph_3P)_6Cl_2]^{3+}$, respectively. The observed isotopic patterns of the tricationic clusters are in good agreement with the simulation (Figure 1 inset). The Au $4f_{7/2}$ and Cu $2p_{3/2}$ binding energies were determined to be 84.3 and 932.9 eV, respectively (Figure S2). These values are slightly higher than corresponding bulk metals (84.0 for Au and 932.4 eV for Cu), indicating the metal atoms are mostly in reduced form.

Structural determination revealed that **1** and **2** are isostructural (Figure S3).⁴² The only difference between **1** and **2** is the R groups in the alkynyl ligands. For simplicity, we focus discussion on **1**. Figure 2 shows that the tricationic cluster $[Au_{19}Cu_{30}(C=C-3-SC_4H_3)_{22}(Ph_3P)_6Cl_2]^{3+}$ consists of 19 gold atoms, 30 copper atoms, $22 H_3C_4S-3-C=C-$ ligands, 6 Ph₃P and 2 chlorides. After removing the benzene ring and alkynyls, the $Au_{19}Cu_{30}$ metal framework clearly show C_{2h} symmetry (Figure S4), and the 6 phosphines can be classified into two types (highlighted in yellow and pink). Accordingly, based on the number of P atoms of each type, the ³¹P NMR should display two peaks at an intensity ratio of 1 : 2. Experimentally, two peaks at 55.88 and 65.58 ppm with a peak area ratio of 1 : 2 were observed for **1** (Figure S5).



Figure 2. Molecular structure of $[Au_{19}Cu_{30}(C=C-3-SC_4H_3)_{22}(Ph_3P)_6Cl_2]^{3+}$.

Anatomy of the Au₁₉Cu₃₀ kernel is illustrated in Figure 3. It has a Russian doll structure Au@Au₁₂@Cu₃₀@Au₆. The central part of the kernel is a conventional Au_{13} (Au@Au_{12}) (Figure 3a), which is enclosed in a second shell of Cu_{30} icosidodecahedron (Figures 3b and 3c). The third shell consists of 6 Au atoms (Figure 3d) forming a chair-like hexagon (Figure S7). The icosidodecahedral structure of the Cu_{30} (Figure 3b) is of special interest, which has not been observed in gold alloy nanoclusters before. An icosidodecahedron is one of the Archimedean solids, consisting of twenty triangular faces and twelve pentagonal faces. Two triangles and two pentagons meet at each vertex. There are 60 identical edges, each separating a triangle from a pentagon. An icosidodecahedron has icosahedral symmetry, and it can be generated with the 30 vertices located at the midpoints of the edges of an icosahedron. For comparison, the 30 Cu atoms are arranged quite differently in [Au₁₂Cu₃₂(SPhCF₃)₃₀]⁴⁻ as a pentagonal dodecahedral Cu₂₀ attached by 6 $Cu_2(SR)_5$ units.³⁴



Figure 3. Anatomy of $Au_{19}Cu_{30}$ kernel structure in **1** or **2**. (a) Centered icosahedron $Au@Au_{12}$ (b) Cu_{30} icosidodecahedron. (c) $Au@Au_{12}@Cu_{30}$ multishelled structure. (d) Six outmost Au atoms highlighted in green.

In the central Au_{13} core, the Au \cdots Au distances from the central Au atom to the peripheral Au₁₂ shell give an average value of 2.783 Å. It is shorter than the 2.88 Å bond length in bulk gold, indicating strong interactions between central Au and peripheral Au. The Au ... Au distances on the Au₁₂ icosahedron has an average value of 2.926 Å. The average Cu $\cdot \cdot$ Cu distance in Cu₃₀ shell is 2.917 Å, which is much longer than that (2.56 Å) in bulk copper. The Au $\cdot \cdot$ Cu bond lengths between Au₁₂ and Cu₃₀ shells can be classified into two groups: shorter distances in the range of 2.651(2)-2.758(2) Å and longer distances in the range of 2.773(2)-3.019(2) Å, together giving an average distance of 2.774 Å, which is comparable to 2.72 Å (sum of the atomic radii of Au and Cu). The six gold atoms (Figure S7, highlighted in orange) at the third shell cap six pentagonal Cu₅ faces of the Cu₃₀ shell, and form a hexametric ring of a chair conformation (Figure S7, blue shadowed).

In the Au₅₅ Mackay icosahedron (Au₅₅-MI)³ and icosahedral-based Au₁₄₄ nanoclutser,^{43,44} there is a icosahedral Au₄₂ shell around the central Au₁₃. This Au₄₂ icosahedron can be taken as Au₃₀@Au₁₂, i.e. 12 gold atoms capping an icosidodecahedral Au₃₀. Au₁₉Cu₃₀ can be derived from icosahedral Au₅₅ by replacing the Au₃₀ by Cu₃₀ and removing 6 Au atoms of the outmost Au₁₂. This structural similarity implies that the Au₃₀ shell in Au₅₅ or Au₁₄₄ may be the substitution positions when these clusters are doped by copper. Previous prediction is that the preferable doping sites are inner metal core and the maximum numbers of Cu atom were 30 and 23 respectively.^{27,45} Calculation by Zeng et al.²⁹ suggests that in gas phase copper-doped multishell structured Au₅₅ prefer to form alloy cluster Au₄₃Cu₁₂, and the preferable doping sites are the inner Au₁₂ shell. The present work offers new possibilities for the doping sites in gold nanoclusters.

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Figure 4. The coordination models of 22 H₃C₄S-3-C=C- ligands on surface of the Au₁₉Cu₃₀: (a) μ_3 - $\eta^1(Cu)$, $\eta^1(Cu)$, $\eta^1(Cu)$, two; (b) μ_3 - $\eta^1(Cu)$, $\eta^1Cu)$, $\eta^2(Cu)$, two; (c) μ_3 - $\eta^1(Cu)$, $\eta^2(Cu)$, $\eta^2(Cu)$, 14; (d) μ_3 - $\eta^1(Au)$, $\eta^2(Cu)$, $\eta^2(Cu)$, four. Color legend: orange = Au; turquoise = Cu; yellow = S; gray = C.

There are 22 H₃C₄S-3-C=C- ligands, 6 Ph₃P and 2 chlorides in **1**. Each of the six Au atoms in the outmost shell is ligated terminally by one Ph₃P ligand, and each chloride bridges two Cu atoms (Figure 2). Although staple motifs such as PhC=C-Au-C₂(Ph)-Au-C=CPh and PhC=C-Au-C=CPh were found in alkynyl-protected Au or Au-Ag nanoclusters,^{21,39,41} there is no such staple motifs in **1** whose surface is dominated by Cu atoms. Formation of staple motifs on the gold surface is facilitated by two factors: gold's preference for a linear twofold coordination; ease of creation of a gold adatom on the surface (energy penalty is about 0.6 eV from DFT; see Table S1 in SI). In contrast, it is harder to create an adatom on the Cu surface (energy penalty is about 1.0 eV), so the PhC≡C groups prefer to bind to the Cu surface individually at the tight Cu₃ triangles (due to the smaller atomic radius of Cu). We found that all the 22 alkynyls in **1** function as μ_3 -bridges on M_3 triangles. The RC=C group can be an exclusively σ donor to bind triangular Cu₃ (Figure 4a) or both σ and π donors to bind Cu₃ (Figure 4b and 4c). Interestingly, the Au atom in Figure 4d is from the inner Au_{12} shell, while the Cu atoms are from the Cu_{30} shell. These interfacial binding structures account for the distinct arrangement of alloy metal atoms in the $Au_{19}Cu_{30}$ cluster.

We next discuss the electronic structure of cluster 1 which has 22 valence electrons according to the superatom complex model: $N^* = N_{Au+Cu}$ - $N_{alkynyl}$ - $N_{chloride}$ - Q = 49 -22 - 2 - 3 = 22.⁴⁶ Because 20 is a magic number corresponding to a spherical shell closing, 22 is hence an unusual number of free electron count in gold nanoclusters, and the previous example is the diphosphine-protected Au₂₂ cluster having a rod-like shape.¹⁰ The jellium model, which the superatom complex model is based on, predicts that the 22-electron system has the shape of a sphere with two elongated poles,⁴⁷ quite different from the roughly spherical shape of 1. Hence the Au₁₉Cu₃₀ cluster with its 22 electron count could be another example whose complexity is beyond the superatom model. On the other hand, our analysis of the HOMO and LUMO orbitals from density functional theory (DFT) does show that they are delocalized around the whole cluster (Figure S8). The HOMO looks like two D-type orbitals with an inversion symmetry, while the LUMO looks like one D-type orbital. In contrast, the superatom model would predict F-type orbitals for the frontier orbitals of a 22-electron system. This again shows that our 22-electron Au₁₉Cu₃₀ cannot be described by the superatom model.48



Figure 5. Comparison of the optical absorption spectrum of the $[Au_{19}Cu_{30}(C \equiv C-SC_4H_3)_{22}(PH_3)_6Cl_2]^{3+}$ cluster between experiment and simulation (TD-DFT).

We measured the optical absorption spectrum of **1** (Figure 5) which shows three main broad bands at 1.36 eV (α), 1.83 eV (β), and 2.34 eV (γ). They are well reproduced in the simulated spectrum from time-dependent DFT, despite the underestimate of the excitation energies. We found that the α peak mainly comes from the HOMO-4 to LUMO+1 transition, while the β and γ peaks all have multiple contributions of similar oscillator strength.

In summary, two novel alkynyl-protected multishell structured $Au_{19}Cu_{30}$ nanoclusters have been synthesized and structurally determined. The novel shell-by-shell structure $Au@Au_{12}@Cu_{30}@Au_6$ offers new mode for understanding the preferable doping sites when Au nanoclusters are doped with copper. The interfacial structures of alkynyl ligands on the Cu_{30} shell via μ_3 -bridges are distinctly different from those of alkynyls on Au or Au-Ag nanoclusters. The 22 electron count of the two clusters is also unusual. The new geometry, interface, and electronic structure of the $Au_{19}Cu_{30}$ nanoclusters offer exciting opportunities to explore their functions in the new future.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest

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