

# Doping Golden Buckyballs: $\text{Cu@Au}_{16}^-$ and $\text{Cu@Au}_{17}^-$ Cluster Anions\*\*

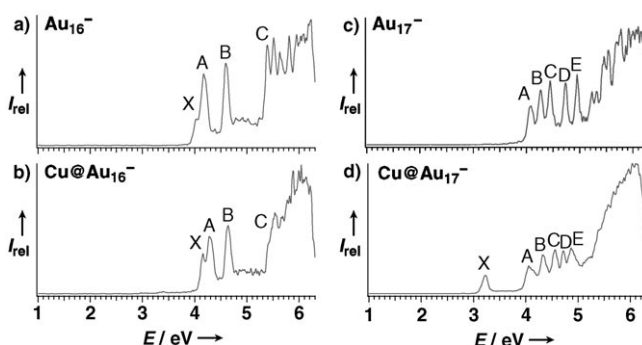
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The discovery of the unique catalytic effects of gold nanoparticles on oxide substrates<sup>[1]</sup> has stimulated a flurry of research into the structures and properties of free gold nanoclusters, which may hold the key to elucidating the catalytic mechanisms of supported gold clusters. One of the most remarkable results has been the discovery of planar gold cluster anions ( $\text{Au}_n^-$ ) of up to twelve gold atoms and the 2D to 3D transition for clusters with  $n$  larger than 12.<sup>[2–4]</sup> Among larger gold clusters,  $\text{Au}_{20}$  has been found to be a perfect tetrahedron.<sup>[5]</sup> A more recent study of the structures of  $\text{Au}_n^-$  cluster anions in the medium size range ( $n=15–19$ )<sup>[6]</sup> has shown that clusters with  $n=16–18$  possess unprecedented empty cage structures. In particular, the  $\text{Au}_{16}^-$  cluster anion has an interesting tetrahedral structure with an inner diameter of about 5.5 Å and can be compared to the fullerenes (buckyballs). Although  $\text{Au}_{32}$  was first suggested to be a “24-carat golden fullerene”,<sup>[7,8]</sup> subsequent studies showed that the  $\text{Au}_{32}^-$  ion is in fact a low-symmetry compact 3D structure.<sup>[9]</sup> Other larger gold cage clusters have also been proposed computationally,<sup>[10,11]</sup> but none has been observed or is expected to be the global minimum. The cage structures of the cluster anions  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  have recently been confirmed by electron diffraction<sup>[12]</sup> and thus they are the first experimentally confirmed and the smallest possible gold cages. The large empty space inside these cage clusters immediately suggested that they can be doped with a foreign

atom to produce a new class of endohedral gold cages<sup>[6]</sup> analogous to endohedral fullerenes.<sup>[13,14]</sup>

A gold cage containing a central atom was first predicted for a series of icosahedral clusters  $\text{M@Au}_{12}$  ( $\text{M} = \text{W}, \text{Ta}^-, \text{Re}^+$ ) based on the 18-electron rule<sup>[15–17]</sup> and was subsequently confirmed experimentally.<sup>[18,19]</sup> However, since  $\text{Au}_{12}$  itself does not possess a cage structure, the dopant atom with the appropriate electron count must play an essential role in holding the cage together. Bimetallic gold clusters have been studied experimentally<sup>[20–24]</sup> as they offer new opportunities to fine-tune the electronic and structural properties of gold nanoclusters. Following the discovery of the hollow gold cages,<sup>[6]</sup> two recent theoretical studies have appeared concerning doping them with a foreign atom.<sup>[25,26]</sup> Since the parent  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  cluster anions are empty cages, many different types of atoms could be used as dopants to form new endohedral gold clusters.<sup>[6]</sup> Herein we report the first observation and characterization of  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  doped with a Cu atom ( $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$ ) by both photoelectron spectroscopy (PES) and density functional theory (DFT) calculations.

The experiment was performed in a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic cluster source.<sup>[27]</sup> Figure 1 shows the spectra of the ions



**Figure 1.** Photoelectron spectra of the cluster anions  $\text{CuAu}_{16}^-$  and  $\text{CuAu}_{17}^-$ , compared to  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$ ; see text for details.

$\text{CuAu}_{16}^-$  and  $\text{CuAu}_{17}^-$  along with those of the parent gold clusters.<sup>[6]</sup> Let us first focus on the  $\text{CuAu}_{16}^-$  ion (Figure 1 b), whose PE spectrum is remarkably similar to that of its parent gold cluster  $\text{Au}_{16}^-$  (Figure 1 a). The first three features (X, A, and B) and the gap between B and C (Figure 1) are all very similar in the PE spectra of both systems, except that the intensity of the ground state band (X) is greater for the doped cluster and its electron-binding energies are slightly higher (Table 1). The similarity between the spectra of these two

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**Table 1:** Experimental adiabatic (ADE) and vertical (VDE) detachment energies for the doped cluster anions  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  along with those for the  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  anions and the calculated VDE values. All energies are given in electron volts.

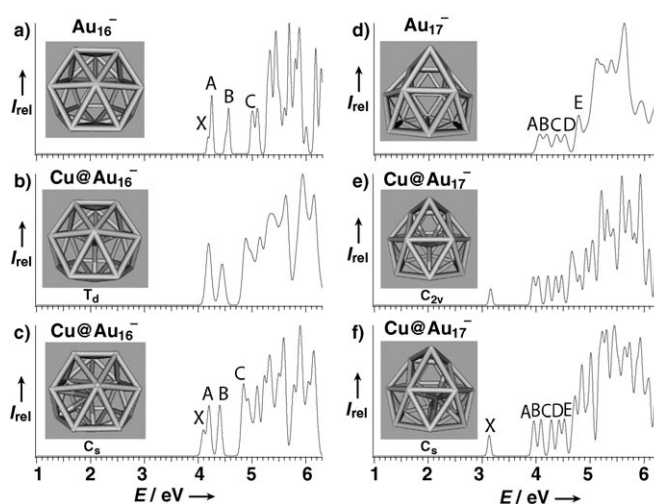
Anion	Experimental ADE	Experimental VDE	Theoretical VDE
$\text{Au}_{16}^-$ [a]	$3.99 \pm 0.03$	$4.03 \pm 0.03$	4.179
$\text{Cu@Au}_{16}^-$ ( $C_s$ )	$4.12 \pm 0.05$	$4.16 \pm 0.03$	4.092
$\text{Au}_{17}^-$ [a]	$4.03 \pm 0.03$	$4.08 \pm 0.03$	4.053
$\text{Cu@Au}_{17}^-$ ( $C_{2v}$ )	$3.16 \pm 0.06$	$3.23 \pm 0.03$	3.155

[a] Taken from ref. [6].

species suggests that the Cu doping does not alter the geometric and electronic structures of the  $\text{Au}_{16}^-$  cluster anion significantly, which is only possible if Cu is trapped inside the  $\text{Au}_{16}^-$  cage. The  $\text{Au}_{16}^-$  cluster anion itself is unique and its PE spectrum does not exhibit an energy gap similar to that for other even-sized gold clusters in this size range.<sup>[4,6,28]</sup> The high electron-binding energies and the lack of an energy gap suggest that the neutral  $\text{Au}_{16}$  cluster is open-shell and probably has two unpaired electrons (a triplet state).<sup>[6]</sup> This means that two extra electrons would be required to reach a closed-shell 18-electron  $\text{Au}_{16}^{2-}$  ion, which is also borne out by a recent theoretical study.<sup>[25]</sup> Because of the high electron affinity of Au, the Cu atom can be viewed as donating an electron to the gold cage in  $\text{CuAu}_{16}^-$ , which gives rise to a closed-shell and stable  $\text{Au}_{16}^{2-}$  dianion. Thus, the  $\text{CuAu}_{16}^-$  cluster anion can best be viewed as  $\text{Cu}^+@Au_{16}^{2-}$ .

The spectrum of the doped cluster anion  $\text{CuAu}_{17}^-$  is also very similar to that of the parent gold cluster  $\text{Au}_{17}^-$ ; except that there is one low-binding-energy peak followed by a large energy gap in the spectrum of the Cu-doped cluster (Figure 1 c,d). The five peaks between 4 and 5 eV in the spectrum of the  $\text{CuAu}_{17}^-$  cluster anion (labeled A–E in Figure 1 d) are remarkably similar to the five characteristic low-binding-energy features in the spectrum of the parent gold cluster ( $\text{Au}_{17}^-$ ; Figure 1 c). This spectral similarity again suggests that the Cu dopant induces very little structural change in the  $\text{Au}_{17}^-$  cage except that it donates one electron.  $\text{Au}_{17}^-$  is a closed-shell species with 18 valence electrons,<sup>[6]</sup> therefore the extra electron is expected to enter its LUMO and give rise to the low-binding-energy peak (X) in the PE spectrum of the  $\text{CuAu}_{17}^-$  cluster anion (Figure 1 d). All these observations again imply that Cu stays in the center of the  $\text{Au}_{17}^-$  ion cage ( $\text{Cu}^+@Au_{17}^{2-}$ ) and does not perturb the electronic and geometric structures of the cage significantly.

We carried out theoretical studies to confirm these observations (see Experimental Section). The results revealed that the endohedral  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  cluster anions are overwhelmingly favored over any other structure with the Cu atom on the outside of the cage. Figure 2 shows the simulated PE spectra for two endohedral structures each for the  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  cluster anions along with those of the parent clusters.<sup>[6]</sup> In one structure, the Cu atom is located in the center of the cages and in the other it is displaced slightly from the center. The energy differences between the two isomers are very small and their simulated PE spectra are also very similar to each other. The endohedral



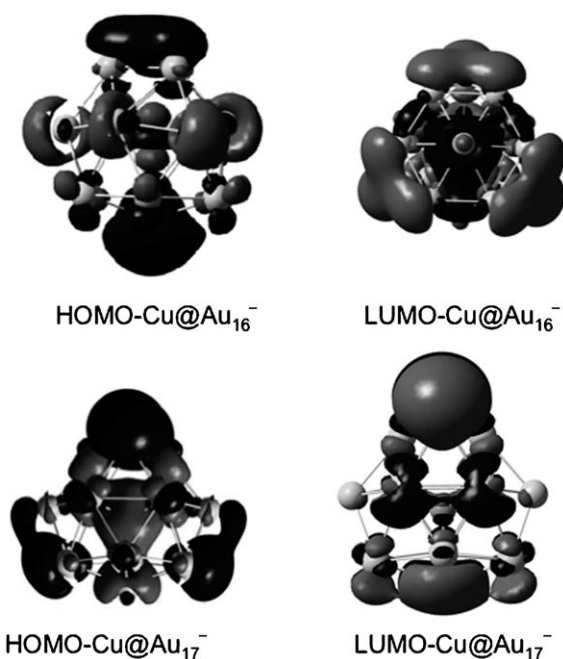
**Figure 2.** Simulated photoelectron spectra for two endohedral structures each for  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  along with those for  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$ .

$\text{Cu@Au}_{16}^-$  cluster anion with Cu in the center has  $T_d$  symmetry with a triply degenerate HOMO, which gives rise to the first band in the simulated PE spectrum (Figure 2 b). In the structure in which the Cu atom is displaced from the center, the  $\text{Cu@Au}_{16}^-$  cluster anion has  $C_s$  symmetry and the triply degenerate HOMO is split, which gives rise to the doublet peaks (X and A) in the simulated PE spectrum (Figure 2 c) and is in perfect agreement with the experimental spectrum (Figure 1 b). The simulated PE spectra of both the  $C_{2v}$  and  $C_s$  structures of the  $\text{Cu@Au}_{17}^-$  cluster anion are similar to each other and are both in good agreement with the experimental spectra, thereby suggesting that the Cu atom in the center of the  $\text{Au}_{17}^-$  anion cage might be somewhat fluxional.<sup>[29]</sup>

The calculated vertical detachment energies (VDEs) for the  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  cluster anions are also in good agreement with the experimental values (Table 1). Overall, the excellent agreement between theory and experiment confirms the endohedral structures of these Cu-doped gold cages unequivocally. It is important to note, however, that the  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  cages are not distorted significantly from those of the parent clusters even in the low-symmetry structures.

Figure 3 shows the frontier orbitals of the two endohedral clusters. The electron densities are clearly dominated by the cages, with little contribution from the central Cu atom; this is consistent with the description of  $\text{Cu@Au}_{16}^-$  and  $\text{Cu@Au}_{17}^-$  as  $\text{Cu}^+@Au_{16}^{2-}$  and  $\text{Cu}^+@Au_{17}^{2-}$ , respectively.<sup>[30]</sup> The charge-transfer interactions between the cage and its dopant are also reminiscent of endohedral fullerenes<sup>[13,14]</sup> and are consistent with the strongly ionic character of the diatomic molecule  $\text{CuAu}$ .<sup>[31]</sup>

Doping gold clusters could be a powerful way to tune their chemical and physical properties,<sup>[24,32,33]</sup> and the results reported herein suggest that a new class of endohedral gold cages is indeed viable. In these examples the cage structures of  $\text{Au}_{16}^-$  and  $\text{Au}_{17}^-$  cluster anions are maintained simply by changing the dopants, which is reminiscent of the behavior of



**Figure 3.** The HOMO and LUMO of cluster anions Cu@Au<sub>16</sub><sup>-</sup> (C<sub>2v</sub>) and Cu@Au<sub>17</sub><sup>-</sup> (C<sub>2v</sub>).

endohedral fullerenes.<sup>[13,14]</sup> It would be particularly interesting to dope transition-metal atoms inside these gold cages to create magnetic gold clusters as these may exhibit new, physical, chemical, and catalytic properties that are distinct from the pure gold clusters.

### Experimental Section

**Photoelectron spectroscopy:** The CuAu<sub>16</sub><sup>-</sup> and CuAu<sub>17</sub><sup>-</sup> cluster anions were produced by laser vaporization of an Au/Cu composite disk target containing about 7% Cu. Negatively charged clusters were extracted from the cluster beam and analyzed with a time-of-flight mass spectrometer.<sup>[27]</sup> The clusters of interest were mass-selected and decelerated before being intercepted by a 193-nm laser beam from an ArF excimer laser for photodetachment. The Cu content in the Au/Cu target was carefully adjusted to minimize multiple Cu doping in the Au<sub>x</sub>Cu<sub>y</sub><sup>-</sup> clusters and provide the Au<sub>x</sub>Cu<sub>y</sub><sup>-</sup> series as the dominant doped species in order to achieve clean mass-selection for the CuAu<sub>16</sub><sup>-</sup> and CuAu<sub>17</sub><sup>-</sup> anions. Photoelectron time-of-flight spectra were calibrated against the known spectra of Au<sup>-</sup> and converted into binding energy spectra by subtracting the kinetic energy spectra from the photon energy. The resolution of the magnetic-bottle PE spectrometer was  $\Delta E/E \approx 2.5\%$  (i.e., about 25 meV for 1-eV electrons).

**Calculations:** We performed global-minimum searches using the basin-hopping method<sup>[34]</sup> for the anionic gold clusters Au<sub>n</sub><sup>-</sup> ( $n = 16, 17$ ) doped with a Cu atom. We combined the global search method directly with DFT calculations.<sup>[6,25,35]</sup> After each accepted Monte-Carlo move a geometry minimization was carried out using a DFT method with a gradient-corrected functional, namely the Perdew–Burke–Erzerhof (PBE) exchange–correlation functional,<sup>[36]</sup> implemented in the DMol<sup>3</sup> code.<sup>[37]</sup> Top low-lying isomers were collected and reoptimized using the PBEPBE functional and LANL2DZ basis set, as implemented in the Gaussian03 package.<sup>[38]</sup> Frequency calculations were also carried out to assure the optimized structures were local minima. Finally, PE spectra were calculated using the

PBEPBE functional and the LANL2DZ basis set. The first VDE was calculated by the energy difference between the anion and neutral clusters at the anion geometry. VDEs to higher detachment channels were computed by adding the occupied orbital energies relative to the HOMO to the first VDE. The simulated PE spectra were obtained by fitting the computed VDEs with Gaussian functions with a width of 0.04 eV. The isomer structures that gave the best match between simulated and measured spectra were identified and are shown in Figure 2. Note that the *T<sub>d</sub>* isomer of the Cu@Au<sub>16</sub><sup>-</sup> ion shown in Figure 2b has four imaginary frequencies (owing to Jahn–Teller distortion), whereas the *C<sub>s</sub>* isomer of the Cu@Au<sub>16</sub><sup>-</sup> ion shown in Figure 2c has no imaginary frequencies and represents a global minimum.

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