The discovery of catalytic effects in gold nanoparticles has accelerated efforts on the characterization and understanding of the structures and properties of bare gold clusters. Doped gold clusters have received increasing attention because of their potential tunable catalytic properties versus dopant. The first highly stable doped gold cluster was a closed-shell icosahedral W@Au12, predicted using density functional theory (DFT) by Pyykkö and Runeberg and confirmed using photoelectron spectroscopy (PES) by Li et al. Subsequent PES studies showed that V-, Nb-, and Ta-doped Au12 clusters also possess the Ih symmetry. Another theoretical study by Gao et al. shows that Au clusters doped with a foreign metal atom tend to form core/shell structures when the number of Au atoms is greater than nine. Very recently, we have provided the first experimental evidence of endohedral doping of the golden cages by Cu in Cu@Au16 and Cu@Au17. Our recent studies of pure gold clusters have shown that Au16 exhibits a novel hollow-cage structure with a large diameter (~5.5 Å), suggesting possibilities of endohedral doping in analogy to the endohedral fullerenes. A following theoretical study by Walter et al. suggests that Si can be doped inside the neutral Au16 cage and the Si-doped Au16 exhibits very different reactivities toward O2. We have provided the first experimental evidence of endohedral doping of the golden cages by Cu in Cu@Au16 and Cu@Au17. Our PES spectra reveal striking similarities between the Cu-doped clusters and the parents, suggesting the Cu dopant does not distort the cages significantly, which is borne out by theoretical calculations. However, what other types of atoms can be doped into the golden cages still remains an open question.

In this communication, we report a joint PES and theoretical study of doping a group IV atom into the Au16 cage cluster. We find surprisingly that the lowest-energy structures of MAu16 (M = Si, Ge, Sn) are no longer in the form of endohedral structures. Instead, the dopant atom is found to be exohedral (Ge, Sn) or becomes a part of the gold cage (Si).

PES spectra of MAu16 (M = Si, Ge, Sn) have been obtained at two detachment photon energies, 193 nm (Figure 1a–c) and 266 nm (Figure S1). The PES spectra are somewhat similar to each other, each revealing a fairly large HOMO–LUMO gap (X–A gap). The spectrum of SiAu16 (Figure 1a) shows a weak feature (X′) in the HOMO–LUMO gap region, suggesting the presence of an isomer. The first feature in the spectrum of SnAu16 (Figure 1c) displays a doublet feature (also see Figure S1), which is also an indication of another isomer (see below). The X band represents the ground state transition, yielding adiabatic and vertical detachment energies (ADE/VDE) of 3.24/3.23 eV, respectively, for M = Si, Ge, and Sn (Table 1).

Table 1. Relative Energies, Experimental ADE, VDE, and Calculated VDE of the Lowest-Energy Isomers of MAu16. All Calculations were at the PBE0/LAN2DZ Level of Theory and All Energies are in Electronvolts

<table>
<thead>
<tr>
<th>isomer</th>
<th>relative energies</th>
<th>ADE (exptl)</th>
<th>VDE (exptl)</th>
<th>VDE (theor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiAu16(1) (C1)</td>
<td>0.00</td>
<td>3.20 (5)</td>
<td>3.23 (3)</td>
<td>3.11</td>
</tr>
<tr>
<td>SiAu16(3) (C1)</td>
<td>0.12</td>
<td>3.63 (3)</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td>GeAu16(1) (C1)</td>
<td>0.00</td>
<td>3.21 (4)</td>
<td>3.26 (3)</td>
<td>3.31</td>
</tr>
<tr>
<td>SnAu16(1) (C1)</td>
<td>0.00</td>
<td>3.21 (4)</td>
<td>3.26 (3)</td>
<td>3.28</td>
</tr>
<tr>
<td>SnAu16(3) (C3)</td>
<td>0.05</td>
<td>3.30 (6)</td>
<td>3.37 (3)</td>
<td>3.37</td>
</tr>
</tbody>
</table>

The number in the parentheses denotes the uncertainty in the last digit.

To affirm if the group IV atoms can be doped into the Au16 cage, we carried out an unbiased search for the global minimum structures of MAu16 (M = Si, Ge, Sn), using the basin-hopping optimization technique coupled with the DFT method. Several randomly constructed initial structures were used, and all yielded consistently similar sets of low-lying isomers (Figures 1 and S2). After 200–300 Monte Carlo moves. These isomers were reoptimized using the PBE0 functional with the scalar relativistic effective core potential and LANL2DZ basis set.
Harmonic vibrational frequencies were calculated to confirm that the lowest-energy isomers are true minima (Table S6). The PBEPBE calculations were performed using the Gaussian03 program.\textsuperscript{14} Single-point energies of the corresponding neutral isomers in the anion geometries were calculated to evaluate the first VDEs of the anion isomers. The binding energies of deeper orbitals were added to the first VDE to yield the VDEs of the excited states. Finally, each calculated VDE was fitted with a Gaussian of width 0.04 eV to yield the simulated PES spectra (Figure 1, right panel).

Surprisingly, our global minimum search shows that the Au\textsubscript{16} clusters doped with a group IV atom are exohedral in nature with significant distortions to the parent cage (Figure 1). The structures with endohedral doping are all higher-lying isomers (Figure S2). The VDEs of all the lowest-energy isomers are in very good agreement with the experiment (Table 1). The simulated spectrum for the global minimum of GeAu\textsubscript{16} agrees well with the experimental spectrum. For the Si- and Sn-doped clusters, there is evidence of an additional isomer present in the PES spectra (Figure 1a,c), as borne out in the simulated spectra (Figure 1d,f). The similarities in the structures of the lowest-energy isomer with the Ge and Sn dopants are reflected in their similar PES patterns (Figure 1b,c). For SnAu\textsubscript{16}, isomers 1 and 3 give nearly identical simulated spectra; isomer 3 seems to contribute significantly to the experimental spectra; isomer 3 for SiAu\textsubscript{16} in that the Si dopant is capped by an extra Au atom that is not a part of the cage but dangling over the Si atom. Isomer 1 for SiAu\textsubscript{16} is the main species, while isomer 3 gives rise to the minor feature (X, Figure 1a and Table 1).

The dangling Au atom atop Si in SiAu\textsubscript{16} is reminiscent of the Au/H analogy\textsuperscript{16} first discovered in the SiAu\textsubscript{5} cluster, which possesses a T\textsubscript{d} geometry similar to SiH\textsubscript{6}.\textsuperscript{16a} We find recently that this Au/H analogy does not exist in GeAu\textsubscript{4} and SnAu\textsubscript{4} since the latter have a square-planar structure.\textsuperscript{17} A closer look at the structures of GeAu\textsubscript{16} and SnAu\textsubscript{16} shows that the local geometry around the Ge/Sn atom is nearly square-planar (Figure 1), just as in GeAu\textsubscript{4} and SnAu\textsubscript{4}. On the other hand, the dangling Au atom atop Si in SiAu\textsubscript{16} reflects the strong Si–Au covalent bonding, similar to that in SiAu\textsubscript{4} or other Si–Au mixed clusters.\textsuperscript{16} Interestingly, the local structure of Si in SiAu\textsubscript{16} is also very similar to that of the SiAu\textsubscript{5} cluster.\textsuperscript{18}

Molecular orbital analyses give rise to further insight into the local interactions between the dopant and Au in MAu\textsubscript{16}. The dangling Au atom in SiAu\textsubscript{16}, besides giving a unique geometry to the doped cluster, has a significant contribution to the HOMO of the doped cluster, resulting in strong bonding with the Si atom (Figure S3). The HOMO pictures of the Ge- and Sn-doped clusters show significant contribution from the dopant atom to the cage: the local electron density distribution around the group IV atom resembles the molecular orbital pictures obtained in the cases of GeAu\textsubscript{4} and SnAu\textsubscript{4}.\textsuperscript{17} Apparently, the strong interactions between Au and the group IV atoms (particularly in the diatomic molecule MAu) lead to reconstruction of the parent Au\textsubscript{16} cage structure in the global minima of MAu\textsubscript{16}. Additionally, Hirshfeld charge analysis on the neutral clusters indicates that all dopants entail a small negative charge.

The neutral MAu\textsubscript{16} clusters all possess 20 valence electrons and are closed-shell species, as evident from the PES spectra which exhibit a sizable HOMO–LUMO gap of ~0.6–0.8 eV (Figure 1). However, because of the strong M–Au local interactions, the MAu\textsubscript{16} clusters may no longer be viewed as 20-electron closed-shell systems in the sense of the jellium model. They should rather be considered as 16-electron systems because four electrons are needed for the local M–Au bonding. This is consistent with the fact that group IV elements tend to form covalent bonds, particularly for Si and Ge.

In summary, we have studied a series of doped gold anion clusters, MAu\textsubscript{16} (M = Si, Ge, Sn), and found that their global minima do not possess the endohedral structures. The global minima are dominated by the strong M–Au local interactions reminiscent of the MAu\textsubscript{16} clusters. In particular, a dangling Au atom is observed in the low-lying isomers of SiAu\textsubscript{16}, which confirms the Au/H analogy found earlier in Si–Au mixed clusters.\textsuperscript{18} Thus, the nature of the dopant–Au local interactions is the key factor in determining if a given atom can be used to dope the golden cages. Just like Cu,\textsuperscript{10} we expect that many transition metals can be doped into the golden cages. This research is being actively pursued in our laboratories.

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Supporting Information Available: Experimental methods, PES at 266 nm, data of Cartesian coordinates and harmonic vibrational frequencies, HOMO picture of the lowest-energy isomers, and the complete ref 14 are collected. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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