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Communication

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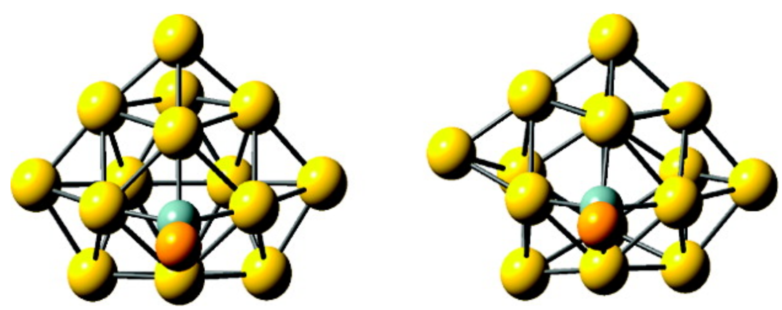

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Doping the Golden Cage Au_{16}^- with Si, Ge, and Sn

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The discovery of catalytic effects in gold nanoparticles[1] has accelerated efforts on the characterization and understanding of the structures and properties of bare gold clusters.[2,3] 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 $W@Au_{12}$, predicted using density functional theory (DFT) by Pyykkö and Runeberg[4] and confirmed using photoelectron spectroscopy (PES) by Li et al.[5] Subsequent PES studies showed that V-, Nb-, and Ta-doped Au_{12} clusters also possess the I_h symmetry.[6] Mass spectra of a number of Au alloy clusters have been observed by Lievens and co-workers.[7]

Our recent studies of pure gold clusters have shown that Au_{16}^- exhibits a novel hollow-cage structure with a large diameter (~5.5 Å),[8] 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 Au_{16} cage and the Si-doped Au_{16} exhibits very different reactivities toward O_2.[9a] 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.[9b] Very recently, we have provided the first experimental evidence of endohedral doping of the golden cages by Cu in $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$.[10] 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 Au_{16}^- cage cluster. We find surprisingly that the lowest-energy structures of MAu_{16}^- (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 MAu_{16}^- (M = Si, Ge, Sn) have been obtained[10,15] 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 $SiAu_{16}^-$ (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 $SnAu_{16}^-$ (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 3.20/3.23, 3.21/3.26, and 3.30/3.37 eV, respectively, for M = Si, Ge, and Sn (Table 1).

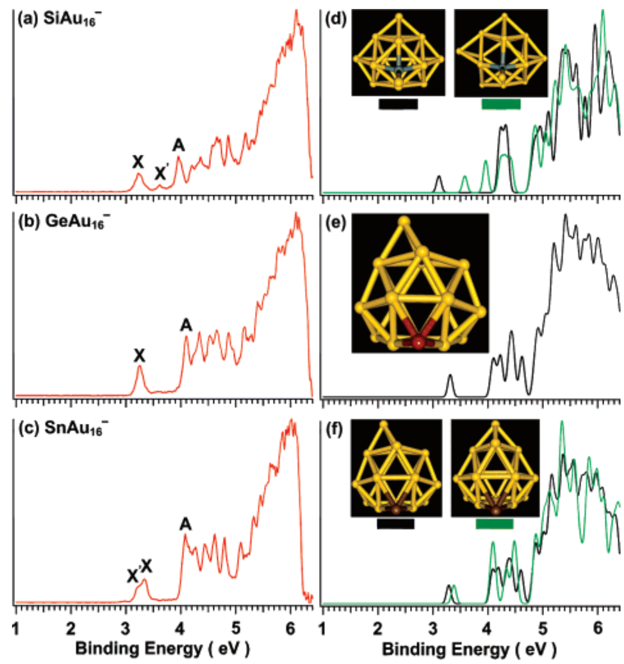

Figure 1. The experimental (left panel) and simulated PES (right panel) of $SiAu_{16}^-$, $GeAu_{16}^-$, and $SnAu_{16}^-$. The inset shows the global minimum and a low-lying isomer (for $SiAu_{16}^-$ and $SnAu_{16}^-$). The dopant atoms are shown in color (Si in gray, Ge in red, and Sn in brown).

Table 1. Relative Energies, Experimental ADE, VDE, and Calculated VDE of the Lowest-Energy Isomers of MAu_{16}^-: All Calculations were at the PBEPBE/LAN2DZ Level of Theory and All Energies are in Electronvolts

isomer	relative energies	ADE (exptl)[a]	VDE (exptl)[a]	VDE (theor)
$SiAu_{16}^-$(1) (C_s)	0.00	3.20 (5)	3.23 (3)	3.11
$SiAu_{16}^-$(3) (C_1)	0.12		3.63 (3)	3.58
$GeAu_{16}^-$(1) (C_1)	0.00	3.21 (4)	3.26 (3)	3.31
$SnAu_{16}^-$(1) (C_1)	0.00	3.21 (4)	3.26 (3)	3.28
$SnAu_{16}^-$(3) (C_s)	0.05	3.30 (6)	3.37 (3)	3.37

[a] The number in the parentheses denotes the uncertainty in the last digit.

To affirm if the group IV atoms can be doped into the Au_{16}^- cage, we carried out an unbiased search for the global minimum structures of MAu_{16}^- (M = Si, Ge, Sn), using the basin-hopping optimization technique coupled with the DFT method.[11] Several randomly constructed initial structures were used, and all yielded consistently similar sets of low-lying isomers (Figures 1 and S2 and Tables 1 and S1–S5) after 200–300 Monte Carlo moves. These isomers were reoptimized using the PBEPBE functional[12] with the scalar relativistic effective core potential and LANL2DZ basis set.[13]

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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.[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 give 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_{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 $GeAu_{16}^-$ 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 $SnAu_{16}^-$, isomers 1 and 3 give nearly identical simulated spectra; isomer 3 seems to contribute significantly to the experimental spectra and is competing for the global minimum. For $SiAu_{16}^-$, the two low-lying isomers are quite different from those of $GeAu_{16}^-$ and $SnAu_{16}^-$ 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 $SiAu_{16}^-$ 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 $SiAu_{16}^-$ is reminiscent of the Au/H analogy[16] first discovered in the $SiAu_4$ cluster, which possesses a T_d geometry similar to SiH_4.[16a] We find recently that this Au/H analogy does not exist in $GeAu_4$ and $SnAu_4$ since the latter have a square-planar structure.[17] A closer look at the structures of $GeAu_{16}^-$ and $SnAu_{16}^-$ shows that the local geometry around the Ge/Sn atom is nearly square-planar (Figure 1), just as in $GeAu_4$ and $SnAu_4$. On the other hand, the dangling Au atom atop Si in $SiAu_{16}^-$ reflects the strong Si−Au covalent bonding, similar to that in $SiAu_4$ or other Si−Au mixed clusters.[16] Interestingly, the local structure of Si in $SiAu_{16}^-$ is also very similar to that of the $SiAu_5$ cluster.[18]

Molecular orbital analyses give rise to further insight into the local interactions between the dopant and Au in MAu_{16}^-. The dangling Au atom in $SiAu_{16}^-$, 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 $GeAu_4^-$ and $SnAu_4^-$.[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_{16}^- cage structure in the global minima of MAu_{16}^-. Additionally, Hirshfeld charge analysis on the neutral clusters indicates that all dopants entail a small negative charge.

The neutral MAu_{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_{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_{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_4 clusters. In particular, a dangling Au atom is observed in the low-lying isomers of $SiAu_{16}^-$, which confirms the Au/H analogy found earlier in Si−Au mixed clusters.[16] 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,[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.

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