Published in final edited form as:

J Inorg Organomet Polym Mater. 2014 January 1; 24(1): 241–249. doi:10.1007/s10904-013-9995-6.

Structures and Stabilities of the Metal Doped Gold Nano-Clusters: $M@Au_{10}$ ($M = W, Mo, Ru, Co$)

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Abstract

The structures and stabilities of a series of endohedral gold clusters containing ten gold atoms $M@Au_{10}$ ($M = W, Mo, Ru, Co$) have been determined using density functional theory. The gradient-corrected functional BP86, the Tao-Perdew-Staroverov-Scuseria TPSS meta-GGA functional, and the hybrid density functionals B3LYP and PBE1PBE were employed to calculate the structures, binding energies, adiabatic ionization potentials, and adiabatic electron affinities for these clusters. The LanL2DZ effective core potentials and the corresponding valence basis sets were employed. The $M@Au_{10}$ ($M = W, Mo, Ru, Co$) clusters have higher binding energies than an empty Au_{10} cluster. In addition, the large HOMO–LUMO gaps suggest that the $M@Au_{10}$ ($M = W, Mo, Ru, Co$) clusters are all likely to be stable chemically. The ionization potentials and electron affinities for these clusters are very high, and the $W@Au_{10}$ and $Mo@Au_{10}$ clusters have electron affinities similar to the super-halogen Al_{13} .

Keywords

Gold nanoclusters; DFT; Binding energy; Electron affinity; Ionization potential

1 Introduction

A major interest in cluster science is to discover highly stable clusters, which may be used as building blocks for novel materials. Gold nanoclusters have attracted considerable interest for two decades due to their applications as catalysts [1–5], as sensors [6] in molecular electronics, and as bioconjugate probes for amplification tags in gene analysis [7], antibody or antigen detection [8], DNA sequencing, and gene mapping [9, 10]. Unlike pure Cu and Ag clusters, small pure Au clusters favor three-dimensional amorphous or planar configurations [11, 12]. The existence of bi-metallic clusters $Au_nX_m^+$ ($X = Al, In, Cs$) [13],

Au_nX_m clusters ($X = Cu, Al, Y, In, n = 1 - 65, m = 1$ and 2) [14], and Au_nX ($X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni$) [15] has been demonstrated experimentally. Torres et al. studied the stability and magnetic behavior of Au_nM^+ clusters ($M = Sc, Ti, V, Cr, Mn, Fe, Au; 1 \leq n \leq 9$) using density functional theory (DFT) [16]. Schwerdtfeger [17] and El-Sayed [18] explained the fundamental properties of gold nanoclusters in mini-reviews. Theoretical work on pure gold clusters and on clusters of gold with other elements was extensively reviewed by Pyykkö [19].

Pyykkö and Runeberg [20] first proposed the highly symmetric endohedral transition metal gold clusters, $M@Au_{12}$ ($M = W, Ta, Re^+$). These clusters have icosahedral symmetry, have closed shell electron configurations, and are stabilized by aurophilic attractions, relativistic effects, and the eighteen-electron rule [20]. The $W@Au_{12}$ cluster was predicted to have a large HOMO–LUMO gap of 3 eV, suggesting that it should be unusually stable chemically. Wang et al. [21] shortly thereafter synthesized the icosahedral $W@Au_{12}$ and $Mo@Au_{12}$ clusters. More recently, detailed investigations of $M@Au_{12}$ ($M = Sc-Ni, W, V, Nb, Tc, Ru, Rh, Ta, Pt, Au, Hg$) clusters have appeared [22–27]. Wang et al. [24] studied the energetics and local spin magnetic moments of single $3d$ and $4d$ metal impurities encapsulated in an icosahedral Au_{12} cage. Zhai et al. [23] investigated $M@Au_{12}^-$ ($M = V, Nb, Ta$), and Qiu et al. [25] reported $M@Au_{12}$ ($M = W, Pt, Au, Hg$). Long et al. studied the geometric and electronic structures of endohedral $M@Au_{12}$ ($M = 5d$ transition metals, from Hf to Hg) [26]. Very recently, Wang et al. [27] investigated structural and photoelectron spectroscopic properties of the anionic $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$ clusters both theoretically and experimentally. Gao et al. [28] theoretically investigated endohedral $M@Au_n$ ($n = 8 - 17, M = Zr, Hf, Sc, Y$), all satisfying the eighteen-electron rule. The $Zr@Au_{14}$ cluster possesses a larger HOMO–LUMO gap than that of the magic number cluster T_d-Au_{20} value of 1.77 eV [28]. The $Sc@Au_{14}$ cluster possesses a higher electron affinity (4.13 eV) than that of the Cl atom [28]. Walter and Häkkinen [29] studied theoretically the endohedral $M@Au_{16}$ [$M = Si$ and Al] clusters by using density functional theory and Born–Oppenheimer molecular dynamics, concluding that $Si@Au_{16}$ is a magic species with 20 delocalized electrons. Chen et al. studied the titanium-doped small gold clusters Au_nTi ($n = 2 - 16$) [30], and Zorriasatein et al. investigated the electronic and structural properties of the copper-doped gold clusters, Au_nCu^- ($n = 12 - 18$) [31]. Doping of the gold cage Au_{16}^- with Si, Ge, and Sn has also appeared in literature [32]. In addition, element-centered ligated gold compounds such as octahedral $[C@Au_6](Ph_3P)_6X_2$ or icosahedral $[Pd@Au_{12}](Ph_3P)_8Cl_4$ [33] have been reported.

Despite this tremendous recent progress on gold clusters, many open questions remain. For example, can a cage exist with a transition metal encapsulated in a cluster of less than 12 gold atoms? Will the size of the encapsulated metal be important in clusters containing only 10 gold atoms? What types of interactions exist between the transition metal and the gold atoms? Although substantial work on endohedral gold $M@Au_{12}$ clusters has been published, studies on metal-encapsulated gold ($M@Au_n$) clusters containing fewer than 12 gold atoms are still in their preliminary stages. Thus, accurate first-principles calculations are important to help understand the structural and electronic properties of gold clusters containing fewer than 12 gold atoms that encapsulate a transition metal. Here we report the relative stabilities, the gap between the highest occupied and lowest unoccupied molecular orbital (HOMO–LUMO gap), adiabatic ionization potentials, and adiabatic electron affinities of a series of metal-doped gold clusters containing only ten gold atoms, $M@Au_{10}$ ($M = Mo, W, Ru, Co$). Since an exhaustive search of all possible transition metal-containing Au_{10} clusters is not currently practical, these four metals were chosen to give a first sampling both across the d block and down the periodic table. In particular, these were chosen because W is directly below Mo on the periodic table, giving an indication as to the role played by the size of the encapsulated atom. Ru and Co are widely used metal centers in homogenous catalysis,

suggesting their incorporation may be of interest. Finally, the Ru@Au₁₀ cluster follows the 18 electron rule, possibly making it unique.

2 Computational Methods

An initial D_{4d} symmetry was used for the Au₁₀ cluster (bicapped square antiprisms), which is a derivative of the I_h (icosahedral) Au₁₂ geometry. The metal atom was situated at the center of the Au₁₀ D_{4d} isomer in the M@Au₁₀ (M = W, Mo, Ru, Co) endohedral clusters, and the structures were optimized. The empty cluster Au₁₀ and all the endohedral clusters were optimized using four different DFT functionals, the gradient-corrected functional BP86 [34, 35], the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA functional [36], the hybrid functional of Perdew, Burke and Ernzerhof (PBE1PBE) [37, 38], and Becke's three-parameter hybrid exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) [35, 39]. The LanL2DZ basis set, along with its effective core potentials, was used. To check the reliability of the LanL2DZ results, the structures were reoptimized with the TPSS functional and the LanL2TZ(f) basis set [40]. The TPSS/LanL2TZ(f) structures were almost identical to the TPSS/LanL2DZ results. No symmetry constraints were imposed during the geometry optimizations. Vibrational frequencies were calculated, and geometries were relaxed until structures with no imaginary frequency were found, indicating that the final structures are local minima on their potential energy surfaces.

To calculate the adiabatic ionization potentials and electron affinities, B3LYP/LanL2DZ optimizations were also performed on the cation and anion clusters using the same procedure. Restricted Kohn–Sham calculations were used for all of the clusters with an even number of electrons, with an unrestricted formalism used for all of the doublets.

The binding energy (E_b) per atom was calculated as $E_b = -[E(M@Au_{10}) - 10E(Au) - E(M)]/11$.

Zero-point energies were included in the E_b values. The adiabatic ionization potentials and electron affinities were calculated as the difference between the energies of the endohedral neutral clusters and their corresponding cationic and anionic clusters, respectively. All of the calculations were performed using the Gaussian 03 computational program package [41].

3 Results and Discussion

The calculated interatomic distances, adiabatic ionization potentials, adiabatic electron affinities, and HOMO–LUMO gaps of the endohedral M@Au₁₀ (M = W, Mo, Ru, Co) clusters are summarized in Tables 1 and 2. Their optimized geometries obtained with a given functional and the LanL2DZ or LanL2TZ(f) basis set are shown in Figs. 1, 2, 3, 4, and 5. The total energies and coordinates for the optimized structures appear in the supplementary material.

With B3LYP/LanL2DZ the W@Au₁₀ cluster has a 4,4-bicapped square octahedron structure with the W atom inside the cage. The distances between the edge Au and the capped Au vary between 2.824 and 2.825 Å. The distance between the gold atoms in the square plane of W@Au₁₀ is 2.96 Å. The nearest neighbor Au–W distances varies in the range of 2.729–2.745 Å, and the vertical W–Au_{cap} distances vary between 2.917 and 2.942 Å. The BP86/LanL2DZ, TPSS/LanL2DZ, TPSS/LanL2TZ(f) and PBE1PBE/LanL2DZ optimized W@Au₁₀ structures have almost the same distorted bicapped square octahedron structure (Figs. 1, 5a). However, the bond lengths obtained for W@Au₁₀ by BP86/LanL2DZ, TPSS/LanL2DZ, TPSS/LanL2TZ(f) and PBE1PBE/LanL2DZ are a little shorter than the bond lengths obtained using B3LYP (Tables 1, 2).

The B3LYP/LanL2DZ Mo@Au₁₀ optimized structure also has a bicapped octahedral structure like W@Au₁₀. However, in the Mo@Au₁₀ structure two of the bonds between the gold atoms to which the cap is attached are elongated, with bond distances of 3.964 and 3.961 Å. The other two bonds between these atoms have bond lengths of 2.965 and 2.966 Å. The remaining Au–Au distances vary in the range of 2.709–2.710 Å. The Au–Au_{cap} distances are 2.888 Å. The nearest neighbor Au–Mo distances are 2.821–2.822 Å, and the vertical Au_{cap}–Mo distances are 2.843 Å. The BP86/LanL2DZ, TPSS/LanL2DZ and TPSS/LanL2TZ(f) optimized structures of Mo@Au₁₀ have essentially the same distorted bicapped square octahedron structure (Figs. 2, 5b). On the other hand, PBE1PBE/LanL2DZ calculations predict that Mo@Au₁₀ has four five-membered and four three-membered rings, closely resembling the structure of Ru@Au₁₀ obtained using B3LYP/LanL2DZ (Fig. 3).

All of the density functionals predict that the Co@Au₁₀ cluster has a bi-capped octahedral structure with D_{4d} symmetry (Figs. 4, 5c). The Au–Au and Au–Au_{cap} bond lengths vary from 2.773 to 3.163 Å and 2.798 to 2.857 Å, respectively. The M–Au and M–Au_{cap} bond lengths vary in the range of 2.583–2.639 Å and 3.123–3.193 Å, respectively. The bond lengths obtained by B3LYP calculations are longer than the bond lengths obtained with the BP86, TPSS, and PBE1PBE functionals.

The unusual case is Ru@Au₁₀. In the Ru@Au₁₀ structure obtained with B3LYP/LanL2DZ, a hollow Au₁₀ cage forms in which four Au–Au bonds are elongated, generating four five-membered rings and four three-membered rings, with the Ru inside the cage. The Au–Au and Au–Au_{cap} lengths in Ru@Au₁₀ vary in the ranges of 2.780–2.781 Å and 2.958–2.963 Å, respectively. The nearest neighbor Ru–Au bond distance is 2.755 Å, and the vertical Ru–Au_{cap} distances are between 2.809 and 2.810 Å. On the other hand, the BP86/LanL2DZ, TPSS/LanL2DZ, TPSS/LanL2TZ(f), and PBE1PBE/LanL2DZ computations all give pentagonal antiprism structures for Ru@Au₁₀ (Figs. 3, 5d). These structures coincide with that obtained by Gao et al. [42]. The same BP86/LanL2DZ-derived pentagonal antiprism structure for Ru@Au₁₀ was also obtained starting from an initial D_{5d} symmetry. Here, the Au–Au bond lengths are 2.714–3.020 Å, and the Ru–Au bond lengths are 2.677–2.736 Å, respectively. In the pentagonal antiprism structure the bond lengths are shortest for TPSS/LanL2TZ(f). The Ru@Au₁₀ cluster has a special feature. It has a total of 18 valence electrons and follows the eighteen electron rule. It is unclear, though, why, or even if, this feature would lead to the vastly different predictions of B3LYP versus the other functionals.

The B3LYP/LanL2DZ binding energy for the empty Au₁₀ cluster is 1.51 eV/atom. The B3LYP/LanL2DZ binding energies for W@Au₁₀, Mo@Au₁₀, Ru@Au₁₀, and Co@Au₁₀ clusters are 1.86, 1.59, 1.66, and 1.62 eV/atom, respectively. These binding energies are lower than those obtained from BP86/LanL2DZ, and PBE1PBE/LanL2DZ computations (see Table 1), except for the PBE1PBE/LanL2DZ computation for Co@Au₁₀. TPSS/LanL2DZ and TPSS/LanL2TZ(f) predicts significantly higher binding energies for these clusters (Table 2). The endohedral (M = W, Mo, Ru, Co) clusters all have higher binding energies than the empty Au₁₀ cluster. This behavior is like that of the W@Au₁₂ cluster, where the icosahedral pure Au₁₂ cage is unstable [24]. However, stability is achieved upon transition metal doping. Adding the transition metal to the hollow Au₁₀ cage is stabilizing.

The HOMO–LUMO gaps of M@Au₁₀ (M = W, Mo, Ru, Co) were calculated to predict their relative chemical stabilities. The B3LYP/LanL2DZ and (PBE1PBE/LanL2DZ) HOMO–LUMO gaps are 1.80 eV (2.07 eV), 1.63 eV (2.01 eV), 2.31 eV (2.68 eV), and 2.68 eV (3.15 eV) for the W, Mo, Ru, and Co systems, respectively. For comparison, the B3LYP/LanL2DZ HOMO–LUMO gap for the empty Au₁₀ cluster is 2.03 eV. These HOMO–LUMO gaps are comparable to or greater than that of the magic-number cluster T_d–Au₂₀ (1.77 eV) [43] or to that of the most chemically stable W@Au₁₂ cluster (1.67 eV) [21]. This

suggests that all four of these $M@Au_{10}$ ($M = W, Mo, Ru, Co$) clusters are likely to have significant chemical stability and could be interesting synthetic targets.

The B3LYP/LanL2DZ adiabatic ionization potentials (IPs) for $W@Au_{10}$, $Mo@Au_{10}$, $Ru@Au_{10}$, and $Co@Au_{10}$ are 7.07, 6.06, 6.78, and 7.82 eV, respectively. These large IPs also suggest that the clusters are stable. The adiabatic electron affinities (EAs) were also calculated with B3LYP/LanL2DZ for $W@Au_{10}$, $Mo@Au_{10}$, $Ru@Au_{10}$, and $Co@Au_{10}$. These EA values are 3.28, 4.36, 2.16, and 2.17 eV, respectively. The EA of the $W@Au_{10}$ cluster is close to that of the Br atom (3.36 eV) [44], while the EA of the $Mo@Au_{10}$ cluster is higher than the EA of a Cl atom (3.61 eV) [45]. The well-known neutral icosahedral Al_{13} cluster behaves like a superhalogen with a very high EA of 3.57 eV [46]. Al_{13} also has a high IP (6.4 eV) [47]. The EA of $Mo@Au_{10}$ is higher than that of the superhalogen Al_{13} , and its IP is only slightly smaller. Similar very high EA values were recently predicted by Gao et al. for $M@Au_{14}^-$ ($M = Sc, Y$) [21].

B3LYP/LanL2DZ calculations were used to compute the charges on each of the central transition metal atoms using the NBO 5.G program. The charges were W (−0.947), Mo (−1.162), Ru (−0.971), and Co (−0.310). These show a transfer of electron density from the Au atoms to the central transition metal d orbitals.

4 Conclusions

This theoretical investigation presents the endohedral transition metal, hollow cage, gold clusters, $M@Au_{10}$ ($M = W, Mo, Ru, Co$). These clusters have large HOMO–LUMO gaps, similar to or greater than those of the magic number T_d-Au_{20} cluster and the chemically very stable $W@Au_{12}$ cluster. The ionization potentials and electron affinities for the $M@Au_{10}$ ($M = W, Mo, Ru, Co$) clusters, are quite large. The $W@Au_{10}$ cluster has an EA similar to the super-halogen Al_{13} . The EA of $Mo@Au_{10}$ is significantly larger than Al_{13}^0 s and is even greater than that of the chlorine atom. The doping of a transition metal atom into the unstable Au_{10} cage cluster stabilizes the hollow Au_{10} cage structure, making these potential targets for future synthetic work. Finally, for $W@Au_{10}$, $Mo@Au_{10}$, and $Co@Au_{10}$, all four functionals give very similar geometries. However, for $Ru@Au_{10}$ B3LYP gives a minimum structure that is quite different from the other three functionals. It may be worth investigating in the future if this is a breakdown of the functional or if $Ru@Au_{10}$ is somehow a fundamentally more difficult system. Most interesting is that all four of the tested endohedral complexes showed signs of significant stability. This suggests that stable $M@Au_{10}$ clusters may be somewhat ubiquitous and would make interesting targets for synthesis.

In this paper we have extended studies on endohedral gold $M@Au_n$ clusters below $n = 12$, where little work has been done, down to $n = 10$. An open question is to what extent it is possible to make clusters with an even smaller number of gold atoms surrounding a metal atom. Studies are underway to assess the stabilities of $M@Au_9$ clusters.

Supplementary Material

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Acknowledgments

This project was financially supported by Grant Number P20RR017661 from the National Center for Research Resources (NCRR), a component of the National Institutes of Health (NIH). Its contents are solely the responsibility of the authors and do not necessarily represent the official views of NCRR or NIH. The authors would like to thank Dr. Svein Saebø for allowing the use of his laboratory space during this work.

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Fig. 1.
Calculated DFT minimum structures for the W@Au₁₀ cluster using the given functional and the LanL2DZ basis set

Fig. 2. Calculated DFT minimum structures for the Mo@Au₁₀ cluster using the given functional and the LanL2DZ basis set

Fig. 3.
Calculated DFT minimum structures for the Ru@Au₁₀ cluster using the given functional and the LanL2DZ basis set

Fig. 4.
Calculated DFT minimum structures for the Co@Au₁₀ cluster using the given functional and the LanL2DZ basis set

Fig. 5.
Calculated DFT minimum structures for the W@Au₁, Mo@Au₁₀, Ru@Au₁₀ and Co@Au₁₀ cluster using the TPSS/LanL2TZ(f) basis set

Table 1

Calculated properties of W@Au₁₀, Mo@Au₁₀ and Ru@Au₁₀, and Co@Au₁₀ with B3LYP/PB86/PBE1PBE and the LanL2DZ basis set

Property	W@Au10	Mo@Au10	Ru@Au10	Co@Au10	W@Au12 [15]
Au–Au bond length (Å)					
Shortest	2.824/2.761/2.744	2.960/2.763/2.792	2.769/2.818/2.714	2.816/2.773/2.777	2.890
Longest	3.335/3.294/3.744	2.973/3.317/2.910	2.960/3.020/3.000	3.163/3.086/3.111	2.894
Au–Aucap bond length (Å)					
Shortest	2.825/2.797/2.772	2.888/2.802/–	2.965/–/–	2.857/2.818/2.798	
Longest	–/2.798/2.776	2.887/2.801/–	2.961/–/–	2.858/2.818/2.799	
M–Au bond length (Å)					
Shortest	2.729/2.694/2.665	2.821/2.706/2.677	2.755/2.734/2.714	2.638/2.583/2.598	2.749
Longest	2.745/2.697/2.720	2.822/2.707/2.781	2.756/2.736/2.716	2.639/2.583/2.598	2.752
M–Acap bond length (Å)					
Shortest	2.917/2.899/2.857	2.843/2.887/–	2.809/–/–	3.193/3.173/3.123	
Longest	2.942/2.913/2.881	2.843/2.887/–	2.810/–/–	3.193/3.173/3.123	
Binding energy (eV/atom)	1.86/2.29/2.12	1.59/2.07/1.85	1.66/2.07/1.88	1.62/1.84/1.01	
HOMO–LUMO gap(eV)	1.80/0.56/2.07	1.63/0.34/2.01	2.31/0.89/2.68	2.68/1.14/3.15	1.68
Ionization potential (eV) ^a	7.07	6.06	6.78	7.82	
Electron affinity (eV) ^a	3.28	4.36	2.16	2.17	2.02

^aB3LYP/LanL2DZ

Table 2

Calculated properties of W@Au₁₀, Mo@Au₁₀ and Ru@Au₁₀, and Co@Au₁₀ using TPSS/LanL2DZ and TPSS/LanL2TZ(f)

Property	W@Au10	Mo@Au10	Ru@Au10	Co@Au10	W@Au12 [15]
Au–Au bond length (Å)					
Shortest	2.750/2.713	2.753/2.716	2.802/2.770	2.834/2.813	2.890
Longest	3.275/3.248	3.270/3.257	2.962/2.929	2.978/3.008	2.894
Au–Aucap bond length (Å)					
Shortest	2.773/2.738	2.777/2.745	—	2.910/2.856	
Longest	2.774/2.739	2.779/2.746	—	2.910/2.858	
M–Au bond length (Å)					
Shortest	2.671/2.646	2.644/2.655	2.707/2.677	2.534/2.512	2.749
Longest	2.672/2.647	2.783/2.657	2.707/2.677	2.535/2.512	2.752
M–Acap bond length (Å)					
Shortest	2.862/2.813	2.671/2.801	—	3.429/3.663	
Longest	2.863/2.813	2.685/2.805	—	3.420/3.666	2.863/2.813
Binding energy (eV/atom)	2.77/2.65	2.74/2.84	2.48/2.58	2.06/2.15	
HOMO–LUMO gap(eV)	0.64/0.70	0.47/0.49	1.06/1.07	0.86/1.01	1.68