ORIGINAL ARTICLE

A density functional study on equilibrium geometries, stabilities and electronic properties of Au$_5$Li binary clusters

Ajanta Deka · Ramesh Chandra Deka

Abstract All electron scalar relativistic calculations have been performed to investigate the electronic structures of isomeric Au$_5$Li binary clusters at the BLYP/DNP level of theory. The properties of these clusters are compared with the pristine Au$_6$ clusters. As in case of the pure Au$_6$ cluster, the minimum energy structure of the bimetallic Au$_5$Li cluster is triangular with the lithium atom at the mid position. It is found that substitution of a gold atom by a lithium atom in the Au$_6$ clusters leads to an increase in the binding energy per atom, the HOMO–LUMO gap and the chemical hardness of the structures. Thus, lithium substitution leads to stabilization of the Au$_6$ clusters. Further, the response of various sites of the minimum-energy triangular Au$_5$Li and Au$_6$ clusters towards impending electrophilic and nucleophilic attacks has been determined using DFT-based local reactivity descriptors. It is found that lithium substitution leads to an increase in the number of sites prone to attack by nucleophiles like CO or H$_2$O.

Keywords Binary clusters · Lithium substitution · Density functional theory · Relative electrophilicity · Relative nucleophilicity

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Introduction

The study of metal clusters is interesting as they provide us an opportunity to examine the size evolution of metals from the atomic to the bulk state. The properties of a material at the nanoscale can be very different from that of the bulk. As nanoclusters contain a large number of low coordinated surface atoms they readily form bonds with other species, and hence, can be very useful as catalysts. Among metal clusters, gold has been very widely investigated due to its applications in a number of fields like catalysis (Pyykkö 2004) biological diagnostics, medicine, molecular electronic devices (Cui et al. 2001; Valden et al. 1998), nanostructured materials (Whetten et al. 1996; Andres et al. 1996), optics, material science and solid-state chemistry. The properties of pristine gold clusters can be altered by doping the cluster with impurities. This tailoring of the cluster composition leads to changes in the structural, electronic, magnetic and reactivity properties, thus increasing their potential applications. The modification of cluster properties by doping can be effected in two dimensions, viz, by varying the nature and amount of the dopant. A number of studies have been carried out on doped gold clusters (Majumder et al. 2006; David et al. 2010), the most common elements used for doping being the transition metals (Li et al. 2005). There are also studies on the doping of gold clusters by s and p block elements. The electronic structure of alkali metals is similar to that of gold as both contain a single s valence electron. This makes the study of alkali-metal-doped gold clusters particularly interesting. Studies on gold aurides have revealed that the gold-alkali metal bond is highly polar with a large charge transfer from the alkali atom to the gold. Due to the high difference in electronegativity between the alkali metals and gold, alkali aurides are found to be highly stable.

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Among the alkali metals, the electronic structure of lithium is different as it presents an unfilled *p* shell (Rajesh and Majumder 2009; Heiz and Bullock 2004). In addition, lithium is the lightest element that is metallic under normal conditions. So it would be interesting to investigate how doping of a gold cluster by a lithium atom modifies its electronic properties and reactivity.

In an earlier study on the structural and electronic properties of Au_n clusters ($n = 2$–13) using DFT (Deka and Deka 2008) we have found that the triangular Au_6 cluster is highly stable. A number of isomeric Au_6 clusters were considered in that study. In this paper, we examine the effect of doping Au_6 clusters with a lithium atom resulting in the formation of Au_5Li clusters. An exhaustive search for enhanced catalytic properties of nanoclusters by doping can be accomplished only if all isomers of the parent cluster are considered. So, we have taken a number of isomeric structures of the highly stable triangular Au_6 cluster from our earlier study as candidate structures for the present investigation.

Computational details

Density functional calculations were performed to obtain full geometry optimization at the level of a generalized gradient approach via the BLYP exchange–correlation functional. This functional incorporates Becke's exchange (Becke 1988) and Lee–Yang–Parr correlation (Lee et al. 1988). All calculations were performed using the DMol³ suite of programs (Delley 1990). Scalar relativistic effects (VPSR) (Delley 1998) were incorporated into our all electron calculations to account for gold, which is a heavy atom. Relativistic effects in gold lead to radial contraction and energetic stabilization of the *s* and *p* orbitals and a consequent radial expansion and energetic destabilization of the *d* and *f* orbitals. This leads to stronger interaction between the valence 5*d* and 6*s* orbitals thus reducing the *s*–*d* energy gap. Relativistic effects lead to shorter metal–metal bonds, and hence, more stable clusters. The planarity of gold clusters up to large system size is attributed to relativistic effects. The effects of relativity on properties like bond length, ionization potential, electron affinity, dissociation energy, etc. for Au_2, AuH and Au (solid) has been listed by Pyykkö (2004) in his excellent review on gold clusters.

Self consistent field procedures were carried out with convergence criteria of 1×10^{-5} a.u. on the total energy and 1×10^{-6} a.u. on the electron density. The basis set used is of double numeric quality with polarization functions (DNP) (Delley and Ellis 1982). This basis set is comparable with the Gaussian 6-31G** basis set, but the DNP basis set is supposed to be more accurate than a Gaussian basis set of similar size. All calculations are spin restricted and the geometry optimizations have been performed without imposing any symmetry constraint.

The average binding energy per atom is computed from:

$$E_b = [5E(Au_1) + E(Li_1) - E(Au_5Li)]/6$$

where $E(Au_5Li)$ is the energy of the Au_5Li cluster.

Chemical hardness is used as a parameter to determine the reactivity of a system. In density functional theory, hardness (η) of an electronic system is defined as the second derivative of energy (E) with respect to the number of electrons (N) at constant external potential, $v(\vec{r})$ (Fukui 1982).

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})}$$

where μ is the chemical potential of the system.

Global hardness, η can be approximated as

$$\eta = \frac{LUMO - HOMO}{2}$$

Fukui function $f(\vec{r})$, as defined by Parr and Yang (Parr and Yang 1984; Yang et al. 1984), is a mixed second derivative of energy of the system with respect to the number of electrons N and constant potential $v(\vec{r})$:

$$f(\vec{r}) = \left(\frac{\partial^2 E}{\partial N \partial v(\vec{r})}\right) = \left[\frac{\delta \mu}{\delta v(\vec{r})}\right]_N = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})}$$

where $\rho(\vec{r})$ represents the electron density at position $\vec{r}$ of the chemical species.

Fukui function expresses the sensitivity of the chemical potential of a system to an external perturbation. Higher the value of Fukui function at a particular site, more is its reactivity. The condensed Fukui function for an atom k in a molecule having N electrons can be obtained from the finite difference approximation as:

$$f_k^+ = [q_k(N+1) - q_k(N)] \quad \text{for nucleophilic attack}$$

and

$$f_k^- = [q_k(N) - q_k(N-1)] \quad \text{for electrophilic attack}$$

where $q_k(N)$, $q_k(N+1)$ and $q_k(N-1)$ are electronic populations on the particular atom k of the molecule with N, $N+1$ and $N-1$ electrons, respectively. The 'relative electrophilicity' and 'relative nucleophilicity' values for the particular atom can be obtained from the ratio of Fukui functions f_k^+/f_k^- and f_k^-/f_k^+, respectively.

A large number of Au_6 isomeric clusters were used as candidate structures. One atom of the pristine gold cluster was replaced by a lithium atom and then the geometry was fully optimized. This replacement by a lithium atom was done for each unique atom of the cluster. Vibrational frequency calculations were then carried out at the optimized

geometry to verify that the obtained structures are global minima on the potential energy surface. The Fukui functions were calculated on the basis of Hirshfeld population analysis.

Results and discussion

We started with eight isomeric structures of the Au_6 cluster and doped each unique atom of each structure by a lithium atom. These isomeric structures are shown in Fig. 1. These clusters have been arranged in the order of increasing energy. The minimum energy structure is triangular. These structures have been taken from our earlier work on the structural and electronic properties of stable Au_n ($n = 2$–13) clusters (Deka and Deka 2008). Substitution of a gold atom by a lithium atom resulted in ten stable structures of the Au_5Li cluster. The other geometries either did not converge or exhibited negative frequencies. The optimized geometries are shown in Fig. 2.

The structures have been named as S_1, S_2, S_3, …, S_{10} by their relative stability, namely, S_1 is the most stable structure and S_{10} is the least stable. Of the ten structures of the Au_5Li cluster, five are found to be planar. The structures of the Au_6 clusters are mostly retained on doping with a lithium atom, the two-triangle S_8 structure being an exception. In case of the Au_6 cluster, this structure is three-dimensional having C_{2h} symmetry, while in case of Au_5Li, it is planar. The structure S_2 which is a capped square pyramid has not been found in case of the Au_6 cluster. As in case of pristine Au_6 cluster, the minimum energy

structure of the Au_5Li cluster is triangular with a small inner triangle housed inside a big outer triangle. The lithium atom occupies the mid position which forms a vertex of the inner triangle. The other stable isomer having a similar triangular structure is S_4 where the lithium atom occupies the apex position forming a vertex of the outer triangle. To the best of our knowledge there has been no theoretical or experimental study on the Au_5Li bimetallic cluster. So, a direct comparison of our parameters with those of other workers is not possible. As seen from Table 1, the average Au–Au distances for the various isomers of the pristine gold clusters lie in the range 2.63–2.79 Å while those for the Au_5Li clusters vary between 2.45 and 2.60 Å, respectively. Another DFT study with the PW91 exchange correlation functional and a plane wave basis set (Li et al. 2006) gives average Au–Au distances varying between 2.58 and 2.82 Å for various isomers of pristine Au_6 clusters. Our study reveals that bond distances for neighbouring Au–Li atom pairs are shorter than those of the Au–Au atom pairs, indicating that Li substitution leads to stronger bonds. However, our Au–Li distances are much larger compared to the AuLi dimer bond length (2.27 Å) (Leonardo et al. 2006), and hence, much weaker.

The binding energy per atom values of the different isomers of the Au_5Li cluster is given in Table 1. In addition, shown in Table 1 are the binding energies per atom of the corresponding pristine Au_6 clusters for comparison. The most stable triangular Au_5Li cluster S_1 with the lithium atom having a coordination number of 4 exhibits the highest binding energy of 1.966 eV. The binding energy per atom of the pristine triangular Au_6 cluster has a value

Fig. 1 Optimized geometries of Au_6 clusters arranged in the order of increasing energy. The unique atoms have been marked
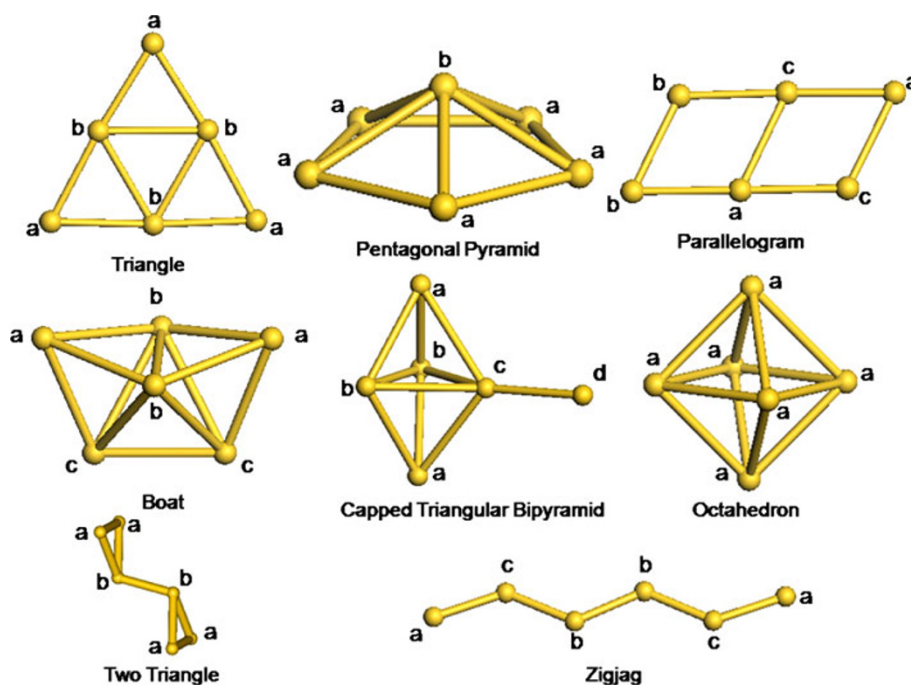
Fig. 2 Isomeric structures of Au$_5$Li clusters arranged in the order of increasing energy. Gold atoms are numbered as *1* and Li atoms as *2*. The relative energies are given in eV
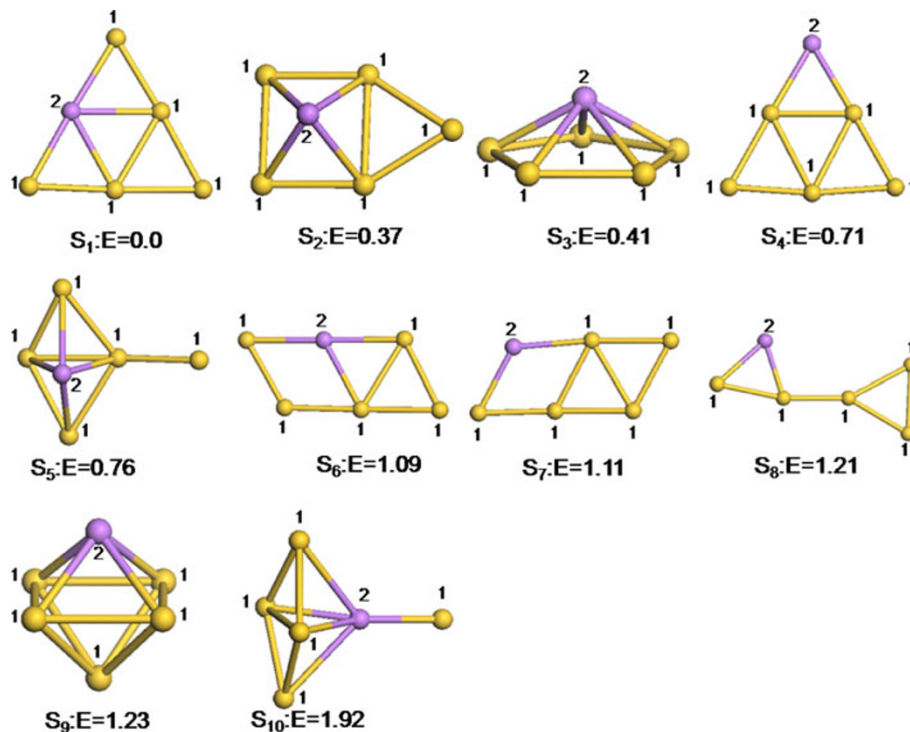

Table 1 Geometric and energetic parameters of pristine Au$_6$ and bimetallic Au$_5$Li clusters

Isomer	Relative energy	Au–Au	Au–Li	E_b		H–L gap		η	
				Au$_5$Li	Au$_6$	Au$_5$Li	Au$_6$	Au$_5$Li	Au$_6$
S$_1$	0.000	2.631	2.645	1.966	1.843	1.736	1.727	0.868	0.864
S$_2$	0.369	2.696	2.602	1.905		1.263		0.632	
S$_3$	0.410	2.664	2.646	1.898	1.690	1.684	1.641	0.842	0.821
S$_4$	0.709	2.703	2.577	1.848	1.843	1.586	1.727	0.793	0.864
S$_5$	0.761	2.686	2.645	1.839	1.588	1.400	0.630	0.700	0.315
S$_6$	1.090	2.649	2.656	1.785	1.676	0.322	0.176	0.161	0.088
S$_7$	1.106	2.677	2.597	1.782	1.676	0.193	0.176	0.096	0.088
S$_8$	1.209	2.639	2.451	1.765		0.735		0.368	
S$_9$	1.225	2.783	2.572	1.762	1.702	0.721	1.806	0.361	0.903
S$_{10}$	1.914	2.785	2.685	1.647	1.588	0.367	0.630	0.184	0.315

Bond lengths are in Å and energies are in eV

of 1.843 eV. Similar GGA calculations at the PW91PW91/6-31G* (Majumder et al. 2006) and PW91/LANL2DZ (Li et al. 2007) levels of theory reveal binding energy per atom values of 1.82 and 1.826 eV, respectively, for the minimum energy triangular Au$_6$ cluster. Our binding energy value for triangular Au$_5$Li cluster is higher than each of these values. Thus, lithium substitution leads to an increase in the binding energy per atom of this structure by 0.123 eV in our case. For the structure S$_4$ where the lithium atom has a coordination number of 2, the binding energy per atom value is 1.848 eV. As can be seen from Table 1 this value is only slightly higher than that of the corresponding pure gold cluster. Thus, gain in binding energy

due to lithium substitution into the minimum energy triangular Au$_6$ cluster is more when the lithium atom has a higher coordination number. On going from the most stable S$_1$ cluster to the least stable S$_{10}$ cluster the binding energies go on decreasing. The S$_{10}$ structure has a binding energy of 1.647 eV. A comparison of the binding energy values of the Au$_5$Li and Au$_6$ clusters reveal that in each case the binding energies increase due to lithium substitution.

The HOMO–LUMO gap is a measure of stability of clusters. Larger the HOMO–LUMO gap, more stable is the cluster. In Table 1 we show the HOMO–LUMO gap of the optimized Au$_5$Li clusters along with those of the corresponding pure Au$_6$ clusters. The most stable Au$_5$Li cluster S$_1$

exhibits the highest HOMO–LUMO gap of 1.736 eV. The other triangular Au$_5$Li cluster S$_4$ has a HOMO–LUMO gap of 1.586 eV. The parent structure of both these clusters is the triangular Au$_6$ cluster having a HOMO–LUMO gap of 1.727 eV. Thus, lithium substitution leads to increase in the LUMO–LUMO gap, the change in HOMO–LUMO gap being larger when lithium occupies the mid position. The pentagonal pyramidal structure S$_3$ with a 5-coordinated lithium atom at the top also has a large HOMO–LUMO gap of 1.684 eV. The analogous Au$_6$ cluster has an energy gap of 1.641 eV. It is seen that in most cases lithium substitution leads to an increase in the HOMO–LUMO gap with the octahedral structure S$_9$ being an exception. In addition, shown in Table 1 are the values of chemical hardness of the clusters. As expected, the most stable cluster has the highest value of chemical hardness. It is seen that for most of the structures, chemical hardness increases due to lithium substitution.

To study the local reactivity at different sites within a cluster, we choose the most stable Au$_5$Li cluster, S$_1$ for our investigation. The Hirshfeld charges and Fukui functions for this structure are shown in Table 2. In addition, shown are analogous values of the pristine triangular Au$_6$ cluster. As can be seen from the table, the lithium atom bears a positive charge of 0.189 q while the gold atoms are negatively charged. In case of the pure Au$_6$ cluster, three atoms, namely, those lying at the vertices of the outer triangle carry negative charges while those forming the vertex of the inner triangle bear positive charges of equal

magnitude, thus making the cluster neutral as a whole. Thus, on doping the Au$_6$ cluster with the lithium atom, lithium donates electrons to the gold atoms becoming positively charged in the process, while the negative charge on the gold atoms increase. In addition, shown in Table 2 are the values of the Fukui functions at different sites within the cluster. For the pure Au$_6$ cluster the atoms lying at the vertex of the outer triangle have higher values of relative electrophilicity f^+/f^- indicating that these atoms are prone to attack by nucleophiles like CO. The atoms forming the vertex of the inner triangle on the other hand having higher values of relative nucleophilicity f^-/f^+ and hence are prone to attack by electrophiles like O$_2$. On substituting the lithium atom at the mid site the outer gold atoms still remain prone to attacks by nucleophiles like CO. But in addition we have a new site which prefers a nucleophile like CO or H$_2$O. A look at Table 2 reveals that the lithium atom has a higher value of f^+/f^- compared to f^-/f^+, and hence, prefers a nucleophile like CO. In case of the pure gold cluster this site is prone to electrophilic attack. Thus, as a result of lithium substitution the number of possible sites for nucleophilic attack on the system increases.

The spatial orientation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels are depicted in Fig. 3. It is seen that the HOMO is strongly delocalized with contribution from all the gold atoms of the cluster. This

Table 2 Hirshfeld charges, Fukui functions, relative electrophilicity and relative nucleophilicity values for unique atoms of pristine Au$_6$ and bimetallic Au$_5$Li clusters

Unique atom	Au$_5$Li				Au$_6$			
	f^+	f^-	f^+/f^-	Charges	f^+	f^-	f^+/f^-	Charges
Au1	0.216	0.203	1.064	−0.013	0.232	0.197	1.178	0.0012
Au2	0.216	0.203	1.064	−0.081	0.232	0.197	1.178	0.0012
Au3	0.279	0.198	1.409	−0.013	0.232	0.197	1.178	0.0012
Au4	0.116	0.172	0.674	−0.081	0.102	0.137	0.745	−0.0011
Li5/Au5	0.056	0.052	1.077	0.189	0.102	0.137	0.745	−0.0011
Au6	0.116	0.172	0.674	−0.003	0.102	0.137	0.745	−0.0011

Fig. 3 Spatial orientations of the highest occupied molecular orbital and lowest unoccupied molecular orbital of the minimum energy triangular Au$_5$Li cluster

HOMO　　　　　　　　　LUMO
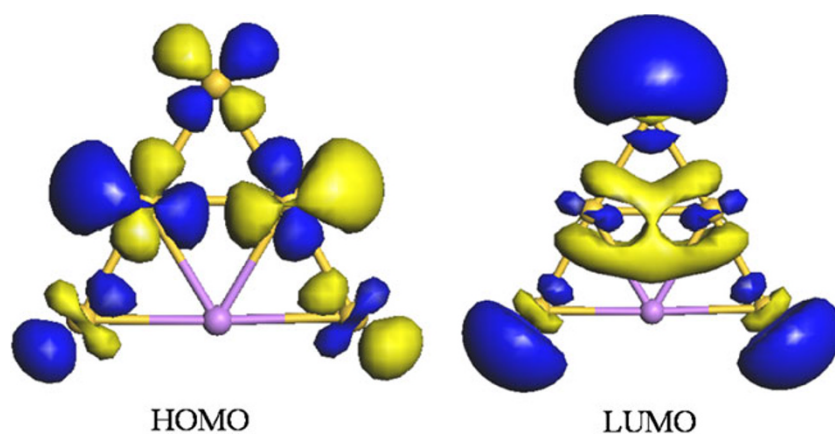
delocalization of the electronic wave-function leads to stabilization of the planar structure. The LUMO is found to be concentrated at the gold atoms forming the vertex of the outer triangle. So the electron accepting power of the cluster is higher at these sites. Thus, an electron-rich species like CO is most likely to be adsorbed at these sites. This further confirms the predictions regarding nucleophilic attack obtained from the Fukui function values.

Summary

We have obtained the optimized geometries of ten isomeric Au_5Li clusters. These structures were obtained by replacing one gold atom of pure Au_6 clusters by a lithium atom. The structure and energetics of these clusters were compared with analogous structures of the pristine Au_6 cluster. It is found that the structures of most of the gold clusters are retained on lithium substitution. Parameters like binding energy per atom, HOMO–LUMO gap and chemical hardness increase on doping the Au_6 cluster by a lithium atom indicating that the bimetallic Au_5Li clusters are more stable than their pristine Au_6 counterparts. Further it is found from Fukui function values that lithium substitution leads to increase in the number of sites prone to be attacked by nucleophiles like CO. The HOMO of the minimum energy planar triangular Au_5Li cluster is strongly delocalized leading to its high stability.

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