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A DFT Study on Morphological Change in Bimetallic Gold Nanocluster

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Abstract: The electronic structures of bimetallic gold clusters with various size, charge and stoichiometry $[Au_aM_b]^n$, (where $M=Au, Cu, Ag, Ni, Pd, Pt, Co, Rh, Ir$; $a=b=1-6$ and $n=0, -1, +1$), have been studied using Density Functional Theoretical methods. The optimization stabilizes the clusters with larger HOMO-LUMO gap. Further, a relaxed geometrical morphology shows that, 2D to 3D conversion can be introduced even in atomic nanoclusters by varying the stoichiometry via inducing heterogeneity. Additionally, the energetics shows that the negatively charged clusters remain highly stable in all the models reported in this work. The presence of a single gold atom in cluster is enough to preserve the trend in redox potential as that in pure gold cluster, where ionization potential is always higher than the electron affinity. The structural relaxation and the influence of heterogeneity in structures and energetics are found to decrease with increase in the size of the cluster.

I. Introduction

The gold is one of the ancient coinage metals with huge amount of potential applications in both macroscopic and nanoscales.¹⁻⁷ The reduction in size of gold material result the nanoclusters, where the novel non-bulk properties emerge with the advantage to be part of science and technological development such as nanodevices,⁸ medicines,⁹⁻¹⁰ catalysts,¹¹⁻²¹ pharmaceuticals,^{22, 23} sensors^{24, 25} and etc, the applications are devoted to physical, structural, redox, optical and magnetic properties of clusters.²⁶⁻²⁹ At nano-scale, gold cluster has size, shape and charge dependent properties,³⁰⁻³² which can be monitored and tuned appropriately according the requirements. And the gold cluster are synthesized in bare form in the gas phase using mass spectrometry³³ and in other media with protecting layer they are always stabilized with protecting layer.^{34, 35} The protecting layer has influence on its physical and chemical properties of the clusters.³⁶⁻⁴⁰ And the protecting layer can control many parameters such as size, shape, stoichiometry, heterogeneity and polarization of the cluster.⁴¹⁻⁴³

Among many parameters, the introduction heterogeneity in the metal core has advantages for being less influenced by environment.⁴⁴⁻⁴⁶ the heterogeneity in the metal core can be generated using any *s*-, *p*- Or *d*-blocks elements in the periodic table. Among these, the bi-metallic clusters with *d*-block elements are considered to be interesting for similar characteristics and having equal weightage in cluster formation. The main disadvantages in these clusters are arises in the predicting the geometry and relative properties. Various experimental and theoretical methods are applied to predict the electronic structure, physical and chemical properties of these cluster,⁴⁷⁻⁴⁹ however, some of their properties are not known and requires detail comparative analysis, which is the main aim of this work.

Nanoclusters are in the range of 1 nm to 100 nm size and the lower end are called sub-nanometres cluster.⁵⁰⁻⁵² The sub-nanometer size cluster is found to be interesting after the experimental realization of them as a building block for larger cluster. For example can be $[Au_{22}(SR)_{18}]$ which is an assembly of Au_7 , one $[Au_6(SR)_6]$ and three $[Au_3(SR)_4]$ clusters.⁵³ Hence, this is become vital to understand the smaller size cluster to larger extend. Specifically, the bimetallic cluster, which give one more dimension in control and selectivity of the physical and chemical properties. Gold cluster has been synthesised and characterised along with many heterometal atom,⁵⁴⁻⁵⁷ Co, Ni, Cu, Rh, Pd, Ag, Ir and Pt using simple kinetic controlled co-reduction route at room temperature and characterized with scanning electron microscopy (SEM),⁵⁸ transmission electron microscopy (TEM),⁵⁹⁻⁶² energy dispersive spectrometer (EDX) elemental mapping⁶³, inductively coupled plasma-atomic emission spectroscopy (ICP-AES)⁶⁴⁻⁶⁵ and UV visible spectra.^{66,67} The reported electronic structural studies show the important of hetero atom in creating the 3D structure and also they found that the polarization had been always dominated by gold atom.³⁹

Using DFT methods the electronic structural, optical, stability and redox properties of $[Au_aM]^n$ clusters, where $a=1-5$, $M=Au, Cu, Ag, Ni, Pd, Pt, Rh, Co, Ir$ and etc. with $n=0, +1$ and few $[Au_aM_2]$ clusters where $a=1-4$, $M=Au, Cu, Ag, Ni, Pd, Pt, Rh$ stoichiometry's have been reported.⁶⁸⁻⁸⁰ However, the possibilities of more than two heteroatoms in the various size clusters have not been explored for other than coinage metals. Hence, in this work, one to six atoms clusters have been studied with all possible stoichiometric and compared with each other in order to obtain the complete picture. The aim of this study is to explore the various stoichiometry's and shape sub-nanometres cluster and understand their lowest energy structure shape, charge and orbital distribution. in three charge states. Finally, the redox properties were calculated along with its stability in order to learn the possible application in electronic devices.

II. Computational Details

All the models studied in this work are generated using parameters already reported for pure gold clusters and all possible structures are relaxed. Only the lowest energy structures are reported in the section below. Geometry optimizations are carried out using Density Functional Theory as implemented in the Gaussian 09 suite of program with the hybrid CAM-B3LYP functional.⁸¹ The LANL2DZ pseudo potential with basis set is used for all metals studied in this work. The method is validated by corroborating the structural parameters and energies with the reported values.^{68-71, 75-80} The single positive and negative charges are considered to be either removing an unpaired electron in odd number cluster or generating an unpaired electron in even number of atoms containing cluster respectively. The stationary structures in the three charged states (positive, neutral and negative) of the bare $[Au_aM_b]$ ($a=b=1-6$) clusters are characterized as minima on the basis of the calculation of their harmonic vibrational frequencies with the options opt=tight (10^{-6} Hartree/bohr for the forces on atoms) and SCF=tight (10^{-8} Hartree convergence threshold). Population analyses are carried out at the same level. The Adiabatic Ionization Potential (AIP), Adiabatic Electron Affinity (AEA) are calculated using the equations below,

$$AIP = E_{(N+1)} (\text{optimized cation geometry}) - E_{(N)} (\text{optimized neutral})$$

$$AEA = E_{(N)} (\text{optimized neutral}) - E_{(N-1)} (\text{optimized anion geometry})$$

$$\Delta = \text{Highest Occupied Molecular Orbitals} - \text{Lowest Unoccupied Molecular Orbitals}$$

III. Results and Discussions

Bimetallic clusters are generated by taking different combinations from three groups of periodic elements, which are d^7 , d^8 and d^{10} metals. These metals are already found to exist with gold atom and a few are characterized using advanced experimental techniques. In order to understand the properties at microscopic level the possible stoichiometry combinations up to M_6 has been discussed in separate sections.

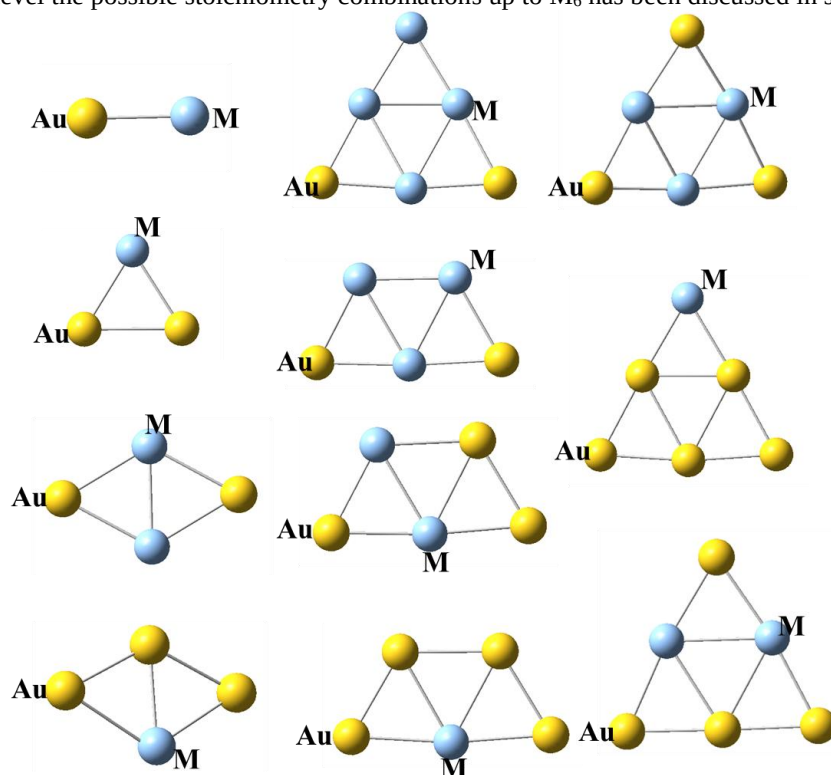


Figure 1. Optimized lowest energy geometries of variously sized bimetallic clusters.

[AuM] cluster

The dimer exists in a linear structure see in (figure 1), where gold atom gets polarised according to hetero atoms as seen in the computed Mulliken charges (Table 1). Among the dimers studied in this work, $[AuCo] \approx [AuRh] \approx [AuNi] \approx [AuCu]$ dimer has been polarized to a larger extent due to its higher electronegativity. And Ir and Pt atom clusters in dimer polarized the cluster minimal as seen in mulliken charge value, The same has been reflected in the bond distance, where copper forms the shortest bond and other coinage metal atom like Ag forms the longest bond in the following order,

$$[AuCu] < [AuNi] < [AuCo] < [AuPt] < [AuIr] < [AuAu] < [AuRh] < [AuPd] < [AuAg]$$

The IP and EA values are calculated by considering one electron oxidation and reduction process. And the computed IP energy values show that [AuCu], [AuNi] and [AuIr] require more than 10 eV of energy to get oxidized. And the EA values indicate the higher stability of negatively charged clusters. Further, even in clusters with two atom size, the addition of electron to the cluster requires lesser energy than removal of electron. And all dimers are chemically stable with almost 5 eV HOMO-LUMO gap. As expected, the bond distance is increased by the addition and removal of an electron, (figure 2) which is due to the repulsion generated at the two centres as can be seen from orbital pictures. The bond distance change is minimal in case of Ni and Ir due to their larger valence.

Table 1. Computed bond distances in Å are given for [AuM]ⁿ, where n=0 (normal), +1 (*italic*) and -1 (**bold**) along with Mulliken charges in e, IP, EA and Δ values in eV. Reported values are given in bracket.

Models [AuM]	Au-M	IP	EA	Δ	Mulliken charges	
					Au	M
M=Au	2.547(2.55) <i>2.688</i> 2.702	9.22(9.50)	1.90(1.94)	5.5	-0.000	0.000
M=Cu	2.386 <i>2.469</i> 2.527	10.23	1.16	5.62	-0.454	0.454
M=Ag	2.573 <i>2.752</i> 2.737	8.33(9.00)	1.33	5.30	-0.379	0.379
M=Ni	2.395 <i>2.348</i> 2.459	11.70	0.19	5.59	-0.452	0.452
M=Pd	2.567(2.56) <i>2.648</i> 2.650	8.14	2.15	5.35	-0.436	0.436
M=Pt	2.527 <i>2.621</i> 2.559	9.25	1.68	5.59	-0.102	0.102
M=Co	2.407 <i>2.597</i> 2.562	5.89	3.49	4.78	-0.509	0.509
M=Rh	2.564(2.52) <i>2.675</i> 2.649	6.70(8.44)	3.12	3.45	-0.473	0.473
M=Ir	2.538 <i>2.533</i> 2.563	10.22	2.56	4.90	-0.117	0.117

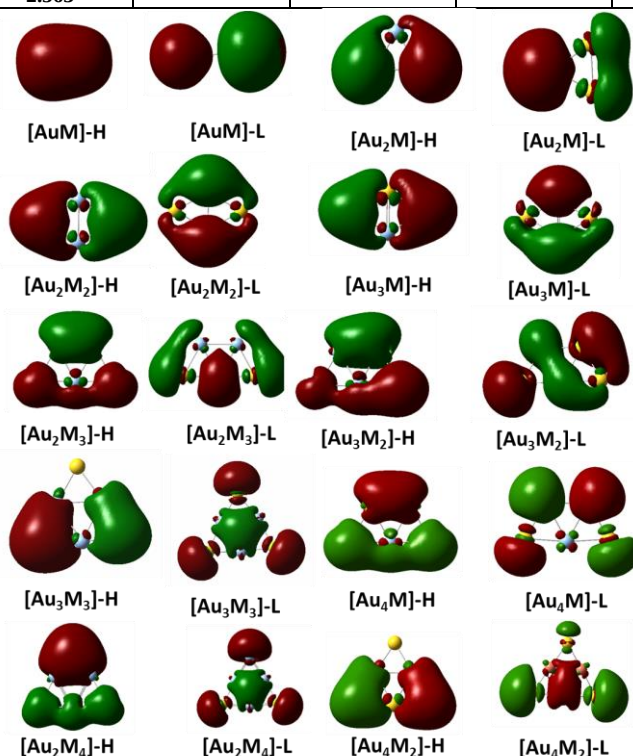


Figure 2. Computed highest occupied (H) and lowest unoccupied (L) molecular orbital of lowest energy conformer of $[\text{Au}_a\text{M}_b]$ clusters plotted with isovalue of $(0.02 \text{ \AA}^{-3})$. Note that the particular stoichiometry with different metal has a same orbital pattern.

[Au₂M] cluster

The triatomic cluster exists in a triangular geometry as a lowest energy conformer (figure 1), where all three atoms exist in same plane resulting in a 2D geometry. Note that other linear, bent geometry for triangular cluster are higher in energy and which is in good agreement with reported energy profile. Hence, the lowest energy geometry has been discussed in this section. Introduction of one more atom does not change the trend; however the Au-Au and Au-M bond distances are increased by 0.5 Å in order to avoid steric hindrance as a result of ring formation. Similarly, addition of an electron and its removal increases the bond distance, however the increase is minimal compared to [AuM] dimer cluster. As a result, the energy required for ionization decreases by 1 to 3 eV. And the negatively charged cluster is more stabilized by the introduction of one more atom in the geometry and increases the EA values in reference to the dimer. And the calculated Mulliken charges show that gold is negatively polarized compared to the hetero metal in accordance due to the electronegativity of gold atom. As a result the Δ values are reduced but still possess insulating nature which represents the molecular behaviour.

Table 2. Computed bond distances in Å are given for [Au₂M]ⁿ, where n=0 (normal), +1 (*italic*) and -1 (**bold**) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

[Au ₂ M]	Au-M	Au-Au	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.646(2.64) <i>2.680</i> 2.721	2.645 <i>2.622</i> 2.646	6.92(8.49)	3.50(3.40)	3.32	-0.024	0.024
M=Cu	2.485(2.642) <i>2.556</i> 2.773	2.754 <i>2.591</i> 2.655	6.80(7.19)	0.08(1.89)	4.04	-0.316	0.316(0.276)
M=Ag	2.683 <i>2.760</i> 2.789	2.743 <i>3.092</i> 2.643	6.63	3.04	3.62	-0.285	0.285(0.236)
M=Ni	2.409(2.84) <i>2.529</i> 2.474	2.682 <i>3.096</i> 2.654	5.86	2.16	4.39	-0.292	0.292
M=Pd	2.666 <i>2.733</i> 2.628	2.761 <i>3.285</i> 2.671	7.61	2.12	4.70	-0.168	0.168
M=Pt	2.582 <i>2.657</i> 2.644	2.773 <i>5.108</i> 2.682	7.55	1.53	4.63	-0.039	0.039
M=Co	2.524 <i>2.555</i> 2.498	2.670 <i>3.045</i> 2.651	9.17	0.60	6.14	-0.323	0.323
M=Rh	2.648 <i>2.712</i> 2.577	2.703 <i>2.808</i> 2.664	8.91(7.37)	1.42	5.52	-0.270	0.270
M=Ir	2.586 <i>2.626</i> 2.556	2.789 <i>2.903</i> 2.608	8.47	1.72	5.01	-0.097	0.097

[Au₂M₂] cluster

Herein, 1:1 ratio concentration for gold and hetero metal in cluster (figure 3) has been maintained to understand the impacts of homogeneity in structure and stability. And the lowest energy conformer has its heteroatom and gold in diagonal position and forms a distorted 2D diamond structure, where the uniformity as observed in dimer, the presence of atoms in 1:1 ratio made the polarization uniform and as a result Δ value is higher than that for [Au₂M] clusters. The addition and removal of electron marginally increases the bond distance compared to neutral, which shows the possibility of absence of structural relaxation during oxidation and reduction. However, the energy required for oxidation increases and the stability of negatively charge cluster decreases which attribute to the differently localized orbital as seen in Eigen function picture of HOMO and LUMO, where HOMO and LUMO are delocalised (figure 4).

Table 3. Computed bond distances in Å are given for $[\text{Au}_2\text{M}_2]^n$, where $n=0$ (normal), $+1$ (italic) and -1 (bold) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

$[\text{Au}_2\text{M}_2]$	Au-M	Au-Au	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.741(2.77) 2.742 2.750	2.650(2.68) 2.712 2.864	7.75(7.94)	2.43(2.42)	4.02	-0.155	0.155
M=Cu	2.539 2.536 2.548	2.380 2.545 2.606	7.84(8.20)	1.26(1.70)	5.28	-0.506	0.506(0.545)
M=Ag	2.744 2.747 2.871	2.724 2.874 2.626	7.65(8.15)	0.91(1.91)	4.86	-0.457	0.457(0.482)
M=Ni	2.588(2.58) 2.669 2.575	2.115(2.40) 2.526 2.221	7.03	3.22	3.70	-0.414	0.414
M=Pd	2.707(2.68) 2.715 2.758	2.820(2.85) 2.730 2.496	7.07	2.43	4.13	-0.208	0.208
M=Pt	2.679(2.70) 2.710 2.700	2.664(2.68) 2.569 2.642	6.79	2.28	3.88	-0.027	0.027
M=Co	2.478 2.528 2.569	2.288 2.331 2.384	6.73	3.87	4.95	-0.611	0.611
M=Rh	2.627 2.732 2.681	3.096 3.109 4.535	4.98(7.15)	3.87	3.07	-0.393	0.393
M=Ir	2.693 2.537 2.742	2.255 2.284 2.334	7.44	2.53	4.41	-0.280	0.280

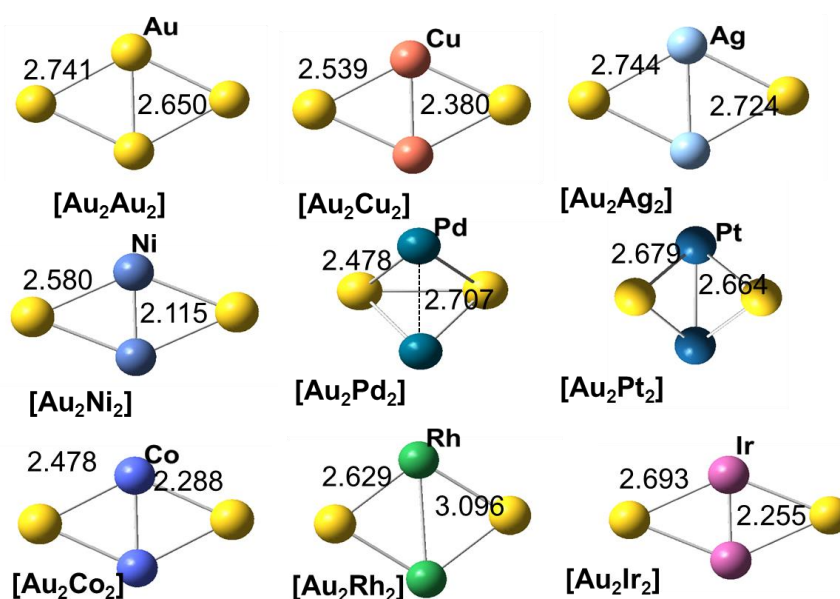


Figure 3. Optimized lowest energy geometries of $[\text{Au}_2\text{M}_2]$ clusters with their important bond distance (Å).

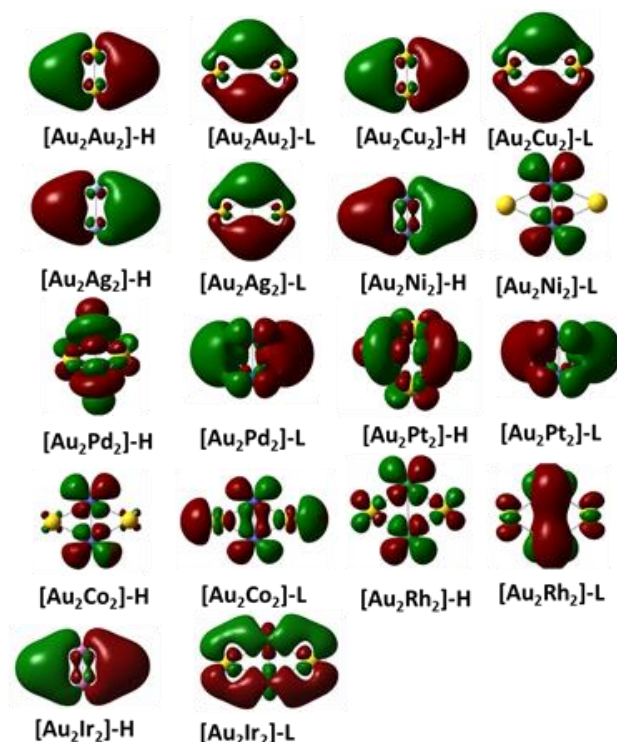


Figure 4. Computed highest occupied (H) and lowest unoccupied (L) molecular orbital of lowest energy conformer of $[\text{Au}_2\text{M}_2]$ clusters plotted with isovalue of $(0.02 \text{ \AA}^{-3})$. Note that the particular stoichiometry with different metal has a same orbital pattern.

$[\text{Au}_3\text{M}]$ cluster

In order to check further the importance of heterogeneity, clusters with 3:1 ratio of gold atom to hetero atom has been generated, where some metal shows 2D to 3D transformation. In lowest energy, $[\text{Au}_3\text{Rh}]$ and $[\text{Au}_3\text{Ir}]$ cluster has perfect tetrahedral geometry, where all other hetero atoms prefer distorted parallelepiped geometry (figure 5). The cluster is polarized towards gold atom and as a result the Au-M bond distance is decreased compared to $[\text{Au}_2\text{M}_2]$ clusters. Nevertheless, the presence of heterogeneity increases the bond distance significantly during one electron oxidation and reduction process. However the redox potential energetics follows the same trend as in homogeneous cluster which is attributed to their delocalised MO as seen in (figure 6).

Table.4. Computed bond distances in $\text{\AA}$ are given for $[\text{Au}_3\text{M}]^n$, where $n=0$ (normal), $+1$ (italic) and -1 (bold) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

$[\text{Au}_3\text{M}]$	Au-M	Au-Au	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.651 2.742 2.751	2.741 2.742 2.751	7.75	2.46	4.02	-0.155	0.155
M=Cu	2.499(2.662) 2.599 2.493	2.741 2.692 2.749	7.76(7.94)	2.03(2.04)	4.52	-0.360	0.741
M=Ag	2.679 2.780 2.712	2.688 2.684 2.829	7.71	1.99	4.50	-0.338	0.635
M=Ni	2.536 2.479 2.447	2.696 2.736 2.491	8.68	1.26	4.54	-0.381	0.779
M=Pd	2.753 2.714 2.819	2.718 2.784 2.718	7.07	2.54	4.58	-0.290	0.587
M=Pt	2.687 2.643 2.609	2.730 2.892 3.548	7.17	2.56	4.17	-0.166	0.254
M=Co	2.523 2.510	2.739 2.698	6.32	3.44	4.67	-0.136	1.088

	2.373	4.035					
M=Rh	2.663 2.664 2.776	2.810 2.651 2.744	6.82	2.62	4.60	-0.224	0.557
M=Ir	2.527 2.639 2.561	3.718 3.419 3.407	7.13	2.04	5.11	-0.059	0.021

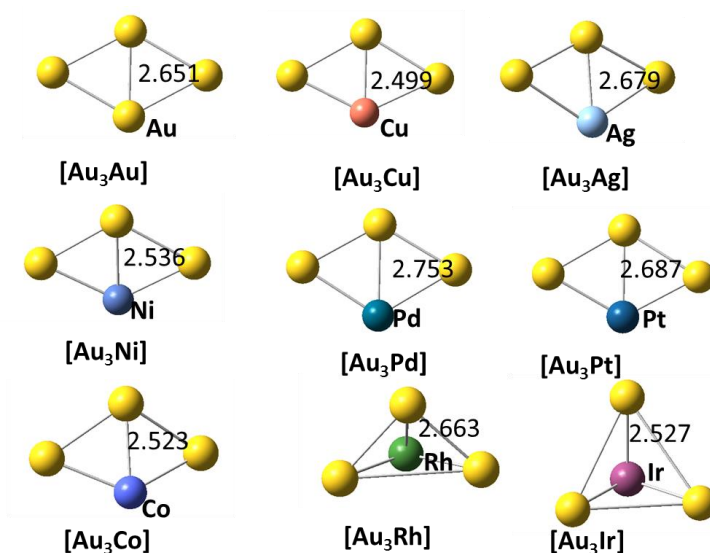


Figure 5. Optimized lowest energy geometries of $[Au_3M]$ clusters with their important bond distance (Å).

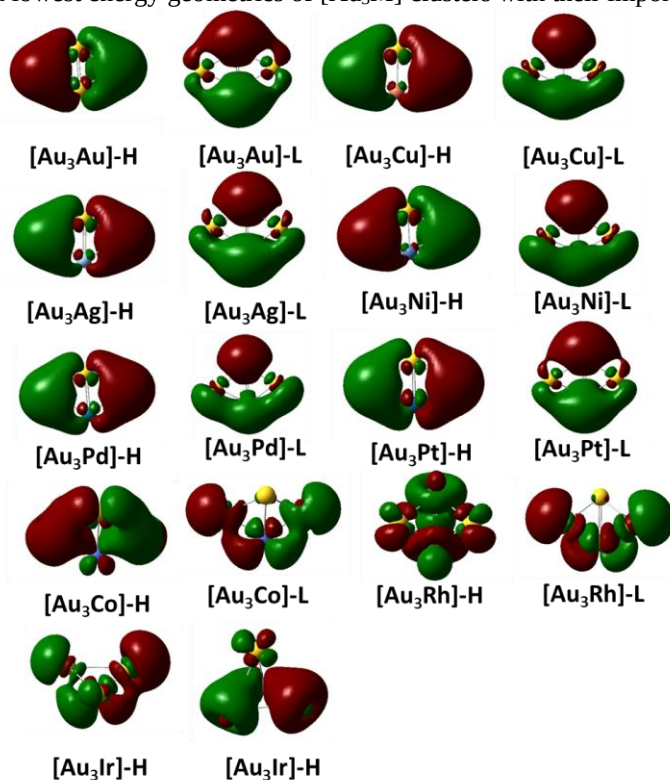


Figure 6. Computed highest occupied (H) and lowest unoccupied (L) molecular orbital of lowest energy conformer of $[Au_3M]$ clusters plotted with isovalue of (0.02 Å^{-3}) . Note that the particular stoichiometry with different metal has a same orbital pattern.

$[Au_2M_3]$ cluster

Further to consider the influence of hetero atom, the hetero atom ratio is increased making it to 2:3 and the effects are studied. Interestingly, at the lowest energy conformation, the hetero and gold atoms are present in a

consequent position forming an internal triangle with three heteroatoms leaving the gold atom at periphery. Among all the clusters, only coinage metal clusters form a 2D planar geometry where d^7 and d^8 group metals distort the geometry from the plane resulting in a 3D geometry (figure 7). This is due to the larger negative Mulliken charge generated at the gold atom due to the presence of hetero atom, which follow it same trend in all stoichiometry. The same are reflected in bond distances where in coinage metal clusters decreases when compared to $[\text{Au}_2\text{M}_2]$ and vice versa for other two group elements. The IP and EA follow the same trend as in other clusters.

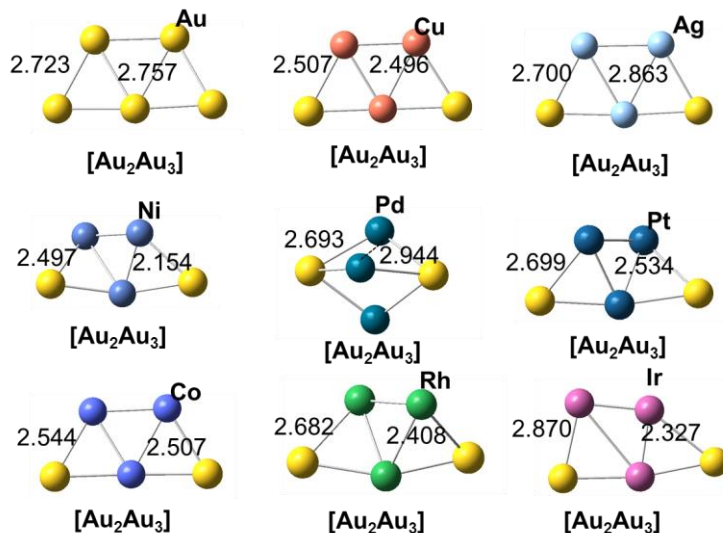


Figure 7. Optimized lowest energy geometries of $[\text{Au}_2\text{M}_3]$ clusters with their important bond distance (Å).

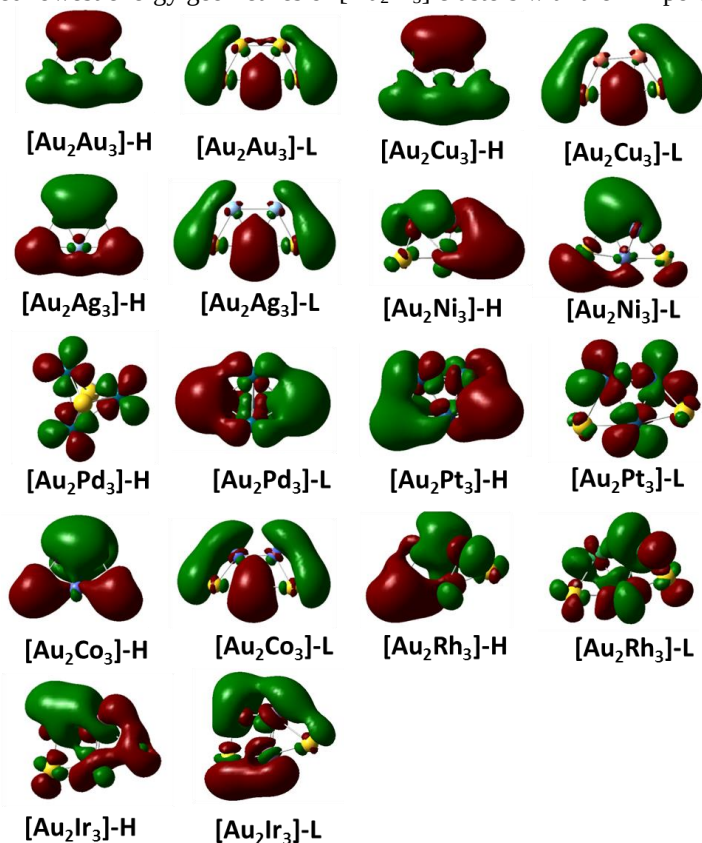


Figure 8. Computed highest occupied (H) and lowest unoccupied (L) molecular orbitals of lowest energy conformers of $[\text{Au}_2\text{M}_3]$ clusters with isovalue ($0.02\text{\AA}^{-3}$). Note that the particular stoichiometric with different metal has a same orbital pattern.

Table 5. Computed bond distances in Å are given for $[\text{Au}_2\text{M}_3]^n$, where $n=0$ (normal), $+1$ (*italic*) and -1 (**bold**) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

[Au ₂ M ₃]	Au-M	Au-Au	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.723	2.757	6.95	2.95	4.48	-0.117	0.117
	2.741	2.741					
	2.937	2.646					
M=Cu	2.507	2.496	6.62	2.19	4.79	-0.450	0.450
	2.444	2.576					
	2.681	2.354					
M=Ag	2.700	2.863	6.39	2.30	4.49	-0.438	0.438
	2.703	2.925					
	2.911	2.677					
M=Ni	2.497	2.154	3.90	3.80	4.87	-0.428	0.428
	2.498	2.490					
	2.614	2.429					
M=Pd	2.693	2.944	6.77	2.88	3.56	-0.323	0.323
	2.748	2.939					
	2.824	2.620					
M=Pt	2.699	2.534	6.87	3.06	3.77	-0.190	0.190
	2.615	2.635					
	2.808	2.539					
M=Co	2.544	2.507	12.15	2.36	5.14	-0.528	0.528
	2.582	2.171					
	2.569	2.516					
M=Rh	2.682	2.408	6.25	2.38	3.71	-0.515	0.515
	2.559	2.441					
	2.843	2.418					
M=Ir	2.870	2.327	7.56	2.42	4.10	-0.257	0.257
	2.732	2.356					
	2.833	2.358					

[Au₃M₂] cluster

Since the electrons are polarized in [Au₂M₃] cluster, one more hetero atom has been replaced with gold atom. The geometric optimization shows that at lowest energy conformation, the heteroatom is making a perfect vertical plane between the three gold atoms and has tried to maintain the ring structure. Unlike [Au₂M₃], even the coinage clusters with Ag and Cu are also distorted from the 2D plane (figure 9). As it obvious that other clusters are in 3D geometry. And the comparison of [Au₂M₃] and [Au₃M₂] shows that both clusters have similar charge distribution because of their counteractive effect. However, IP and EA increase for coinage metal and for other groups IP increases and EA decreases in line with their different orbital pattern as seen in (figure 10).

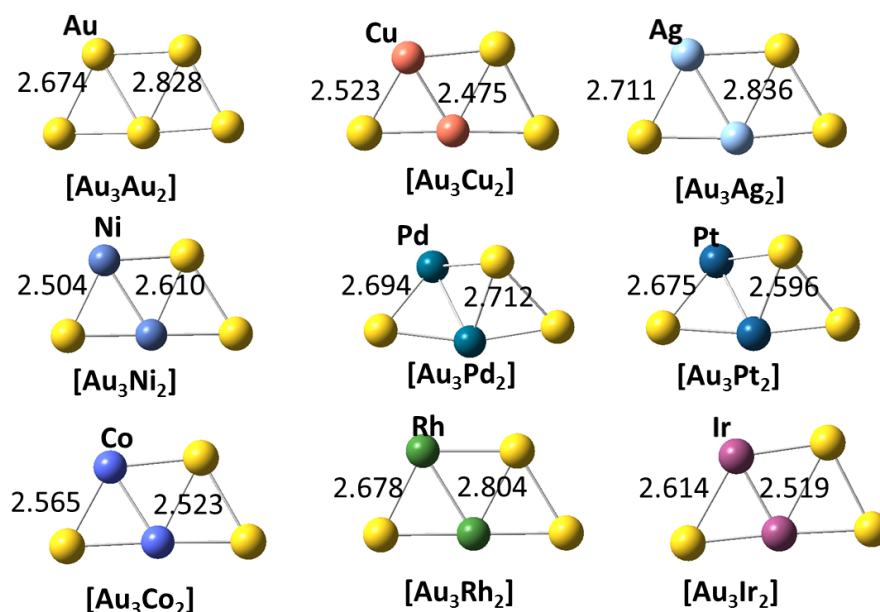


Figure 9. Optimized lowest energy geometries of [Au₃M₂] clusters with their important bond distance (Å).

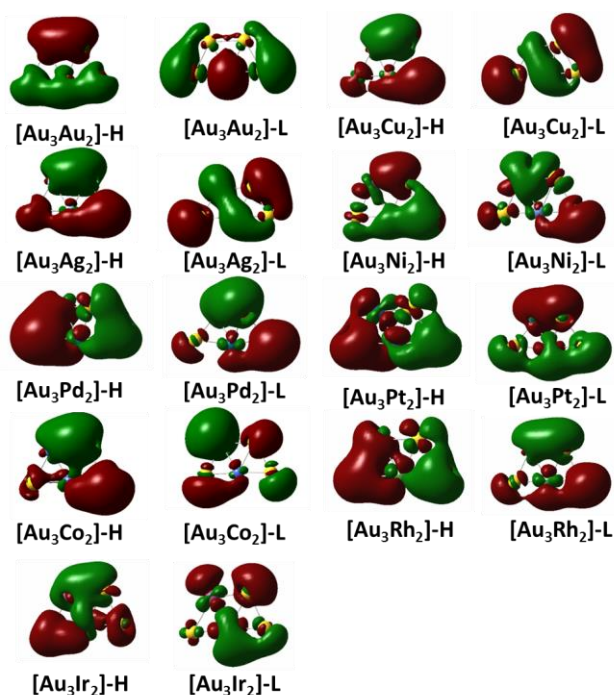


Figure 10. Computed highest occupied (H) and lowest unoccupied molecular orbitals of lowest energy conformers of $[\text{Au}_3\text{M}_2]$ clusters with isovalue ($0.02\text{\AA}^{-3}$). Note that the particular stoichiometric with different metal has a same orbital pattern.

Table 6. Computed bond distances in $\text{\AA}$ are given for $[\text{Au}_3\text{M}_2]^n$, where $n=0$ (normal), $+1$ (*italic*) and -1 (**bold**) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

$[\text{Au}_3\text{M}_2]$	Au-M	M-M	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.674(2.78) 2.740 2.654	2.828 2.740 2.940	6.95	2.95	4.32	-0.116	0.116
M=Cu	2.523 2.478 2.471	2.475 2.469 2.476	7.09	2.69	4.97	-0.473	0.473
M=Ag	2.711 2.697 2.746	2.836 2.919 2.871	6.81	2.59	4.70	-0.726	0.726
M=Ni	2.504(2.60) 2.470 2.515	2.610(2.47) 2.125 2.176	8.02	1.73	3.83	-0.492	0.492
M=Pd	2.694(2.83) 2.709 2.678	2.712(2.89) 2.998 2.825	6.95	2.45	4.40	-0.441	0.441
M=Pt	2.675(2.67) 2.743 2.695	2.596(2.48) 2.448 2.465	7.51	2.83	4.30	-0.195	0.195
M=Co	2.565 2.433 2.498	2.523 2.221 2.075	11.32	1.93	5.25	-0.553	0.553
M=Rh	2.678 2.680 2.641	2.804 2.430 3.047	8.02	0.87	4.35	-0.530	0.530
M=Ir	2.614 2.558 2.670	2.519 2.287 2.292	7.53	2.77	4.47	-0.258	0.258

$[\text{Au}_4\text{M}]$ cluster

Following the extensive generation of heterogeneity, one more hetero atom has been replaced with gold atom resulting in metal clusters with 4:1 ratio. Unlike, other 5 atom containing clusters, all $[\text{Au}_4\text{M}]$ clusters have

planar 2D geometry where the hetero atom is present at the centre and as a result the homogeneity has been increasingly induced. And the MOs are delocalised more which is the reason behind the decreased polarisation observed due to the heteroatom as seen in (figure 11). The computed Δ values are almost similar to $[\text{Au}_5]$ clusters which provide an evidence for their homogeneity. This has been further reflected in the bond distances, IP and EA values. In summary, the presences of more gold atoms in five atom containing clusters reduce their heterogeneity and vice versa. In order to check the similar effect with respect to size, $[\text{Au}_6]$ clusters are analysed in similar patterns.

Table 7. Computed bond distances in Å are given for $[\text{Au}_4\text{M}]^n$, where $n=0$ (normal), $+1$ (*italic*) and -1 (**bold**) along with Mulliken charges in e, IP, EA and Δ in eV. Reported values are given in bracket.

[Au ₄ M]	Au-M	Au-Au	IP	EA	Δ	Mulliken charges	
						Au	M
M=Au	2.828 2.732 2.854	2.757 2.622 2.646	6.95(7.48)	1.91(2.99)	4.34	-0.116	0.116
M=Cu	2.545(2.956) 2.600 2.646	2.754 2.591 2.655	7.06(8.41)	2.87(3.79)	4.47	-0.274	0.274
M=Ag	2.743 2.789 2.875	2.743 3.092 2.643	7.13	2.69	4.48	-0.295	0.295
M=Ni	2.509 2.616 2.650	2.682 3.096 2.654	6.16	3.77	4.20	-0.307	0.307
M=Pd	2.699 2.647 2.787	2.761 3.285 2.671	7.66	2.81	4.37	-0.220	0.220
M=Pt	2.660 2.717 2.682	2.773 5.108 2.682	7.34	2.88	4.37	-0.151	0.151
M=Co	2.509 2.553 2.656	2.670 3.045 2.651	8.45	1.64	4.40	-0.342	0.342
M=Rh	2.707 2.618 2.785	2.703 2.808 2.664	7.25(7.13)	2.81	3.83	-0.275	0.275
M=Ir	2.653 2.629 2.718	2.789 2.903 2.608	7.95	1.88	4.22	-0.221	0.221

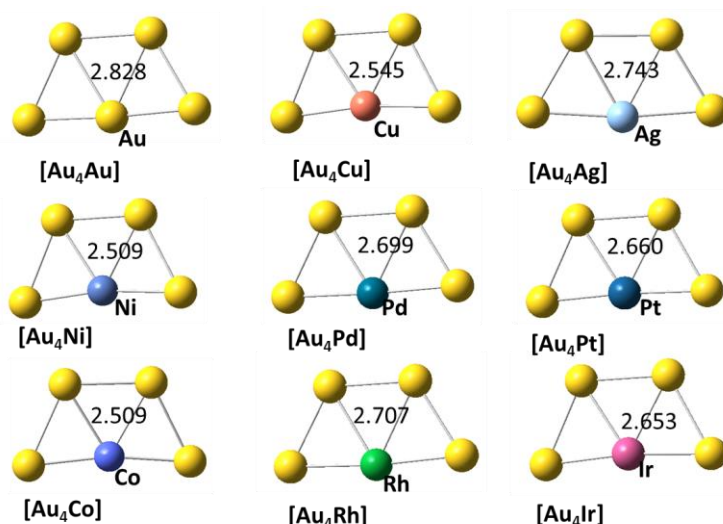


Figure 11. Optimized lowest energy geometries of $[\text{Au}_4\text{M}]$ clusters with their important bond distances (Å).

$[\text{Au}_a\text{M}_b]$ where $a=b=1,6$ cluster

Similar to $[\text{Au}_6]$ and $[\text{Au}_4\text{M}]$, all heterometallic combinations in this stoichiometry exist in 2D geometry as shown in figure 2 with an internal and external triangle, where the hetero atom prefers to be in the internal triangle at its lowest energy geometry. The delocalisation due to homogeneity reduces the polarization (figure 13) and as a result larger stabilization is observed with higher Δ values. And the Au-M distance increases in

following order, $[Au_5Ag] > [Au_5Rh] \approx [Au_5Pd] > [Au_5Au] > [Au_5Pt] > [Au_5Ir] > [Au_5Co] > [Au_5Ni] \approx [Au_5Cu]$. Like other clusters with various sizes, M_6 exist in 2D geometry at all stoichiometry (figure 1) with coinage metals because of the similar size. However, d^8 and d^7 metals included bimetallic cluster possess 3D geometry, due to larger polarization difference (figure 12). The same reflected in bond distances in (table 8). The change in dimension makes ionization and electron affinity processes less energetic compared to 2D geometry as given in (table 9), which might be due to the different orbital patterns as seen in (figure 13).

Table 8. Computed bond distances in Å are given for $[Au_aM_b]^n$, where n=0 (normal), +1 (*italic*) and -1 (**bold**), a=b=1-6, Reported values are given in bracket.

Models	$[Au_5M]$		$[Au_4M_2]$		$[Au_3M_3]$		$[Au_2M_4]$	
Bond distance	Au-M	Au-Au	Au-M	M-M	Au-M	M-M	Au-M	M-M
M=Au	2.680 2.718 2.752	2.776 3.048 2.776	2.680(2.70) 2.762 2.754	2.864(2.90) 2.768 2.775	2.679 2.751 2.751	2.866 2.697 2.776	2.680 2.692 2.752	2.865 2.932 2.778
M=Cu	2.529(2.70) 2.629 2.530	2.750 2.787 2.779	2.656 2.718 2.539	2.613 2.483 2.572	2.497 2.478 2.569	2.571 2.499 2.454	2.495 2.612 2.536	2.568 2.580 2.409
M=Ag	2.712 2.794 2.728	2.761 2.905 2.749	2.880 2.803 2.742	2.923 3.467 2.887	2.692 2.760 2.776	2.922 3.166 2.793	2.690 2.669 2.783	2.817 2.959 2.751
M=Ni	2.530 2.549 2.426	2.772 2.793 3.082	2.665(2.70) 2.557 2.555	2.161(2.27) 2.631 2.610	2.516 2.452 2.615	2.557 2.403 2.187	2.473 2.501 2.481	2.359 2.389 2.441
M=Pd	2.696 2.766 2.635	2.776 2.788 2.848	2.871(2.83) 2.868 2.686	2.578(2.77) 2.771 2.632	2.647 2.612 2.770	2.838 2.708 2.476	2.637 2.729 2.777	2.722 2.757 2.655
M=Pt	2.667 2.580 2.586	2.867 2.627 3.018	2.899(2.95) 2.927 2.664	2.496(2.53) 2.433 2.631	2.494 2.782 2.802	2.628 2.580 2.483	2.603 2.636 2.679	2.692 2.685 2.762
M=Co	2.547 2.615 2.550	2.778 2.931 2.789	2.700 2.771 2.577	2.063 2.626 2.612	2.510 2.507 2.594	2.573 2.464 2.504	2.525 2.516 2.616	2.450 2.379 2.486
M=Rh	2.698 2.716 2.618	2.874 2.862 2.999	2.830 2.771 2.697	2.856 2.832 2.740	2.734 2.741 2.686	2.493 2.437 2.353	2.618 2.739 2.837	2.446 2.877 2.620
M=Ir	2.640 2.657 2.580	2.874 2.877 3.202	2.903 2.952 2.681	2.306 2.345 2.418	2.557 2.663 2.730	2.479 2.520 2.662	2.619 2.682 2.722	2.485 2.676 2.591

Table 9. Computed IP, EA and Δ in eV of $[Au_aM_b]$ clusters, where a=b=1-6, Reported values are given in bracket.

Models	$[Au_5M]$			$[Au_4M_2]$			$[Au_3M_3]$			$[Au_2M_4]$		
	IP	EA	Δ	IP	EA	Δ	IP	EA	Δ	IP	EA	Δ
M=Au	8.43(8.52)	1.91(2.02)	5.63	8.43	1.91	5.63	8.43	1.91	5.63	8.43	1.91	5.62
M=Cu	7.56(8.16)	1.68(2.03)	5.36	8.41	1.86	5.63	8.41	1.56	5.93	7.33	1.29	5.49
M=Ag	7.81	1.69	5.27	8.34	1.81	5.65	7.68	1.62	5.79	7.57	1.42	5.22
M=Ni	8.90(10.16)	1.12(2.03)	5.37	4.65	4.88	4.46	10.48	0.53	5.37	5.14	2.76	3.92
M=Pd	7.44	2.95	5.26	7.43	3.74	3.68	8.19	2.82	3.47	5.02	3.10	3.66
M=Pt	9.68	2.84	5.64	7.97	3.21	4.41	7.38	3.29	4.37	7.48	3.59	3.80
M=Co	5.26(7.42)	4.23(2.09)	5.23	6.30	3.46	4.62	7.70	0.54	4.73	9.28	1.30	4.48
M=Rh	6.25(7.02)	3.44	4.32	5.85	4.40	4.20	6.13	4.08	3.92	7.28	2.50	4.10
M=Ir	6.91	3.79	4.16	7.05	2.48	4.69	7.23	1.93	4.07	6.24	2.86	4.07

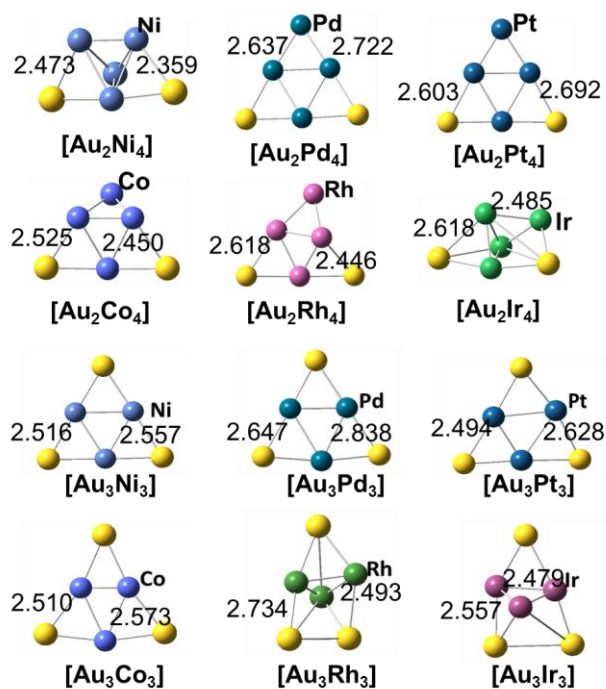


Figure 12. Optimized lowest energy geometries of $[Au_aM_b]$ clusters, where $a=b=1-6$ with their important bond distances (Å).

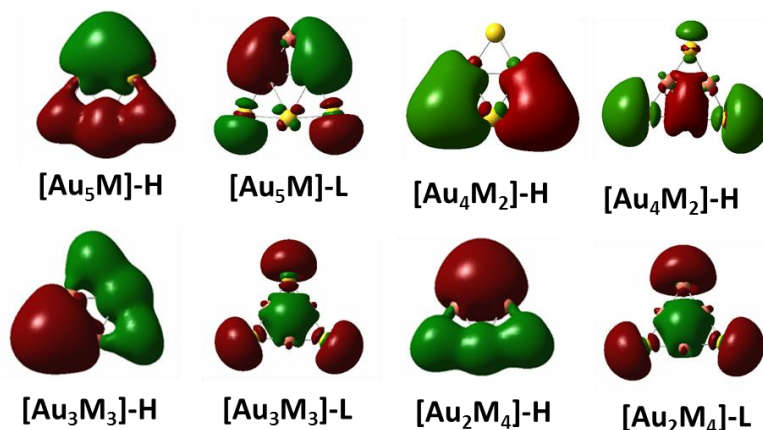


Figure 13. Computed highest occupied (H) and lowest unoccupied (L) molecular orbitals of lowest energy conformers of $[Au_aM_b]$ clusters, where $a=b=1-6$ with isovalue ($0.02\text{\AA}^{-3}$). Note that the particular stoichiometric with different metal has a same orbital pattern.

IV. Conclusion

We have studied the lowest energy conformers of different clusters with the stoichiometry $[AuM]$, $[Au_2M]$, $[Au_2M_2]$, $[Au_2M_3]$, $[Au_2M_4]$, $[Au_3M]$, $[Au_3M_2]$, $[Au_3M_3]$, $[Au_4M]$, $[Au_4M_2]$, $[Au_5M]$, where $M=Au, Cu, Ag, Ni, Pd, Pt, Rh, Co, Ir$. And the negatively charged clusters are comparatively more stable than neutral and positively charged clusters. Among these clusters, $[AuM]$ and $[Au_2M]$ clusters exist in 2D planar geometry. And other clusters exist in a distorted 2D or 3D geometry. And increase in the heterogeneity by introducing heterometal in the cluster increases the distortion from their regular geometry up to six atoms containing clusters as observed in $[Au_3M_2]$, $[Au_2M_3]$, $[Au_3M]$, $[Au_4M_2]$ and $[Au_2M_4]$. In the clusters, heterogeneity is minimal, when there is equal ratio of hetero and gold atom resulting complete delocalisation in orbitals and vice versa. The hetero metal atom containing clusters with more gold atoms have higher chemical stability than smaller gold bimetallic clusters. This is reflected in their larger Δ value and higher IP and EA. Irrespective of stoichiometry, addition of electron required less energy than removal of electron.

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