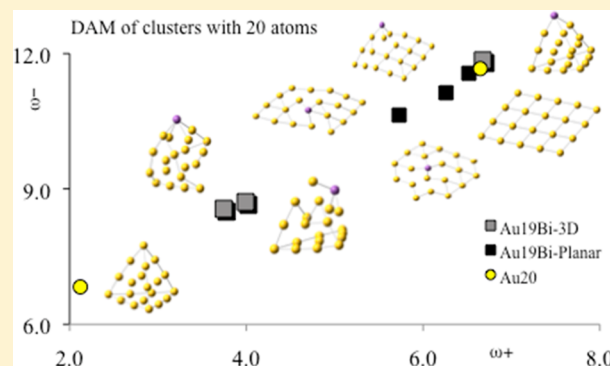


Gold–Bismuth Clusters

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ABSTRACT: Metal clusters have interesting characteristics, such as the relationship between properties and size of the cluster. This is not always apparent, so theoretical studies can provide relevant information. In this report, optimized structures and electron donor–acceptor properties of Au_nBi_m clusters are reported ($n + m = 2-7, 20$). Density functional theory calculations were performed to obtain optimized structures. The ground states of gold clusters formed with up to seven atoms are planar. The presence of Bi modifies the structure, and the clusters become 3-D. Several optimized geometries have at least one Bi atom bonded to gold or bismuth atoms and form structures similar to NH_3 . This fragment is also present in clusters with 20 atoms, where the formation of Au_3Bi stabilizes the structures. Bismuth clusters are better electron donors and worse electron acceptors than gold clusters. Mixed clusters fall in between these two extremes. The presence of Bi atoms in gold clusters modifies the electron donor–acceptor properties of the clusters, but there is no correlation between the number of Bi atoms present in the cluster and the capacity for donating electrons. The effect of planarity in Au_{19}Bi clusters is the same as that in Au_{20} clusters. The properties of pure gold clusters are certainly interesting, but clusters formed by Bi and Au are more important because the introduction of different atoms modifies the geometry, the stability, and consequently the physical and chemical properties. Apparently, the presence of Bi may increase the reactivity of gold clusters, but further studies are necessary to corroborate this hypothesis.



INTRODUCTION

Metal clusters or aggregates comprise a collection of interacting atoms.¹ The study of these nanomaterials offers a very attractive area for research. Questions regarding the effect of size on chemical reactivity as well as the catalysis and optical and magnetic properties have probably been the most analyzed during the last years. Synthetic techniques and modifications to chemical reactivity, as affected by cluster size, are subjects that make these systems very interesting with many potential applications. Altering properties by varying the size or shape of the clusters is important and relevant for new potential applications.¹⁻¹⁰ However, the relationship between properties and size of clusters is not always known; therefore, theoretical studies can provide relevant information.⁵⁻⁸

Physical and chemical properties of clusters are different from those in the bulk. The main reason is that these nanomaterials present more atoms at the surface. These atoms have fewer neighbors and lower coordination. Therefore, these are unstable with unsatisfied bonds and are, as a consequence, more reactive. Probably the best examples of nanomaterials with very different properties when compared with bulk are gold clusters. Gold is a yellow, shiny noble metal used in jewelry because it is very stable and does not tarnish. Because it is a metal, it is a good electrical conductor. Gold clusters are electrical insulators and manifest unexpected catalytic activity.² Depending on the size, the most stable structure changes from planar to 3-D; consequently, chemical properties are modified.

From theoretical studies, it has been predicted that size matters, but planarity is also important and could make a difference.^{5,6} Small planar clusters are very reactive for the activation of C–C multiple bonds and for reactions with radicals; 3-D nanoparticles of gold are more reactive than planar for redox reactions.

In addition to the study of gold clusters, the investigation of bismuth nanoparticles has been reported.^{9,11} The evolution of metallic properties has been investigated using synchrotron radiation-excited photoelectron spectroscopy, and the most stable structure of neutral and cationic bismuth clusters has been theoretically analyzed. Clusters with more than eight atoms represent structures with highly directional bonds and present three or four coordination numbers. For these clusters, fragmentation thresholds exist, which indicate that subclusters are more stable than large clusters. Therefore, reactivity is predictably different than that for other clusters that are stable large-size clusters.

The properties of pure metal clusters are certainly interesting. However, the clusters formed by two or more distinct atoms are also important because the introduction of

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different atoms may modify their geometry, stability, and consequently their physical and chemical properties.^{12–21} For example, doping gold clusters with a single Mg atom dramatically alters ground-state geometries, chemical stability, and magnetic moments.¹² The low-lying energy structures of Ag-doped Au clusters with up to 13 atoms are planar; generally, clusters with an even number of atoms are more stable than clusters with an odd number of atoms.¹³ Gold–silver clusters formed with eight atoms are 3-D when there are three Ag atoms.¹⁴ Gold clusters doped with vanadium present higher capacity for absorbing CO compared with bare gold clusters.¹⁵ When titanium enters gold clusters, it also modifies geometries, stability, and magnetic properties.¹⁶ Bismuth-doped tin clusters present different structural and dielectric properties compared with bare clusters.¹⁷ The structure and bonding of gold–sulfur clusters are unique because these mixed clusters can be either linear or planar.¹⁸ The reactivity of bismuth oxide clusters with ethane is quite different from the corresponding bismuth clusters,¹⁹ and boron as an intruder in gold clusters modifies geometry as well as reactivity.²⁰

Despite all of these studies, little is known concerning the structure and the reactivity of bismuth–gold clusters. A theoretical report exists,²¹ providing equilibrium geometries, relative stability, aromaticity, and the HOMO–LUMO gap of small Au_nBi_m clusters of up to five atoms. This constitutes a thorough investigation about Cu_nBi_m clusters, where bismuth–gold clusters are used for comparison. Because the structure is closely related to reactivity, in this work, an extensive study about the structures and the electron donor–acceptor properties of Au_nBi_m clusters of up to 20 atoms is reported. Quasi-planar structures are stable, but 3-D geometries constitute low-lying energy structures. Large clusters are not stable. Instead, Au_3Bi fragments are formed. This may be important in terms of the stability and reactivity of these clusters and for further applications.

■ COMPUTATIONAL DETAILS

Geometry optimizations and frequency calculations have been undertaken, using the B3LYP²² and M06-2X²³ functional in conjunction with the LANL2DZ^{24–26} basis set. Several initial geometries were used for each cluster. The initial geometries were proposed following different growth patterns and according to chemical intuition. Local minima were identified by the absence of imaginary frequencies. All electronic calculations were performed with Gaussian 09 program series.²⁷ To compute vertical ionization energy (IE) and vertical electron affinity (EA), further single-point calculations are necessary. IE is calculated as the difference between the energy of the cation and the neutral molecule, assuming that both of these have the ground-state nuclear configuration of the neutral molecule. EA is also calculated as vertical and represents the energy difference between the neutral and the anion, calculated with the ground-state nuclear configuration of the neutral molecule. IE and EA are used to calculate electron donor and electron acceptor indexes (ω^- and ω^+) according to Gázquez and Vela.^{28–30} The electrodonating power (ω^-) measures the propensity to donate charge, may be defined as

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \quad (1)$$

The propensity to accept charge or electroaccepting power (ω^+) is defined as

$$\omega^+ = \frac{(I + 3A)^2}{16(I - A)} \quad (2)$$

Lower values of the electrodonating power (ω^-) indicate a greater capacity for donating charge; higher values of the electroaccepting power (ω^+) imply a greater capacity for accepting charge. A donor–acceptor map (DAM) that was reported³¹ is constructed from ω^- and ω^+ . (See Figure 1.) This

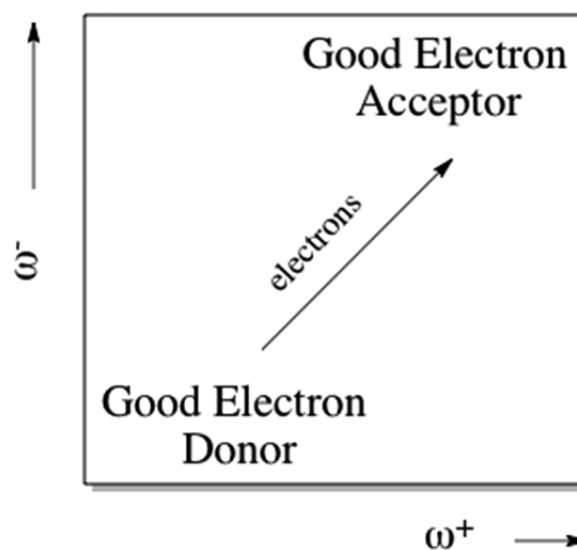


Figure 1. Electron donor–acceptor map (DAM).

map makes it possible to compare different molecules as either electron donors or acceptors. Molecules situated in the lower left corner represent good electron donors, and those situated in the upper right corner are good electron acceptors. Electrons will be transferred from species located in the bottom left of the map to species located in the upper right.

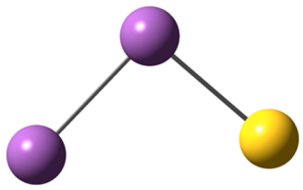
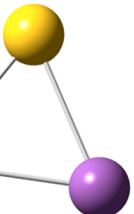
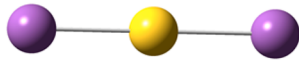
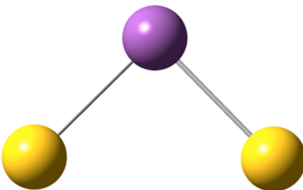

M06-2X functional has been used before to analyze the stability of metal clusters. The mean absolute deviations from benchmark CCSD(T) structural parameters for optimized geometries are $<0.1 \text{ \AA}$, and the cohesive energy is comparable to that calculated with other functionals.^{32–34}

■ RESULTS AND DISCUSSION

Optimized Structures. Tables 1–7 report the low-lying energy structures for the systems being studied. The energy difference between different optimized geometries is also included. The smallest clusters are those with three atoms, either $AuBi_2$ or Au_2Bi . Ground states are triangular structures and linear molecules are less stable by $>20 \text{ kcal/mol}$. For $AuBi_2$, there are two triangular structures with an energy difference of 7.9 kcal/mol . The distinction relates to the Bi–Au–Bi bond angle. Previously, the most stable structure reported²² was optimized with M06-2X functional and different basis sets and is similar to the equilateral triangle of Table 1. To analyze the effect of the functional, we also optimized the structures were with M06-2X functional. Similar results were revealed, with an energy difference of 10 kcal/mol .

Table 2 presents the optimized structures of clusters with four atoms. They are $AuBi_3$, Au_2Bi_2 , and Au_3Bi . For $AuBi_3$, there are four stable geometries: two 3-D and two planar structures. The latter are less stable than the first by $>30 \text{ kcal/mol}$. The ground state presents a planar triangle of three Bi

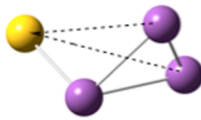
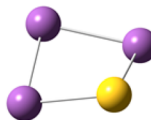
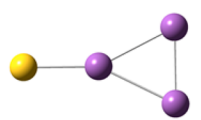

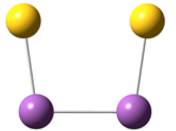
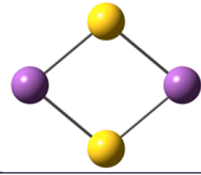
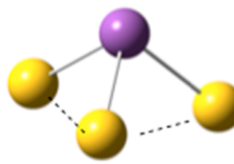
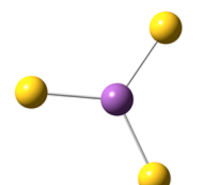
Table 1. Optimized Geometries of Au_nBi_m ($n + m = 3$)^a

Formula	Optimized Geometry	ΔE (kcal/mol)
AuBi_2		0.0
		7.9
		22.5
Au_2Bi		0.0
		35.8

^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

atoms, and the gold atom is bonded to one Bi atom. The second structure is also 3-D, with the gold atom out of the plane. In this molecule, each Bi atom presents only two bonds, while in the ground state there is one Bi atom with three bonds. Apparently, it is more stable to have Bi bonded to three atoms. The optimal structure previously reported for this cluster is planar.²¹ Our results obtained applying M06-2X are the same as the results reported in Table 2 that were optimized with B3LYP. The discrepancies with previously reported results may be due to the basis set. However, Bi is in the same family of the periodic table as nitrogen, and predictably the most stable structure is that where Bi is bonded to three atoms. In any case, the energy difference is small, and both structures could be present under experimental conditions. For Au_2Bi_2 , there are two stable planar stable structures. The 3-D geometries (not shown) are less stable by >20 kcal/mol. The results obtained with M06-2X functional are similar. A discrepancy is also evident in terms of the ground states previously reported, for which it is stated that the rhombic structure is the most stable.²¹ It is well known that the optimized structures are strongly dependent on the initial geometries used for optimization. It is possible that the authors did not use initial geometries with Bi atoms bonded together, which would explain why they do not report the same low-lying energy structure. The ground state of Au_3Bi is like NH_3 , in complete agreement with previous results. For Au_3Bi , the planar structure is 43.7 kcal/mol less stable.

Table 2. Optimized Geometries of Au_nBi_m ($n + m = 4$)^a

Formula	Optimized Geometry	ΔE (kcal/mol)
AuBi_3		0.0
		12.7
		33.9
Au_2Bi_2		92.6
		0.0
Au_2Bi_2		12.7
		0.0
Au_3Bi		43.7
		0.0

^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

The clusters formed with five atoms are reported in Table 3. Planar structures are less stable than 3-D ones, in all cases. The energy differences reported in this Table are very small, and they are at the limits for these calculations. For AuBi_4 , the stable isomers are 3-D structures, and no planar structures were found. There is one 3-D stable structure and two planar structures with similar energy for Au_2Bi_3 . For this cluster, the 3-D structure was previously reported as representing the most stable, in complete agreement with our results. The ground states of Au_3Bi_2 and Au_4Bi are similar to the low-lying structure of AuBi_3 , with a planar structure and one gold atom that is out of the plane. It is reassuring to find in these structures that there is a gold atom bonded to one Bi atom. These gold atoms have

Table 3. Optimized Geometries of Au_nBi_m ($n + m = 5$)^a

Formula	Optimized Geometry	ΔE (kcal/mol)
AuBi_4		0.0
		3.9
Au_2Bi_3		0.0
		2.6
		6.2
Au_3Bi_2		0.0
		3.5
		7.5
Au_4Bi		0.0
		0.7
		12.6

^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

fewer neighbors and lower coordination, and for this reason reactivity should be different. The ground-state structures previously reported²¹ do not include these low-lying structures of Table 3.

In Table 4, the results for clusters with six atoms are presented. All are 3-D. Some of these present one gold atom bonded to only one atom (either Au or Bi). For Au_2Bi_4 , the

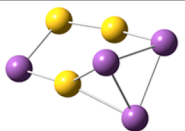
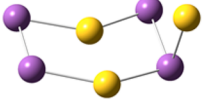

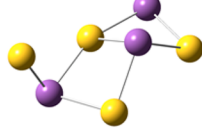
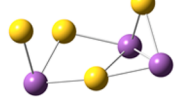
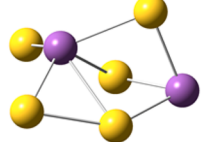
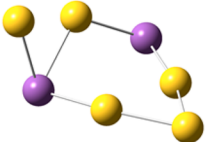
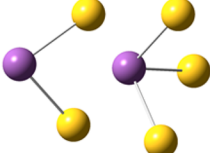
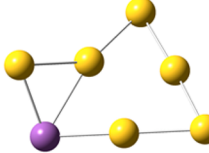
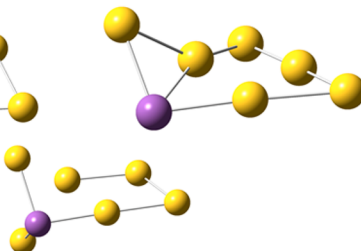
Table 4. Optimized Geometries of Au_nBi_m ($n + m = 6$)^a

Formula	Optimized Geometry	ΔE (kcal/mol)
AuBi_5		0.0
		3.8
Au_2Bi_4		0.0
		14.8
Au_3Bi_3		0.0
		9.1
		11.6
Au_4Bi_2		0.0
		0.2
Au_5Bi		0.0
		9.4

^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

ground state is a tetrahedral structure with one gold atom bonded to Bi. The square bipyramid is more symmetric and less stable by 14.8 kcal/mol. Au_3Bi_3 presents three stable isomers. Two triangles (Au_3 and Bi_3) are perpendicular form the low-lying energy structure. A stable structure exists, which is 9.1

Table 5. Optimized Geometries of Au_nBi_m ($n + m = 7$, $m = 1-4$)^a

Formula	Optimized Geometry	ΔE (kcal/mol)
Au_3Bi_4		0.0
		0.9
Au_4Bi_3		0.0
		8.0
		8.4
Au_5Bi_2		0.0
		0.5
		2.5
Au_6Bi		0.0
		8.0

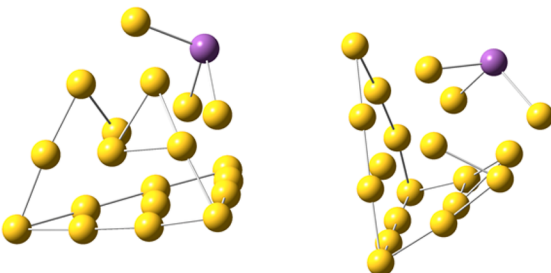
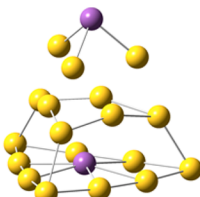
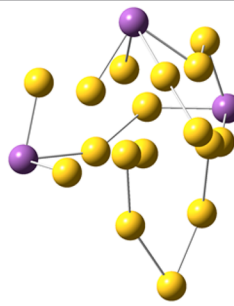
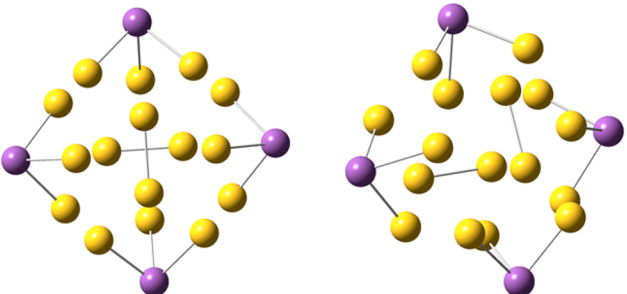
^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

kcal/mol greater in energy and in the form of a Bi_3 triangle, with the gold atoms bonded to one or two atoms. The third structure of Au_3Bi_3 that is reported in Table 4 is also 3-D with two planar squares bonded together. For Au_4Bi_2 , there are two stable structures with the same energy. A rhombus is formed with two Au and two Bi. There are two gold atoms out of the plane that are bonded to one Bi atom each. The gold atoms can

be located either “up” and “down” or both “down” from the rhombus. The ground state of Au_5Bi is similar to the low-lying structure of Au_3Bi_2 , Au_4Bi , and AuBi_3 , with a planar structure and one gold atom that is out of the plane.

Table 5 shows the ground states for clusters with seven atoms. All structures are 3-D. The ground state of Au_4Bi_3 is similar to the ground states of Au_4Bi_2 . For Au_5Bi_2 , there is an

Table 6. Optimized Geometries of Au_nBi_m ($n + m = 20$, $m = 1-4$)^a

Formula	Optimized Geometry
Au_{19}Bi	
$\text{Au}_{18}\text{Bi}_2$	
$\text{Au}_{17}\text{Bi}_3$	
$\text{Au}_{16}\text{Bi}_4$	

^aRelative energies (ΔE) with respect to the most stable structure are reported. Yellow are gold atoms and purple are bismuth atoms.

optimized geometry that presents two fragments: AuBi_2 and AuBi_3 . The energy of these two fragments is similar to the energy of the ground state. The low-lying energy structure of Au_3Bi is planar with one gold atom out of the plane.

The optimized structures for clusters formed with 20 atoms are reported in Table 6. In all structures, fragments of AuBi_3 are formed and dissociated from the gold cluster. For $\text{Au}_{16}\text{Bi}_4$, four AuBi_3 fragments and two Au_2 clusters form a highly symmetric structure. The Au_{19}Bi cluster requires more attention. In Table 7, all optimized structures for this cluster are presented. The structures based on the 3-D ground state of Au_{20} are more stable than those where Au_{20} is forming a quasi-planar structure. Interestingly, the most stable structure has a fragment of AuBi_3 , but there are two structures that are not fragmented, which are very close in energy. The presence of Bi in the planar gold clusters produces a distortion of planarity in all cases and probably increases reactivity. This is something that deserves further studies.

Electron Donor–Acceptor Properties. To analyze the electron donor/acceptor properties of the systems being studied, the DAM was constructed for all clusters and is reported in Figure 2. Evidently, the best electron donor is Bi_4 , and the best electron acceptor is $\text{Au}_{18}\text{Bi}_2$. In general, bismuth clusters are located down to the left of the DAM, that is, there are better electron donors and worse electron acceptors than gold clusters. The best electron acceptor of the pure gold clusters is Au_3 . According to these results, electrons will be transferred from the Bi_n to the Au_n . Analyzing the position on the DAM in more detail, it becomes apparent that pure gold clusters are the best electron acceptors for clusters with three, four, five, and seven atoms, and pure bismuth clusters are the best electron donors for clusters with two, three, four, and seven atoms. Au_6 and Bi_6 are similar in terms of their ability to donate or accept electrons. The AuBi cluster is a better electron acceptor than Au_2 . Au_2Bi_3 is a better electron donor than Bi_5 .

It might be expected that the replacement of gold atoms by bismuth would result in molecules that were better electron

Table 7. Optimized Geometries of Different Isomers of Au₁₉Bi. Relative Energies (ΔE) with Respect to the Most Stable Structure Are Reported^a

Au ₁₉ Bi Optimized Geometry	ΔE (kcal/mol)
	0.0
	6.5
	7.0
	29.3
	34.3
	39.1

^aYellow are gold atoms and purple are bismuth atoms.

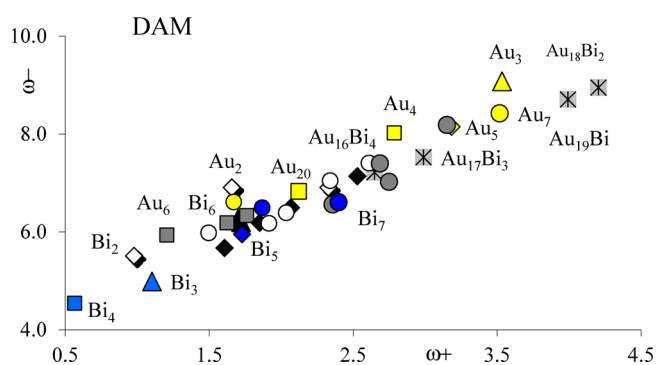


Figure 2. Electron donor–acceptor map of the systems under study.

donors; however, this is not always the case. Clusters with more Bi atoms are not always better electron donors than those with fewer Bi atoms. The clusters with six and seven atoms are good examples of this behavior. Figure 3 reports the DAM for clusters with six atoms. These systems can be put in the following order, according to their electron acceptor capacity

$$\text{Au}_2\text{Bi}_4 > \text{Au}_6 > \text{Bi}_6 > \text{Au}_4\text{Bi}_2 > \text{AuBi}_5 > \text{Au}_3\text{Bi} > \text{Au}_3\text{Bi}_3$$

and also in the following order, according to their electron donor capacity

$$\text{Au}_2\text{Bi}_4 > \text{Au}_4\text{Bi}_2 > \text{AuBi}_5 > \text{Au}_6 = \text{Bi}_6 > \text{Au}_3\text{Bi} > \text{Au}_3\text{Bi}_3$$

In Figure 4, the DAM for clusters with seven atoms is presented. In this case, up to four gold atoms were substituted

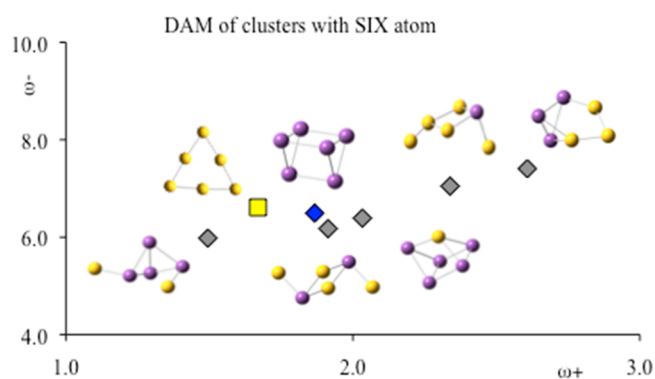


Figure 3. DAM for clusters formed with six atoms. Gold atoms are yellow and bismuth atoms are purple.

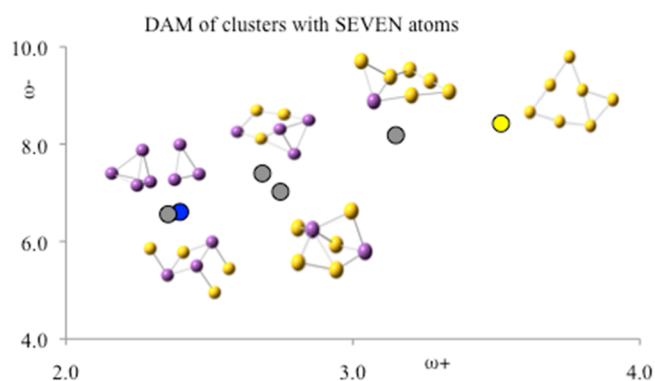


Figure 4. DAM for clusters formed with seven atoms. Gold atoms are yellow and bismuth atoms are purple.

by bismuth atoms. Au_7 is the best electron acceptor and the worst electron donor, followed by Au_6Bi . Up to this cluster, the capacity to donate electrons is increasing, along with the increase in the number of bismuth atoms. However, the next examples are contradictory because Au_4Bi_3 is a better electron donor than Au_3Bi_4 and Au_5Bi_2 . In fact, the electron donor–acceptor capacity of Au_4Bi_3 is almost the same as that for Bi_6 .

Results for clusters with 20 atoms are totally different, as the presence of Bi decreases electron donor capacity while increasing electron acceptor capacity. As apparent in Figure 2, Au_{20} is located down to the left of clusters with Bi; that is, it is the best electron donor and the worst electron acceptor, followed by $\text{Au}_{16}\text{Bi}_4$, $\text{Au}_{17}\text{Bi}_3$, Au_{19}Bi , and $\text{Au}_{18}\text{Bi}_2$. The last one of these is the best electron acceptor and the worst electron donor. It is important to remember that different fragments of Au_3Bi and pure gold clusters form these clusters. Au_{19}Bi and Au_{18}Bi present one Au_3Bi fragment; $\text{Au}_{17}\text{Bi}_3$ and $\text{Au}_{16}\text{Bi}_4$ have three and four fragments of Au_3Bi , respectively. Apparently, the formation of these fragments increases capacity to accept electrons and decreases capacity to donate electrons.

Clusters formed from 19 gold atoms and one Bi atom can be either planar or 3-D. To analyze the influence on the planarity of these clusters on the electron donor–acceptor properties of these clusters, we report in Figure 5 the DAM for Au_{19}Bi .

Comparing pure gold clusters, 3-D forms comprise better electron donors and worse electron acceptors than quasi-planar structures. This result is similar for clusters with one Bi atom. In general, quasi-planar structures of Au_{19}Bi are in the upper right of the map, indicating that they are better electron acceptors than the 3-D ones. The exception is one 3-D structure with Bi

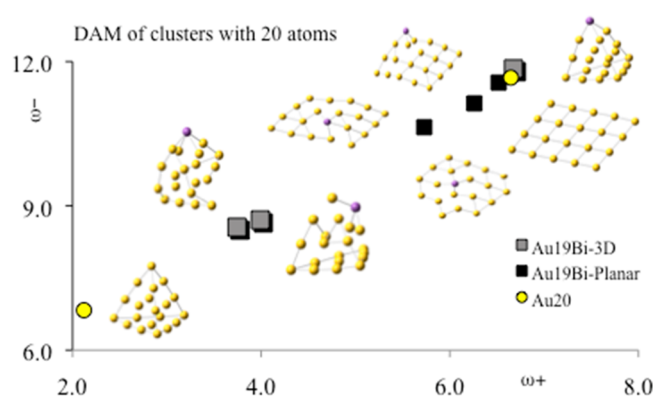


Figure 5. DAM for the different isomers of Au_{19}Bi . Gold atoms are yellow and bismuth atoms are purple.

located at the “tip” of the pyramid. This structure is not fragmented and represents the best electron acceptor.

With all of these results, it can be concluded that the presence of Bi atoms in gold clusters modifies the electron donor–acceptor properties of the clusters, but there is not a correlation between the number of Bi atoms present in the cluster and capacity for donating electrons. The effect of planarity in Au_{19}Bi clusters is the same as that in the Au_{20} clusters.

CONCLUSIONS

The presence of Bi in gold clusters modifies the structure and the electron donor–acceptor properties. The ground states of gold clusters formed with up to seven atoms are planar. The presence of Bi modifies the structure, and the clusters become 3-D.

Several optimized geometries have at least one Bi atom bonded to gold or bismuth atoms and forming structures similar to NH_3 . This fragment is also present in clusters with 20 atoms, where the formation of Au_3Bi stabilizes the structures.

For all systems being studied, at least two optimized geometries exist with similar stability. The energy difference is very small, and the presence of several isomers in an experiment is to be expected.

In general, bismuth clusters are better electron donors and worse electron acceptors than gold clusters. Mixed clusters fall in between these two extremes. The presence of Bi atoms in gold clusters modifies the electron donor–acceptor properties of the clusters, but there is no correlation between the number of Bi atoms present in the cluster and the capacity to donate electrons. The effect of planarity in Au_{19}Bi clusters is the same as that in the Au_{20} clusters.

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Notes

The authors declare no competing financial interest.

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