Size Matters, but Is Being Planar of Any Relevance? Electron Donor−Acceptor Properties of Neutral Gold Clusters up to 20 Atoms

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The main goal of this investigation is to analyze the electron donor−acceptor properties of planar and three-dimensional gold clusters (Au_N (with $N = 2-20$), and for this purpose, a new simple model based on density functional theory is used. Calculations at the B3LYP level permit us to determine the electrodonating ($\chi-$) and electroaccepting (χ^+) electronegativity of Au_N. On the basis of this analysis, it is possible to conclude that gold clusters with an odd number of atoms are better electron acceptors and better electron donors than clusters with an even number of atoms. Likewise, planar clusters are better electron acceptors than three-dimensional ones. These parameters are used to explain previous results concerning the reactivity of neutral clusters with O_2 and CO. The interaction of these neutral gold clusters with adenine−uracil (AU) and guanine−cytosine (GC) base pairs is also described. A rather particular correlation was found between $\chi+$ or $\chi-$ and the binding energies, which indicates the usefulness of this simple model to anticipate the direction of the charge transfer process and to estimate the magnitude order of the binding energies. The relevance of being planar with reference to these results is also analyzed.

Introduction

The importance of gold clusters refers to their potential for applications in catalysis, medical sciences, and in new materials that may be useful as sensors.[1−9] The well-known relativistic effects they exhibit constitute unique properties, and they can also adopt several geometrical structures. Experimental and theoretical investigations have shown that gold clusters present a number of structures, including two-dimensional planar, flat cage, spherical cage, pyramidal, hollow cage, and spherical type.[10−39] The chemical properties of these nanostructures are structurally dependent and may play an important role in nanotechnology. Therefore, there are several works reported in the literature that attempt to elucidate the geometrical structure of gold clusters.[10−39] However, these investigations reveal that a controversy still exists in determining the size that is necessary for a cluster to make the transition from a planar to a three-dimensional structure. This evolution occurs at different sizes in the case of anionic as opposed to cationic gold clusters, and forthwith, the size will also be experimentally determined for neutral clusters. Certain theoretical results indicate that the transition from planar to three-dimensional takes place in the Au cluster when it registers 15 atoms,[21] whereas others report that neutral gold clusters are planar for up to 13 atoms,[34,39] and recently a three-dimensional structure of Au_{15} was labeled as the ground state.[24] Whatever the case, the energy difference between three-dimensional and planar structures is small (10.8 kcal/mol[39] in the case of Au_{13} and approximately 6 kcal/mol[24] in the case of Au_{15}). Moreover, for up to 14 or 15 atoms, the energy difference between planar and three-dimensional structures decreases as the size of the cluster increases. Once the cluster reaches this size, the trend of the two-dimensional clusters to be more stable than the three-dimensional ones reverses.[21] At this point, the energy differences between three-dimensional and planar structures increase along with the size of the cluster: reaching approximately 46−48 kcal/mol in the case of Au_{20} (tetrahedral cluster is clearly more stable than the planar[35−37]). Probably in the case of Au_{20}, the tetrahedral cluster is the principal isomer in an experiment, but it may be that, for smaller clusters, three-dimensional and planar structures coexist under experimental conditions.

More important than the *planar-three-dimensional dilemma* is the relationship between chemical reactivity and the structure of these clusters. An extremely large energy gap was previously reported[35−38] in the case of Au_{20} between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with the greatest difference being registered between the medium-sized three-dimensional clusters. In contrast, the Au_{20} planar structures[35,37] possess a very small HOMO−LUMO gap. Since the HOMO−LUMO gap is related to the stability of the molecule, higher reactivity for the planar can be expected than for the three-dimensional Au_{20} system. There are also reports about the reactivity of smaller clusters that include the discussion about molecular and dissociative chemisorption of small molecules,[40−50] such as CO, O_2, and C_2H_4. Recently,[50] Shukla et al. reported the interaction between gold nanoclusters (Au_N, $N = 2, 4, 6, 8, 10$, or 12) and guanine (G) and guanine−cytosine (GC) nitrogen base pair. They described stable compounds and concluded that there is a charge transfer from the G and the GC base pair to the gold cluster. Only even numbers of gold atoms were taken into account by Shukla et al. because they only considered closed-shell configurations. They also reported that neutral gold clusters will oxidize G and GC, but they did not analyze gold clusters that comprised an odd number of atoms.

In spite of all these reports, no studies have investigated how the electronic properties of these small neutral gold clusters are modified when the structure changes from planar to three-

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dimensional, beyond the HOMO−LUMO gap. Due to the fact that, in most of the reactions, there is a charge transfer process between the neutral gold clusters and the adsorbed molecules, in this report, the electrodonating ($\chi-$) and electroaccepting ($\chi+$) electronegativity of Au_N (with $N = 2-20$; planar and three-dimensional) are presented. The main goal of this investigation is to analyze the electron donor−acceptor properties of planar and three-dimensional gold clusters, and for this purpose, a recently described new simple model based on density functional theory (DFT) was employed.[51−53] Applying this analysis, it is possible to conclude that gold clusters with an odd number of atoms are better electron acceptors and better electron donors than clusters with an even number of atoms. Likewise, planar clusters represent better electron acceptors than three-dimensional ones. An explanation of previous reports[40−50] concerning the reactivity of neutral clusters is offered by applying this simple model. The interaction of the best electron acceptor gold clusters with adenine−uracil (AU) and guanine−cytosine (GC) base pairs is also reported. A rather particular correlation between $\chi+$ or $\chi-$ and the binding energies was revealed, indicating the usefulness of this simple model and the relevance of planarity in these clusters.

Computational and Theoretical Details

Density functional approximation[54−56] as implemented in Gaussian 03[57] was used for all calculations. Full geometry optimizations without symmetry constrains and frequency analysis were carried out for all the stationary points using the three parameters B3LYP[58−60] density functional and the LANL2DZ for Au and D95 V basis sets for the light atoms.[61−63] Harmonic frequency analyses allowed us to verify optimized minima. Local minima were identified by the number of imaginary frequencies (NIMAG = 0). Previous studies indicate that DFT reproduces equilibrium geometries and relative stabilities with hybrid functionals, which partially include the Hartree−Fock exchange energy. These results are largely consistent with those obtained using the Møller−Plesset perturbational theory at second order and basis sets of medium quality, such as 6-31G(d,p), and cc-pVDZ.[64−66] As was reported before,[22,49] the density functional approximation calculations using LANL2DZ pseudopotentials is an adequate descriptor of Au cluster chemistry, which also included the relativistic effects.

In density functional theory, the first derivative of the energy with respect to the number of electrons at constant external potential is identified as the chemical potential, μ. The chemical potential determines the charge flow direction and the capacity of the system to donate or accept charge. Gázquez and co-workers[51−53] reported two different chemical potentials in order to distinguish the response to charge donation from the response to charge acceptance. They determined the following equations in terms of the vertical ionization energy (I) and vertical electron affinity (A), for the charge donation and the charge acceptance processes, respectively:

$$\mu^- = -\frac{1}{4}(3I + A) \quad (1)$$

$$\mu^+ = -\frac{1}{4}(I + 3A) \quad (2)$$

Since the additive inverse of the chemical potential is the electronegativity (χ), from these equations, it is possible to define two different electronegativities for the charge transfer process: one that describes the donation ($\chi-$) and another one that is useful for the electron acceptance ($\chi+$).

$$\chi^- = \frac{1}{4}(3I + A) \quad (3)$$

$$\chi^+ = \frac{1}{4}(I + 3A) \quad (4)$$

It is important to emphasize that lower values of $\chi-$ imply a better electron donor and larger values of $\chi+$ represent a greater capacity for accepting electrons. I and A refer to one electron transfer processes while $\chi-$ and $\chi+$ consider fractional charge transfer reactions. In most of the reactions with gold neutral clusters, there is a partial electron transfer. Since the partial charge transfer is one of the main intermolecular factors that dominates the binding energies in gold clusters, $\chi-$ and $\chi+$ will be better parameters than I and A to describe the electron donor−acceptor properties of these systems.

Results and Discussion

Figure 1 presents the optimized structures of planar gold clusters. Most of the structures in this figure have been reported before.[10−39] They are reoptimized in this investigation in order to obtain I and A. For Au_N with N equal to 9, 10, 15, or 17−20, three-dimensional (3D) structures were also optimized. The results are shown in Figure 2. It was previously reported that, for up to at least 13 atoms, gold clusters are planar. This study demonstrates that Au_9 and Au_{10} (3D) are less stable than the planar, but both are included in this analysis for comparison. Optimized geometries with B3LYP present slightly greater bond distances with respect to other calculations, but the structures are very similar to those previously reported.

The properties of clusters are known to depend on both their size and shape. Properties change with the size of the cluster, but what can we say concerning the planarity and the electron transfer properties of these clusters? The main goal of this investigation is to analyze the electron donor−acceptor properties of gold clusters, depending on the shape. To this end, $\chi+$ and $\chi-$ (eqs 3 and 4) were obtained. The calculated values of $\chi+$ and $\chi-$ for Au_N are presented in Table 1 for planar and 3D structures. According to these results, the best electron acceptor is Au_{15} (planar) and the worst is Au_{10} (3D). Three-dimensional clusters generally represent worse electron acceptors ($\chi+$ smaller) than planar clusters, and some 3D clusters such as Au_{17} and Au_{20} are worse electron donors ($\chi-$ larger) than the corresponding planar clusters. Planar Au_{20} not only has a smaller HOMO−LUMO gap, it is also a better electron acceptor and better electron donor than the three-dimensional one. These results may have further important applications because planar and 3D structures of gold neutral clusters are isomers with similar values in terms of the total energy.

To extend this analysis to other small neutral gold clusters, $\chi+$ and $\chi-$ for Au_N ($N = 2-20$), planar structures are obtained. Only planar clusters are considered, due to the fact that planar structures are more stable than 3D structures, in the case of most clusters. For Au_{20}, both (Au_{20}(P) and Au_{20}(3D)) are included, as they manifest the greatest difference in terms of the total energy. The results are reported in Figure 3. This figure consists of a graph that is based on $\chi+$ and $\chi-$ and appears to facilitate comparisons between electron donor and electron acceptor substances, permitting a rapid evaluation of the electron transfer processes. In this diagram, on the lower left side are

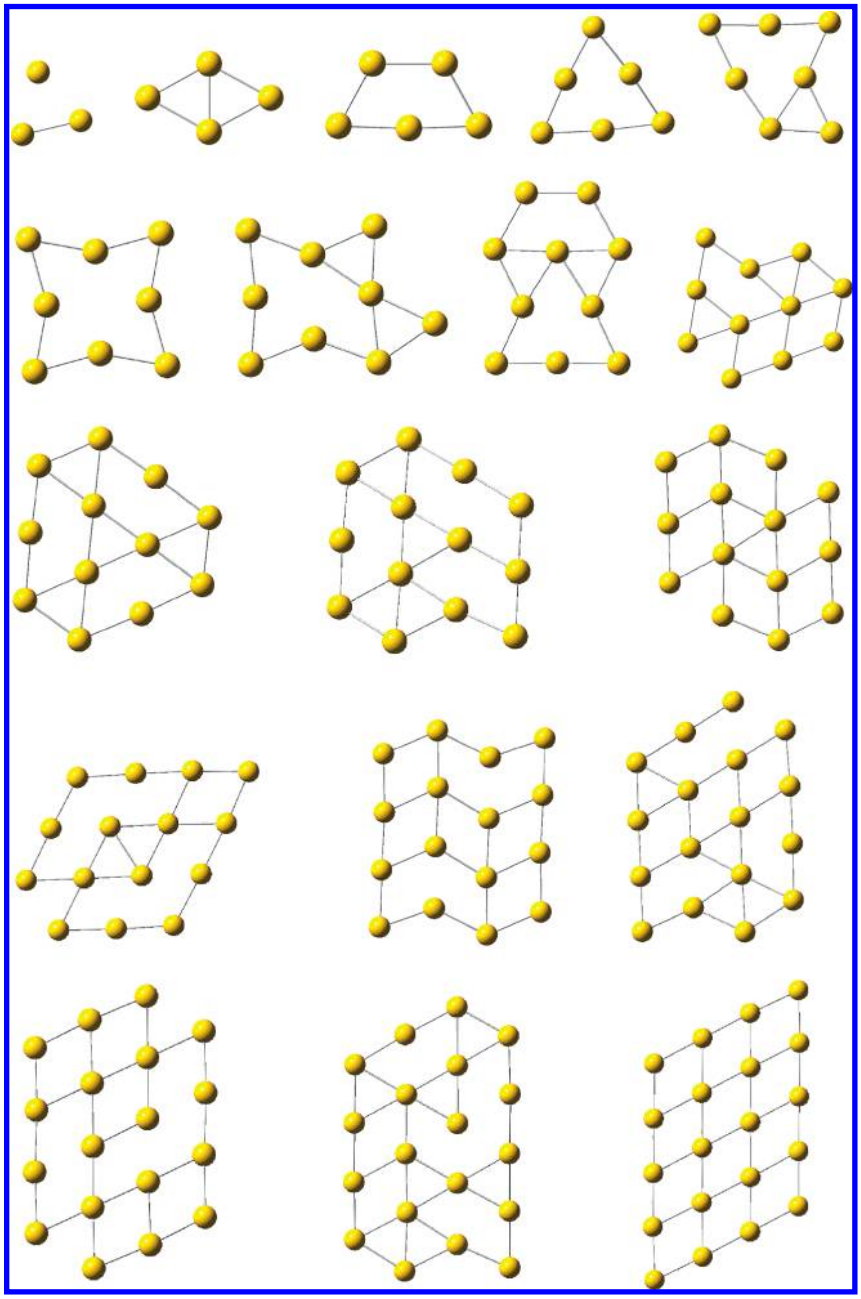


Figure 1. Planar optimized structures of neutral Au_N ($N = 3-20$) clusters.

located those systems that represent better electron donors ($\chi-$ is smaller) and worse electron acceptors ($\chi+$ is smaller), whereas those situated on the upper right side represent the opposite. This map permits a straightforward qualitative comparison between substances. On the basis of Figure 3, it is possible to conclude that generally gold clusters with an odd number of atoms are better electron acceptors ($\chi+$ larger) and better electron donors ($\chi-$ smaller) than clusters with an even number of atoms.

Figure 3 also includes $\chi+$ and $\chi-$ for O_2, CO, C_2H_4, adenine (A), adenine−uracil (AU), guanine (G), and guanine−cytosine (GC). Gold clusters are better electron donors ($\chi-$ smaller) than O_2 and CO. For small gold clusters (up to 10 atoms), the electron acceptor capacity of gold clusters is similar to the electron acceptor capacity of these small molecules. In conformity with these results (gold clusters are better electron donors), a charge transfer process from the neutral gold clusters to O_2 or CO can be anticipated. This is exactly the result that was found previously.[42,45,46] On the other hand, C_2H_4, A, AU, G, and GC are as good electron donors as large neutral gold clusters, but they are worse electron acceptors than Au_N. A charge transfer process from C_2H_4, AU, or GC to the neutral Au_N can be expected. This concurs with previous results indicating the interaction between nitrogen base pairs and gold clusters,[48−50] but it does not completely agree with recently reported results[46] for C_2H_4. However, it is important to note that the reaction with C_2H_4 was explained in terms of a balance between *donation* and *back-donation* processes; so that this reaction mechanism between neutral gold clusters and C_2H_4 cannot be seen as a simple charge transfer process in only one direction. In this situation, $\chi+$ and $\chi-$ are not enough to provide insights concerning the reaction mechanism.

In order to test whether this simple model can be used to rationalize the experimental behavior of these gold clusters, it is important to correlate the Au_N-O_2 and Au_N-CO binding energy (BE) with $\chi-$ of the gold cluster, since the gold cluster

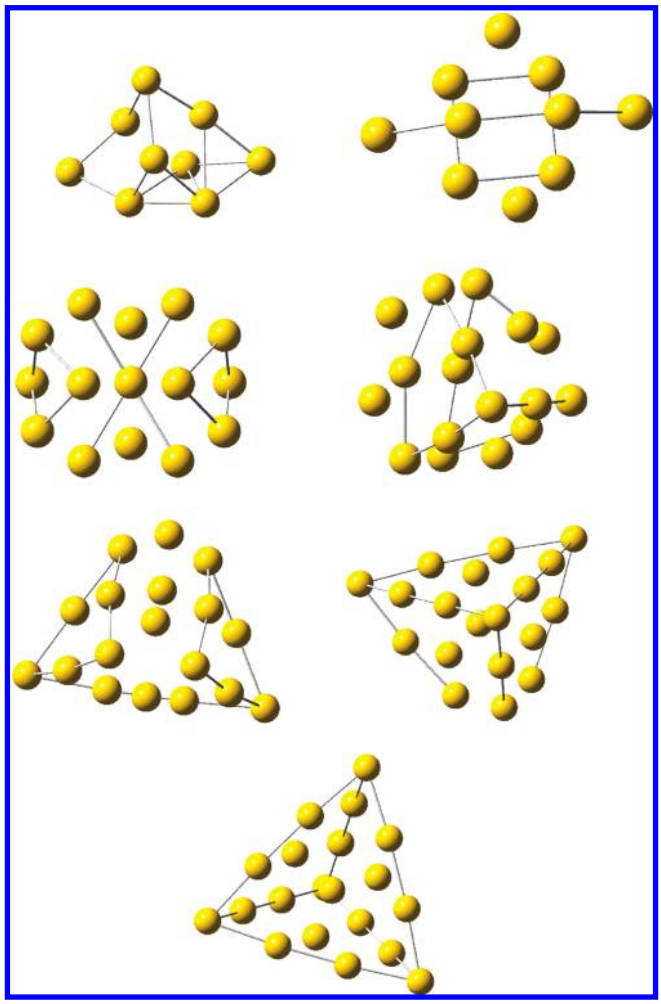


Figure 2. Three-dimensional optimized structures of neutral Au_N (N = 9, 10, 15−20) clusters.

TABLE 1: Two Different Electronegativities (in eV) Distinguish the Response to Charge Donation ($\chi-$) from the Response to Charge Acceptance ($\chi+$)[a]

cluster	3D		planar	
	$\chi-$	$\chi+$	$\chi-$	$\chi+$
Au_9	5.78	3.91	6.22	4.38
Au_{10}	6.07	3.67	6.43	4.02
Au_{15}	6.02	4.35	6.23	4.74
Au_{17}	6.20	4.62	6.09	4.67
Au_{18}	6.07	4.23	6.06	4.51
Au_{19}	5.84	4.31	5.93	4.57
Au_{20}	6.23	3.70	6.16	4.60

[a] Lower values of $\chi-$ imply a better electron donor, and larger values of $\chi+$ represent a greater capacity for accepting electrons. Equations 3 and 4 are used.

acts as the electron donor. Figure 4 shows that there is an inverse correlation between these two quantities, that is, as $\chi-$ decrease, the charge donation increases and the BE also increases. It is important to remember that better electron donors show small values for $\chi-$. In Figure 4, the best electron donors present higher BE. This expedient correlation indicates that $\chi-$ is a useful parameter for quantifying electron donor capacity and may be related to BE.

To analyze the electron acceptor capacity of gold clusters, it is necessary to compare $\chi+$ with BE for reactions where the gold cluster acts as the electron acceptor. This is the case with the DNA bases. The interaction of neutral gold clusters with

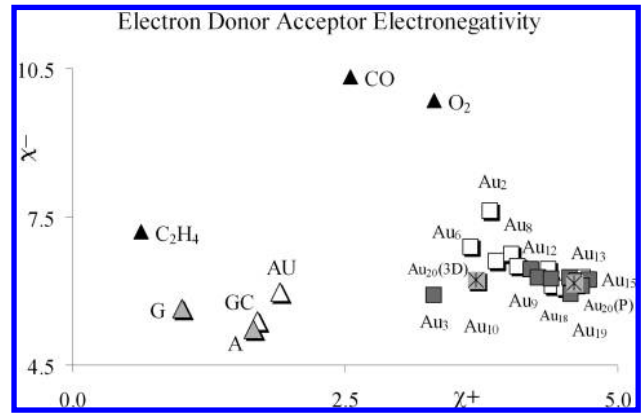


Figure 3. Two different electronegativities distinguish the response to charge donation ($\chi-$) from the response to charge acceptance ($\chi+$). Lower values of $\chi-$ imply a better electron donor, and larger values of $\chi+$ represent a greater capacity for accepting electrons. Equations 3 and 4 are used. For Au_N (N = 2−20), black squares represent for clusters with an odd number of atoms, and white squares represent clusters with an even number of atoms. Au_{20} is indicated by a star inside the square.

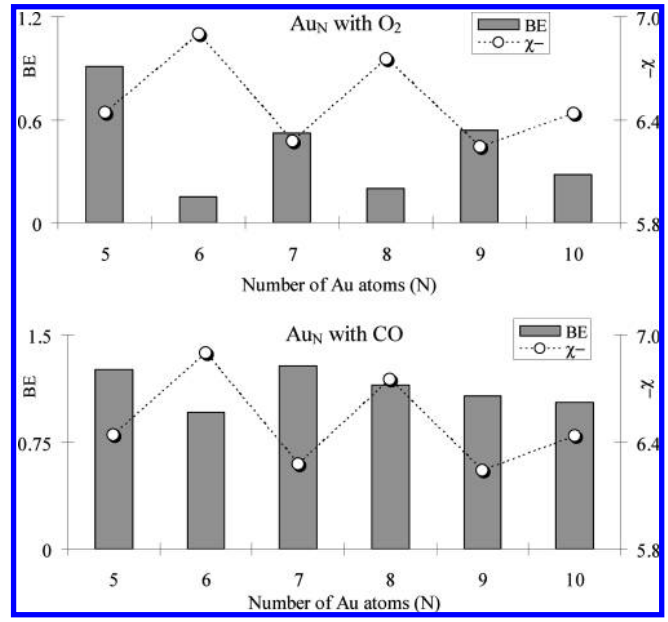
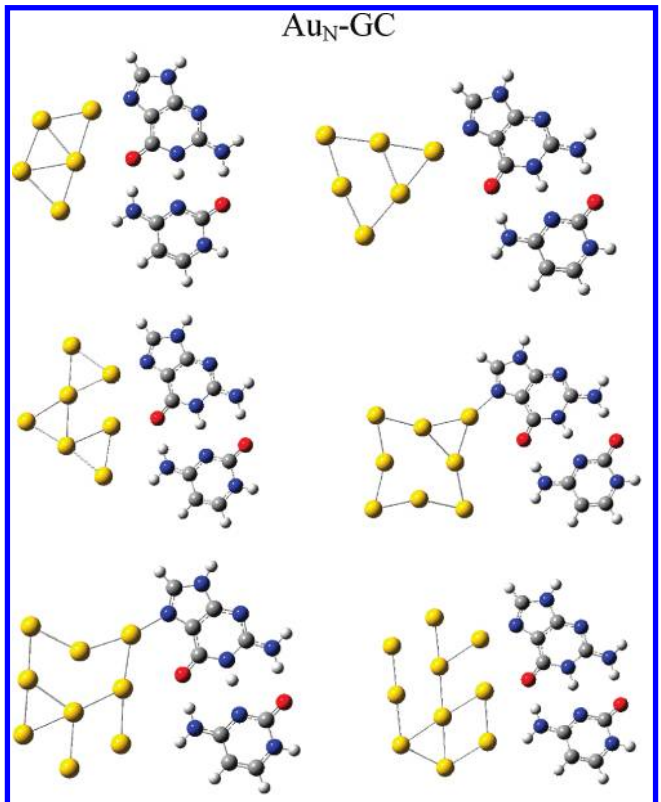


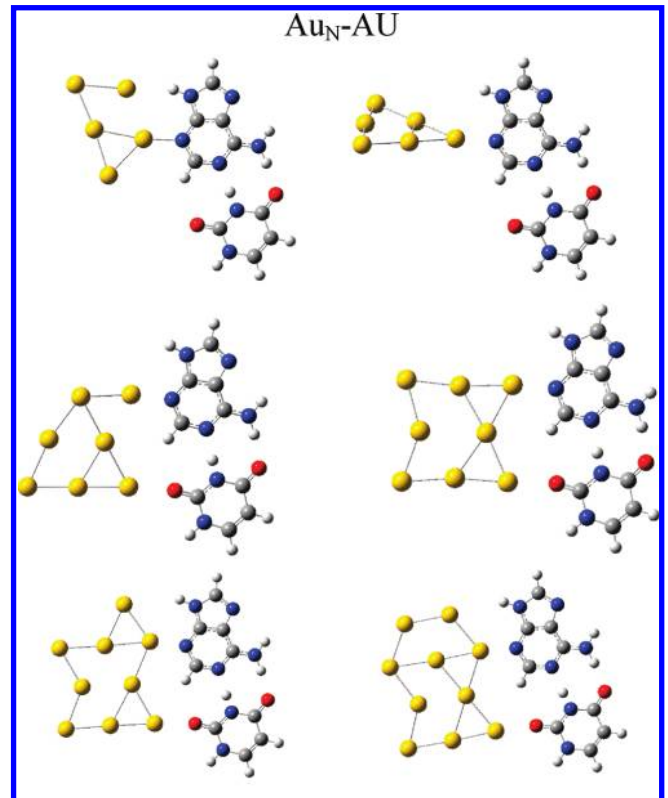
Figure 4. $\chi-$ of gold clusters and binding energy (BE in eV) for the reaction between neutral gold clusters and O_2 and CO. BE values are from ref 42.

DNA bases involves a charge transfer process from the nitrogen bases to the neutral gold cluster. Since gold clusters with an odd number of atoms are better electron acceptors, it can be hypothesized that gold clusters with an odd number of atoms will react more with DNA nitrogen bases than gold clusters with an even number of atoms. In a previous work, Shukla et al.[50] reported an investigation of the interaction of neutral Au_N (N = 2, 4, 6, 8, 10, 12) with a guanine and guanine−cytosine base pair. They did not include clusters with odd numbers of atoms in their study, even though they are better electron donors and also better electron acceptors. Moreover, the optimized geometries that they reported included 3D structures for Au_N (with $N \geq 6$), but it would appear that they did not consider the planar structures that are the most stable for Au_6, Au_8, and Au_{10}. Because of this and in order to analyze the interaction between neutral gold planar clusters and the nitrogen base, the optimized structures of guanine−cytosine (GC) and adenine−uracil (AU) base pairs bonded to neutral and planar Au_N clusters



Molecule	BE (in eV)	Bond Distance (in Å) Au-N7 (guanine)	Au-O6 (guanine)	Au-H_2N (cytosine)
Au_5-GC	1.16	2.16	3.01	3.02
Au_6-GC	1.10	2.19	4.61	6.93
Au_7-GC	1.24	2.17	2.68	2.93
Au_8-GC	1.20	2.16	4.15	4.44
Au_9-GC	1.36	2.15	3.08	2.98
Au_{10}-GC	1.29	2.17	2.55	2.88

Figure 5. Optimized structures of Au_N−(guanine−cytosine) (N = 5−10). Binding energy (BE in eV) for the reaction between the neutral cluster and GC is reported. Selected bond distances are included.



Molecule	BE (in eV)	Bond Distance (in Å) Au-N3 (adenine)	Au-HN (adenine)	Au-O (uracil)
Au_5-AU	1.06	2.16	2.59	5.60
Au_6-AU	0.95	2.20	4.53	7.50
Au_7-AU	1.01	2.20	3.40	2.48
Au_8-AU	1.01	2.22	3.42	2.49
Au_9-AU	1.34	2.18	3.40	2.44
Au_{10}-AU	1.32	2.18	3.35	2.46

Figure 6. Optimized structures of Au_N−(adenine−uracil) (N = 5−10). Binding energy (BE in eV) for the reaction between the neutral cluster and GC is reported. Selected bond distances are included.

(N = 5−10) are reported in Figures 5 and 6 (for Au_N−GC and Au_N−AU, respectively). Selected bond distances and the binding energy results (BE) are also included. BE was calculated according to the following:

$$Au_N\text{−}GC \rightarrow GC + Au_N \quad BE = [E(GC) + E(Au_N)] - [E(Au_N\text{−}GC)]$$

$$Au_N\text{−}AU \rightarrow GC + Au_N \quad BE = [E(AU) + E(Au_N)] - [E(Au_N\text{−}AU)]$$

It is evident from Figure 5 that the interaction of the Watson−Crick guanine−cytosine base pair with Au_N is mainly through N7, which concurs with previous results for nonplanar gold clusters.[50] All the structures presented in Figure 5 are planar with the gold cluster parallel to the GC base pair. The only exception is Au_{10}−GC. Neutral Au_{10} and GC are planar structures, but they are not completely parallel, rather the dihedral angle is approximately 140 degrees. In the case of Au−-AU, the structures are also planar with only one exception: Au_6−AU. The gold cluster in this compound is perpendicular to the AU base pair plane, and only one Au atom is bonded to the adenine. The Au−N bond distance is slightly greater when bonded to AU than when bonded to GC, and the BE is slightly smaller for Au_N−AU than it is for Au_N−GC.

It is possible to correlate the BE with the $\chi+$ parameter that was obtained in this work. Figure 7 shows that a direct correlation exists, confirming the hypothesis that reactivity increases among gold clusters that have an odd number of atoms. All these results make it possible to affirm that $\chi+$ and $\chi-$ are likely to be very useful parameters for anticipating the direction of the charge transfer process and for estimating the magnitude order of the binding energies.

Importance of Being Planar. The comparison between the results shown in Figure 5 with those reported by Shukla et al.[50] shows that the BE energies of the planar structures of Au_6, Au_8, and Au_{10} bounded to GC are slightly greater than for the 3D reported in ref 50. Apparently, planar and 3D structures form similar bonds with GC, and planarity is not crucial for stability. Until now, for the purpose of analyzing the interaction between nitrogen base pairs and neutral gold clusters, only planar structures where the gold clusters are located "outside" and "parallel" to the nitrogen base pair were considered. However, it is possible to include planar gold clusters located in between the base pair (thus dissociating the hydrogen bonds). In order to analyze the energy difference between these structures and the planar structures described previously, in Figure 8, the optimized structures of Au_5 and Au_9 interacting with adenine−uracil are included. Neutral Au_5 and Au_9 bound within the nitrogen base pair are approximately 0.7 eV less stable than those where

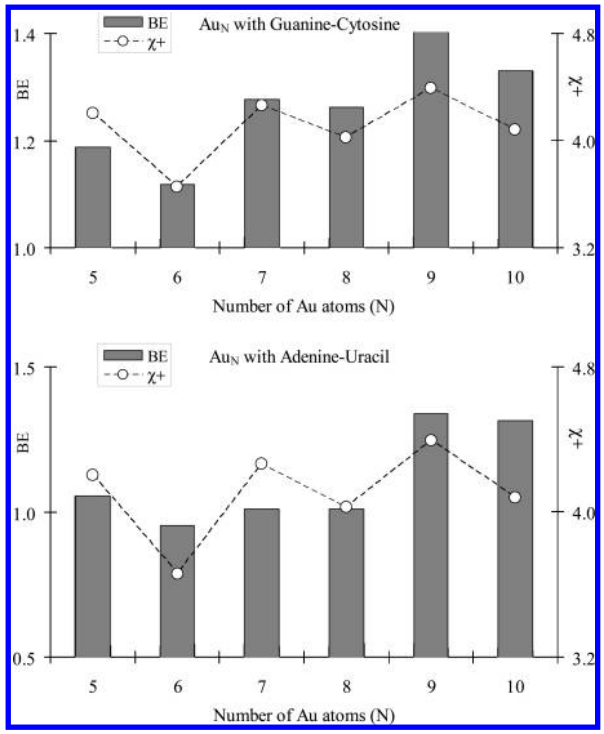


Figure 7. $\chi+$ of gold clusters and binding energy (BE in eV) for the reaction between neutral gold clusters and guanine−cytosine or adenine−uracil base pairs.

the neutral cluster is found "outside" the nitrogen base pairs. This destabilization is due to two factors: the breaking of the hydrogen bonds and the disappearance of the planarity of the nanoclusters. In a previous work,[49] it was reported that anionic gold clusters may dissociate the adenine−uracil base pair. Anions remain planar and form nonconventional hydrogen bonds that stabilize the system, but neutral gold clusters in between the nitrogen base pair are not planar and do not produce such hydrogen bonds.

The neutral gold cluster with 20 atoms is interesting as planar and 3D manifest very different electron donor−acceptor properties. Both present different ability in terms of accepting or donating electrons with the planar structures being better electron acceptors and better electron donors than the 3D. In the interaction of Au_{20} with guanine (it has lower $\chi-$, i.e., is a better electron donor than Au_{20}), a greater binding energy can be predicted for the planar structure than for the 3D, due to the fact that the planar structure represents a better electron acceptor than the 3D. To corroborate this hypothesis, optimized structures of guanine−Au_{20} (planar and 3D) are presented in Figure 9. The BE is included for comparison. The BE for the planar structure is approximately 0.2 eV greater than the BE for the 3D, corroborating the hypothesis referring to the importance of being planar.

It was reported in a previous work[39] that a planar conformation offers the best conditions for concomitant oxidation and reduction reactions. This conclusion is based on local reactivity descriptors. With $\chi-$ and $\chi+$, which are both global reactivity descriptors, the conclusion is similar.

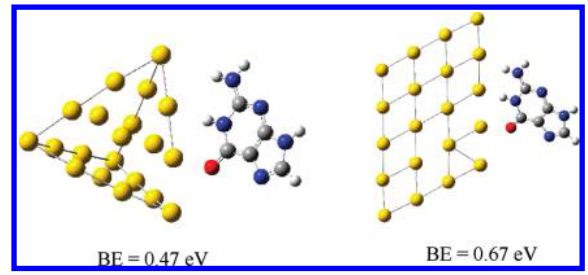


Figure 9. Optimized structures of guanine−Au_{20} (planar and 3D).

Concluding Remarks

Planar structures represent better electron acceptors than 3D. These results indicate that it would be a useful experimental challenge to control conditions by creating the necessary structure, depending on the reaction desired. In the interaction between gold neutral clusters and nitrogen base pairs, gold clusters act as electron acceptors and nitrogen bases as electron donors. This means that planar clusters may be more reactive with a nitrogen base than 3D clusters. Thus, in order to optimize this reaction, it is important to employ small planar gold clusters. On the other hand, it was previously reported that small molecules such as O_2 and CO react with neutral gold clusters by means of a charge transfer process. In these reactions, the small molecules accept charge from the neutral gold clusters. Au_9, Au_{10}, Au_{15}, and Au_{19} are better electron donors when the structure is 3D. Therefore, 3D structures of Au_9, Au_{10}, Au_{15}, and Au_{19} will be better for the interaction with O_2 and CO.

Gold clusters with an odd number of atoms are better electron acceptors and better electron donors than clusters with an even number of atoms. Consequently, the BE for GC−Au_N and AU−Au_N where N is an odd number is greater than in systems where N is an even number.

In summary, if the shape of neutral gold clusters is modified, it is possible to change their electron donor−acceptor capacities. Since the electron donor capacity is an important driving force for reactivity, it can be concluded that the shape of the clusters directly affects the level of reactivity. These results may be useful for further experimental studies and may be important for future applications.

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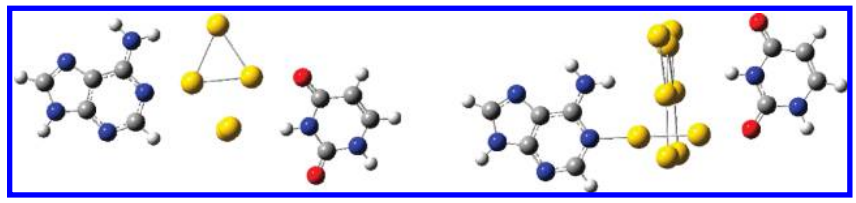

Figure 8. Optimized structures of Au_5 and Au_9 interacting with adenine−uracil. Planar gold clusters are located in between the base pair (thus dissociating the hydrogen bonds).

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