Do Anionic Gold Clusters Modify Conventional Hydrogen Bonds? The Interaction of Anionic Au$_n$ (n = 2−4) with the Adenine−Uracil Base Pair

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Density functional approximation (B3LYP) calculations have been used in order to analyze the interaction of gold anionic clusters (Au$_n$ with $n = 2-4$) with uracil ([uracil-Au$_n$]$^{-1}$), adenine ([adenine-Au$_n$]$^{-1}$), and the adenine−uracil base pair ([uracil-adenine-Au$_n$]$^{-1}$). It was found that there is only one stable isomer for [uracil-Au$_2$]$^{-1}$ and [uracil-Au$_3$]$^{-1}$, whereas there are two or more stable structures for [uracil-Au$_4$]$^{-1}$, [adenine-Au$_n$]$^{-1}$, and [uracil-adenine-Au$_n$]$^{-1}$. For all these systems, nonconventional hydrogen bonds are formed. Strengthening the bond between anionic gold clusters and the nitrogen base pair weakens the conventional hydrogen bond of the adenine−uracil base pair. This destabilization is not very strong (2−4 kcal/mol) and is at the limits of calculations, but anionic gold clusters bound in between the uracil−adenine base pair indicate that gold anionic clusters may dissociate it. These results will be useful for further experimental studies and may be important for future applications.

Introduction

The most important directional intermolecular interaction was discovered almost 100 years ago, and it is called the hydrogen bond.[1−5] A dozen different hydrogen bonds exist that are covalent or electrostatic in nature, or that can be produced as a result of dispersion contributions such as van der Waals interactions. The dissociation energy of the hydrogen bond spans from 0.2 to 40 kcal/mol and may be viewed as the beginning of the proton transfer reaction, which is very important for determining molecular conformation and as a consequence, the function of enormous chemical and biological systems. One fundamental molecule, where hydrogen bonds are crucial, is DNA. In this molecule, the orientation of hydrogen bonds is critical for the formation of the double helix structure.[6]

The interactions of metal atoms and ions with the DNA molecule have been the subject of several investigations in recent years, and it has been suggested that these interactions can induce structural modifications[7−40] in this molecule. It has been concluded that metal atoms and ions stabilize certain tautomers, modifying the orientation of hydrogen bonds in the DNA. Recently, Kryachko and Remacle[27a] carried out a theoretical study of gold neutral clusters interacting with DNA bases. They reported that "in the most stable planar base complexes, the Au−N or Au−O anchor bonds are reinforced by N−H−Au bonds". They termed this interaction the "non-conventional H-bonds" and concluded that "one of the unanchored gold atoms served as a non-conventional proton acceptor". The attachment of gold clusters to guanine−cytosine (GC) and adenine−thymine (AT) Watson−Crick DNA base pairs was also previously studied and reported.[27b,40] Geometries of the neutral and the anionic GC-Au$_n$ and AT-Au$_n$ (n = 4,8) indicated that gold clusters in the neutrals have a T-shape conformation, whereas in the anionic they have extended zigzag and T-shape structures. The authors[40] report that the adiabatic electron affinities of the GC-Au$_n$ complexes are much larger than those found in isolated pairs.

In previous works,[10−13] nonconventional hydrogen bonds that are also present when metal and non metal anions interact with DNA bases were described. Some atoms (Cu, Ag, and Au) with an extra electron have a stable closed-shell electronic configuration. These anionic systems have an extra electron localized on the metal atom and form stable complexes with RNA and DNA. In these compounds, metal atoms serve as nonconventional proton acceptors and nonconventional hydrogen bonds are formed, playing an important role in stabilizing, as well as destabilizing, DNA base pairs. One valuable conclusion which can be reached in the light of all of these investigations[7−40] is that metal cations and anions, attached to conjugated molecular systems such as the nitrogen bases of RNA and DNA are associated with substantial charge-transfer effects. These ions may function as electron donors or acceptors and thereby modulate the properties of the system.

In spite of the existence of previous studies describing the interaction of metal atoms and clusters with DNA base pairs, the influence of anionic gold clusters on the hydrogen bonds of the nitrogen base pairs has not been yet portrayed. The nonconventional hydrogen bonds that can be formed between anionic metal clusters may modify the orientation of hydrogen bonds in a way which is critical for the formation of the double helix structure. An important question addressed in the present work is whether nonconventional hydrogen bonds formed between gold anionic clusters (Au$_n$ with $n = 2-4$) and the adenine−uracil base pair affect the conventional hydrogen bond that exists between adenine and uracil. Optimized geometries, Mulliken atomic charges, and dissociation energies are used to provide insights into the binding mechanism of these complexes. As will be observed, the atomic charge distribution is related to the dissociation energy. Gold ions may function as electron acceptors and therefore change the properties of the system. This information may be useful for further experimental studies

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and may be important for future applications, where the movement of electrons is important.

Computational Details

Density functional approximation[41−43] as implemented in Gaussian 03[44] was used for all calculations. The hybrid, three-parameter B3LYP[45−47] functional was used for the calculation of complete optimizations without symmetry constraints. Two basis sets were employed: LANL2DZ[48−50] for Au and 6-311G(d,p)[51] for C, H, O, and N. Harmonic frequency analyses permitted us to verify optimized minima. The interaction energies were not corrected for basis set superposition error (BSSE).

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.[52−54]

The potential energy surface was extensively explored, in search of the global minimum. The number of initial geometries examined here is sufficient to reliably identify the global minima. It should also be note that the systems under study contain Au$_n$ anionic clusters interacting with uracil, adenine, and uracil−adenine. Geometries with fragmented Au$_n$ anionic clusters were not used because the aim was to study the clusters' reactivity. Uracil and adenine major tautomeric form are the more stable structures by at least 10 kcal/mol. However, the interaction of metal atoms with the nitrogen base may alter the stability order of certain tautomers. This is the case for neutral and cationic systems and for some anionic systems, as made evident in previous works.[10−13] The third tautomer of adenine and uracil is less stable than the correspondent major tautomeric forms by more than 10 kcal/mol. To analyze if the interaction with gold clusters modified the stability order of the tautomers, the optimization of Au$_2$ with the third tautomer of adenine and uracil was obtained. Optimized geometries are less stable than the correspondent major tautomeric forms by more than 12 kcal/mol. For this reason and for the purpose of analyzing the interaction of the nitrogen base with gold anionic clusters, two tautomers were used: the most stable and the second most stable. To compute the vertical electron detachment energies (VEDEs) of anionic species, further single-point calculations were required. Compounds were considered to be at their lowest electronic state (singlets and doublets).

Although there is no universally accepted method for assigning electrostatic charges to atoms and no experimental technique is currently available, in a previous study, de Oliveira et al.[55] made a comparison of the recorded charges using the Mulliken and Bader population analysis methods. The qualitative description of the atomic charges was the same, using either of these methods. For this reason, in this paper Mulliken atomic charges are used for the discussion of the qualitative behavior involved in the charge-transfer process.

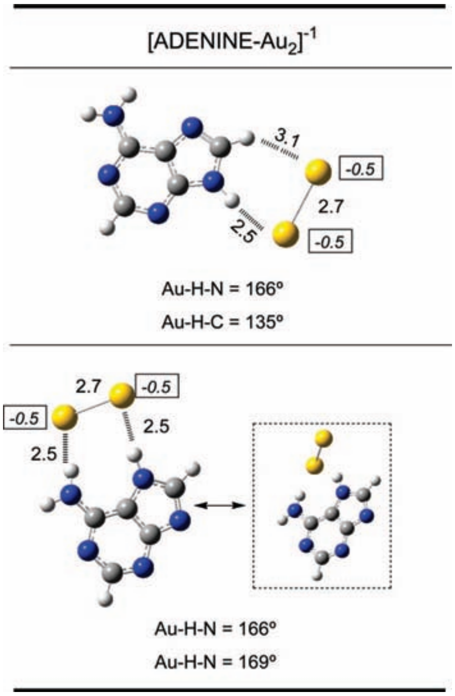

Figure 1. Most stable tautomers of [adenine-Au$_2$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

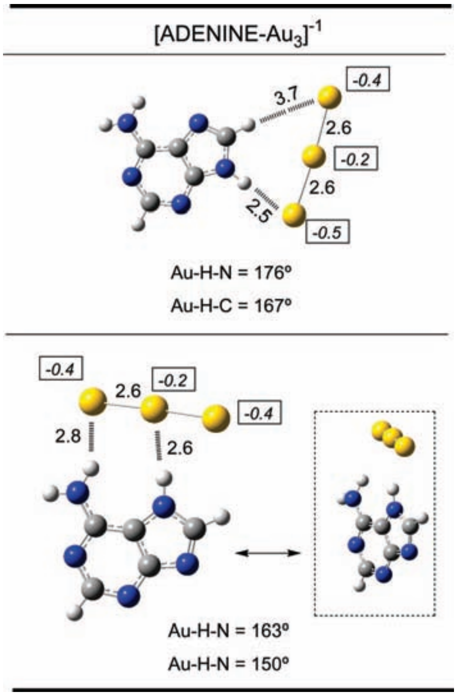

Figure 2. Most stable tautomers of [adenine-Au$_3$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

Results and Discussion

The results of the geometry optimization for [uracil-Au$_n$]$^{-1}$, [adenine-Au$_n$]$^{-1}$, and [uracil-adenine-Au$_n$]$^{-1}$ (n = 2−4) are presented in Figures 1−7. Several structures exist, each manifesting almost the same energy. Some of them are planar and related to the canonic tautomer of uracil and adenine. Other structures employ the second tautomer of adenine or uracil, and some are not planar. The isomers have similar energy. Evidently in the case of all the anionic systems described in this paper, the extra electron is localized on the gold clusters. The charge distribution of the systems closely coincides with the electron affinity (EA) values. The EA of the gold clusters (2.02, 3.85, and 2.77 eV for Au$_2$, Au$_3$, and Au$_4$, respectively[56]) is greater than the EA of the uracil (−0.05 eV) and guanine (−0.84 eV) molecules,[57] and for this reason, the extra electron is localized on the gold atoms. In any isomer, the negatively charged metal atoms of the cluster are found close to two positive hydrogen atoms of the uracil or adenine molecule.

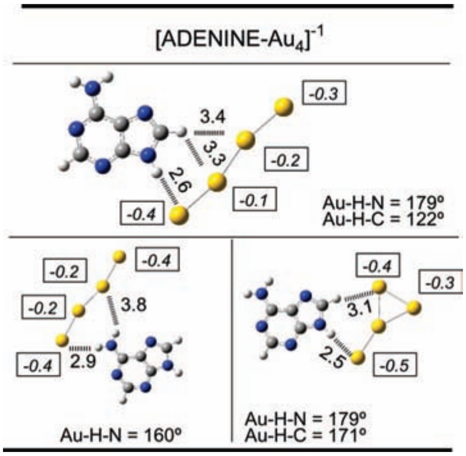

Figure 3. Most stable tautomers of [adenine-Au$_4$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

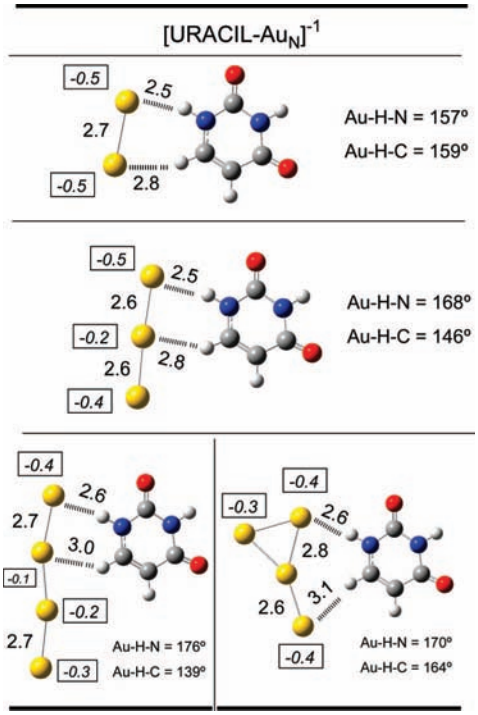

Figure 4. Most stable tautomers of [uracil-Au$_n$]$^{-1}$ ($n = 2-4$). Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

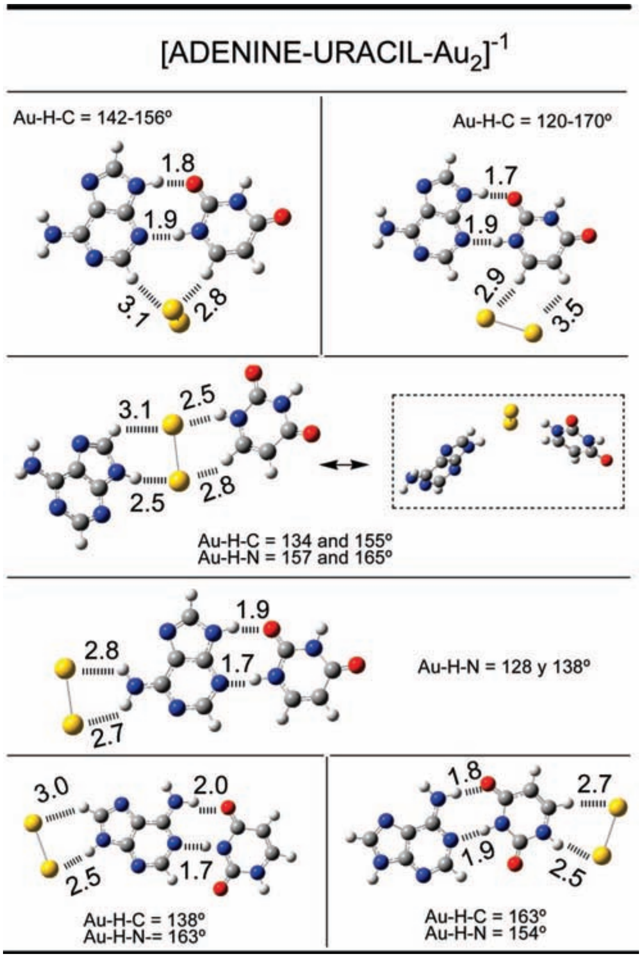

Figure 5. Most stable tautomers of [adenine-uracil-Au$_2$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

Negatively charged gold clusters represent proton acceptors containing lone-pair electrons and the interaction between the clusters and the nitrogen base is similar to those of a hydrogen bond. The bond is formed between proton donor groups (N−H and C−H) and a proton acceptor (Au$_n$$^{-1}$) containing lone-pair electrons. In the case of all these systems, the orientation of the bonds is similar to the nonconventional hydrogen bonds described by Kryachko and Remacle.[27] They call this bond a "non-conventional hydrogen bond" as it fulfills the prerequisites that are necessary for this type of interaction. Referring to the compounds reported in this paper, they fulfill at least four of the prerequisites for nonconventional hydrogen bonds, namely: (i) there is evidence of bond formation (one Au−H stretching mode is found around 80 cm^{-1}); (ii) this bond involves a hydrogen atom which is bonded to Au along the N−H bond direction; (iii) the N−H bond elongates in the compound, relative to the isolate uracil or adenine; (iv) the sum of the van der Waals radii (2.86 Å for H−Au) is larger than the hydrogen bond distances (2.5 Å for H−Au). In the case of nonconventional hydrogen bonds, the negative metal atoms (Au) represent a proton acceptor.

Regarding the metal clusters' configuration, Au$_3$ is always linear (the triangular structure is less stable) and Au$_4$ adopts two different configurations: an extended zigzag conformation and a structure that is reminiscence of a "kite" or T-shaped arrangement. Similar structures for gold clusters interacting with nitrogen base pairs were previously described[40] for AT and GC bonded to anionic Au$_4$ and Au$_8$. In this report, the initial geometries of AT-Au$_n$ and GC-Au$_n$ (neutral and anionic) complexes for optimization "were generated by placing two or four gold atoms, four or eight in total in each case, near the electron-rich sites of the AT and GC base pairs". In this work, several initial geometries for the optimization were used, including those that localized the gold atoms near the electron-rich sites of the nitrogen base. The most stable structures are shown in Figures 1−7, and evidently, all of these present the N−H−Au and C−H−Au bond interactions. In the previous report,[40] the authors do not study the interaction of Au$_4$ as a cluster with the nitrogen base pairs. Either they split the cluster into two gold dimers or they used two Au$_4$ clusters in order to analyze the AT-Au$_8$ and GC-Au$_8$ systems. For this reason and because they used different nitrogen base pairs, the results of the present report cannot be compared to theirs. The bonding scheme depends on the structure of the cluster and is determined by the atomic charge distribution. It is not to be expected that

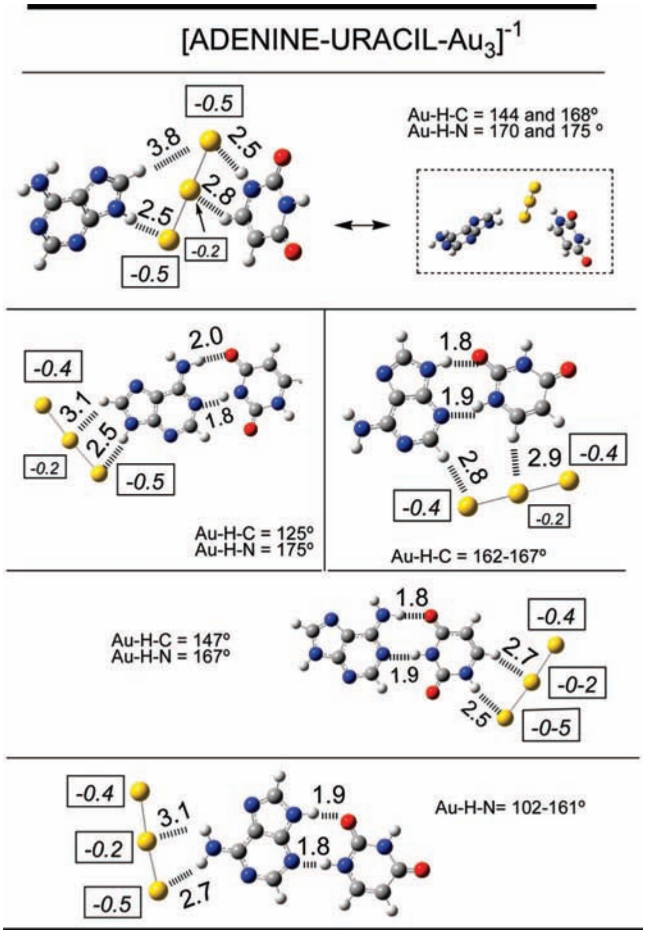

Figure 6. Most stable tautomers of [adenine-uracil-Au$_3$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

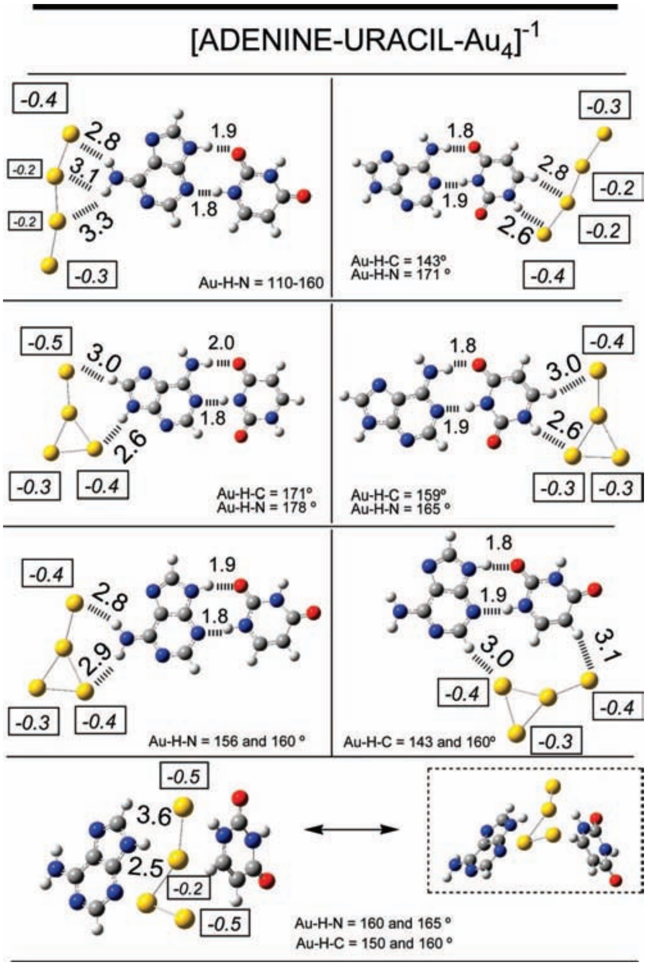

Figure 7. Most stable tautomers of [adenine-uracil-Au$_4$]$^{-1}$. Selected bond distances (in angstroms), angles, and Mulliken atomic charges (in italics) are reported.

the same interaction would take place between two Au$_2$ clusters and the nitrogen base pairs as that which takes place between one Au$_4$ with the nitrogen base pairs. The distribution of the atomic charge must necessarily be very different. In their paper, Kumar et al.[40] do not report the Mulliken atomic charges for the system with four gold atoms, but the results that they included for Au$_8$ indicate that the gold atom that is bonded near the electron rich sites of the nitrogen base is positively charged. When the Au$_4$ cluster is not split (as is the case for the results presented in this paper), the negative atomic charges are distributed along the clusters and the positively charged gold atoms do not interact with the nitrogen base. Instead, negatively charged gold atoms interact with positive hydrogen atoms of uracil and/or adenine, forming nonconventional hydrogen bonds.

[Uracil-Au$_n$]$^{-1}$ and [Adenine-Au$_n$]$^{-1}$ (n = 2−4). ***Geometry Optimization, Atomic Charges, and Dissociation Energies.*** Figures 1−4 present the most stable structures for [uracil-Au$_n$]$^{-1}$ and [adenine-Au$_n$]$^{-1}$ (n = 2−4) It may be observed that there is only one stable isomer in the case of [uracil-Au$_2$]$^{-1}$ and [uracil-Au$_3$]$^{-1}$, whereas there are two or more stable structures (with similar total energy value) in the case of [uracil-Au$_4$]$^{-1}$ and [adenine-Au$_n$]$^{-1}$. The energy difference between the structures shown in Figures 1−4 is less than 5 kcal/mol. As previously mentioned, all the structures comprise nonconventional hydrogen bonds consisting of two positively charged hydrogen bonds and two negatively charged gold atoms.

It has been stated[58,59] that in the case of hydrogen bonds, in order to achieve the optimal hydrogen bonding interactions between D−H (D being a donor atom) with anion's acceptor atom (A), certain geometric features must be presented; specifically a D−H···A interaction distance which is sufficient to produce the strongest interactions. Also, hydrogen bonds tend to be linear, because energetic stabilization results from the orientation of the D−H bond dipole, which is attracted toward the acceptor atom. Optimal hydrogen bonding corresponds to higher dissociation energies and is related to the strongest interactions. In Table 1, the dissociation energies for all the systems in this study are presented as well as the reaction schemes relating to uracil and adenine. It is evident that the dissociation energies of [Au$_n$-uracil]$^{-1}$ are larger than the dissociation energies of [Au$_n$-adenine]$^{-1}$. It is possible to rationalize these results analyzing the Au···H−N and Au···H−C bond distances and angles. For both systems, Au···H−N bond distance is close to 2.5 Å. For [Au$_n$-uracil]$^{-1}$, Au···H−C bond lengths are shorter than 3.0 Å, whereas in the case of [Au$_n$-adenine]$^{-1}$ the Au···H−C bond distance is greater than 3.0 Å. The shorter the D−H···A bond distance the stronger the interactions. The bond angles indicate that the bond is more linear in the case of [Au$_n$-adenine]$^{-1}$ than it is in the case of systems comprising uracil. These results would appear to indicate that systems comprising adenine are more stable than systems comprising uracil. However, this is not the case, which may be observed in Table 1.

By comparison of the results when employing the same nitrogen base and different sizes of gold clusters, it is evident that the compounds that include the gold anionic dimers have

TABLE 1: Dissociation Energies (in kcal/mol) According with the Reaction Schemes that Are Also Included

dissociation scheme	dissociation energies (kcal/mol)		
	Au_2	Au_3	Au_4
$[Au_n\text{-adenine}]^{-1} \rightarrow [Au_n]^{-1} + \text{adenine}$	14.9	13.1	10.7
$[Au_n\text{-uracil}]^{-1} \rightarrow [Au_n]^{-1} + \text{uracil}$	18.4	16.3	13.8
$[Au_n\text{-adenine-uracil}]^{-1} \rightarrow [Au_n]^{-1} + \text{adenine-uracil}$	12.4	10.4	8.8
$[\text{adenine-uracil-}Au_n]^{-1} \rightarrow \text{adenine-uracil} + [Au_n]^{-1}$	14.1	12.0	9.5
$[Au_n\text{-adenine-uracil}]^{-1} \rightarrow [Au_n\text{-adenine}]^{-1} + \text{uracil}$	16.1	15.9	16.6
$[\text{adenine-uracil-}Au_n]^{-1} \rightarrow \text{adenine} + [\text{uracil-}Au_n]^{-1}$	14.2	14.3	14.3
$[Au_n\text{-adenine-uracil}]^{-1} \rightarrow [Au_n]^{-1} + \text{adenine} + \text{uracil}$	31.0	29.0	27.3
$[\text{adenine-uracil-}Au_n]^{-1} \rightarrow \text{adenine} + \text{uracil} + [Au_n]^{-1}$	32.6	30.6	28.1
$[\text{adenine-}Au_n\text{-uracil}]^{-1} \rightarrow \text{adenine} + [Au_n]^{-1} + \text{uracil}$	30.2	27.4	22.9

The adenine−uracil calculated dissociation energy is equal to 18.6 kcal/mol. All the calculations were done at B3LYP level with 6-311G** for C, H, N, and O and LAND2DZ for Au.

higher dissociation energies than those that have gold anionic trimers and tetramers. It is possible to explain these results using the analysis of the Mulliken atomic charges. The gold anionic dimer has the biggest negative atomic charge for each gold atom in the cluster, and therefore the electrostatic interactions of the nonconventional hydrogen bonds for these systems are the strongest. For the systems with the gold anionic trimer and tetramer, the negative atomic charges on the gold atoms are similar. They show one gold atom with 0.5 (negative) and others with smaller and varying negative values for the gold atomic charges. In spite of the atomic charge distribution that is similar for systems with gold anionic trimers than for those that present gold anionic tetramers, the dissociation energy for compounds with trimers is greater than that of the tetramers, possibly due to stereochemical impediments that are present with four atoms.

$[\text{Uracil-Adenine-}Au_n]^{-1}$ ($n = 2-4$). ***Geometry Optimization, Atomic Charges, and Dissociation Energies.*** There are two possible binding schemes for the almost degenerated adenine-uracil base pair (see Supporting Information); thus, both structures were used as initial geometries in order to study the interactions with gold anionic clusters. Figures 5−7 indicate the most stable structures for $[\text{uracil-adenine-}Au_n]^{-1}$ ($n = 2-4$). There are many stable isomers in each case. The energy difference between the isomers shown in the figures is less than 5 kcal/mol, so they may be considered as almost degenerated. As is evident, the anionic gold clusters are bounded to the base pairs in different positions. It can be close to the uracil (adenine-uracil-Au_n), close to the adenine (Au_n-adenine-uracil), or in between the adenine−uracil base pair (adenine-Au_n-uracil). In all the systems, two negative gold atoms interact with positive hydrogen atoms. One of these two hydrogen atoms corresponds to a proton donor group (N−H) of uracil or adenine. The shortest Au−H bond distance is with the most negative gold atom of the cluster that interacts with the N−H group in all the systems. Also in this system, the orientation of the bonds is similar to the nonconventional hydrogen bonds reported by Kryachko and Remacle,[27] and the same four prerequisites relating to the nonconventional hydrogen bonds are fulfilled (as described earlier in this paper).

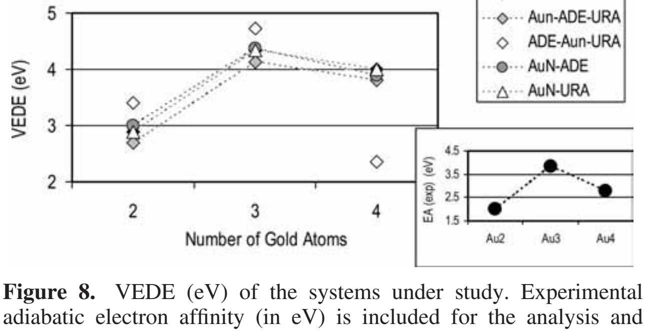

Figure 8. VEDE (eV) of the systems under study. Experimental adiabatic electron affinity (in eV) is included for the analysis and discussion of the results.

Table 1 presents the dissociation energies for two isomers in each case: one with the gold anionic cluster bonded to the uracil molecule of the base pair (adenine-uracil-Au_n) and the other with the cluster linked to the adenine molecule of the base pair (Au_n-adenine-uracil). In 1, the total dissociation energies are also presented, corresponding to the following reaction schemes

$$[\text{adenine-uracil-}Au_n]^{-1} \rightarrow Au_n^{-1} + \text{adenine} + \text{uracil}$$

$$[Au_n - \text{adenine} - \text{uracil}]^{-1} \rightarrow Au_n^{-1} + \text{adenine} + \text{uracil}$$

$$[\text{adenine} - Au_n - \text{uracil}]^{-1} \rightarrow Au_n^{-1} + \text{adenine} + \text{uracil}$$

In the cases of structures with gold clusters close to uracil (row IV, Table 1), the dissociation energies are greater than the dissociation energies for the isomers with the metal cluster close to adenine (row III, Table 1). It is possible to rationalize these results using the same arguments applied for anionic uracil-Au_n and adenine-Au_n. Bond distances are shorter in the case of systems with higher dissociation energies than they are for those with lower dissociation energies. Bond angles are also important, and the energetic stabilization that results from the orientation of the D−H bond dipole toward the acceptor atom is less significant than the energetic stabilizations related to the bond length.

The fact that the dissociation energies of $[\text{adenine-uracil-}Au_2]^{-1}$ isomers are higher than those of $[\text{adenine-uracil-}Au_3]^{-1}$ and $[\text{adenine-uracil-}Au_4]^{-1}$ isomers is also explained with the analysis of the Mulliken atomic charges. Au atoms in $[\text{adenine-uracil-}Au_2]^{-1}$ have the greatest negative atomic charge, and therefore, the electrostatic interactions of the nonconventional hydrogen bonds for these systems are the strongest.

VEDEs. VEDEs of all the anionic compounds were obtained using single point energy calculations for the neutrals when the anions manifest an optimized geometry. The results are presented in Figure 8. The experimental values of the EA (EA exp) of the neutral gold clusters are also included for the analysis. As can be seen, there is an extensive even/odd alternation of the VEDEs in the systems, corresponding to a large even/odd alternation of the gold clusters' electron affinity. Gold dimer and tetramer present smaller electron affinity than the trimer because Au_3^{-1} has a closed-shell electronic configuration, which is stable, whereas Au_2^{-1} and Au_4^{-1} have an open-shell electronic configuration, which is less stable. Au_3 has higher electron affinity than Au_2 and Au_4, and consequently, the attachment of an extra electron to the anionic systems that include Au_3 is stronger than when an extra electron is added to the anionic systems that include Au_2 or Au_4. Therefore, the VEDEs relating to the anionic systems with Au_3 must be greater than the VEDEs relating to the anionic systems with Au_2 and Au_4. These are exactly the results that we can observe in Figure 8. It is also important to note that the lowest VEDE is that relating to adenine-Au_4-uracil. This also has the lowest value of the total dissociation energy (rows VII, VIII, and IX of Table 1). This is something that may be useful for further experiments or have other possible applications.

Adenine-Uracil Hydrogen Bonds. To define whether anionic gold clusters modify conventional hydrogen bonds of the adenine–uracil base pair, hydrogen bond dissociation energies associated with the following reaction schemes are also presented in Table 1

$$[\text{adenine-uracil-Au}_n]^{-1} \rightarrow \text{adenine} + [\text{uracil-Au}_n]^{-1}$$

$$[\text{Au}_n\text{-adenine-uracil}]^{-1} \rightarrow [\text{Au}_n\text{-adenine}]^{-1} + \text{uracil}$$

The corresponding hydrogen bond lengths are included in Figures 5–7. If we compare the dissociation energy of the nonconventional hydrogen bonds, i.e., $[Au_n]^{-1}\cdots$[adenine-uracil] and [adenine-uracil]$\cdots[Au_n]^{-1}$ (rows III and IV of Table 1) with the following hydrogen bond dissociation energy $[Au_n$-adenine$]^{-1}\cdots$(uracil) and (adenine)$\cdots$[uracil-$Au_n]^{-1}$ (see rows V and VI of Table 1), it can be seen that conventional hydrogen bonds are stronger than nonconventional hydrogen bonds in these systems, in spite of the big negative atomic gold charge.

The calculated hydrogen bond dissociation energy of adenine–uracil base pair is 18.6 kcal/mol. As can be seen in Table 1 (rows V and VI), with the anionic gold clusters bonded to the base pair, the hydrogen bond dissociation energy of adenine–uracil base pair is lower by 2–4 kcal/mol. This represents a small destabilization of the adenine–uracil hydrogen bonds due to the presence of gold anionic clusters. Also the hydrogen bond lengths of the nitrogen base pair are elongated by 0.1–0.2 Å, where the anionic gold cluster is involved. It should be pointed out that this destabilization is not very strong and that we are at the limit of these calculations, but the anionic gold clusters bonded in between the nitrogen base pairs have almost the same stability (similar total energy) as the other structures presented in Figures 5–7. This means that the gold anionic cluster could be able to dissociate the adenine–uracil base pair. If this to be the case, the conventional hydrogen bonds may be modified.

Conclusions

In the case of all the anionic compounds described in this paper, the extra electron is localized on the gold clusters. Nonconventional hydrogen bonds are formed with the negatively charged gold clusters and positive hydrogen atoms of the nitrogen base.

The dissociation energy of the compounds, including the gold anionic dimer is greater than the dissociation energy of the systems that comprise gold anionic trimers and tetramers. These results correlated highly with the atomic charges. The gold anionic dimer manifests the highest negative atomic charge in the case of each gold atom in the cluster, and therefore, the electrostatic interactions of the nonconventional hydrogen bonds are the strongest in these systems.

There is a large even/odd alternation of the VEDEs of the compounds under study that corresponds with a large even/odd alternation of the gold clusters' electron affinity. Gold anionic dimers and tetramers present less electron affinity than the trimer because Au_3^{-1} has a stable, closed-shell electronic configuration, whereas Au_2^{-1} and Au_4^{-1} have less stable open-shell electronic configurations.

The uracil–adenine hydrogen bond dissociation energy of the compounds with gold anionic clusters is lower than the uracil–adenine hydrogen bond dissociation energy of the isolated nitrogen base pair by 2–4 kcal/mol. This means that there is a small destabilization of the conventional hydrogen bond that exists in the adenine–uracil base pair. This destabilization is not very strong and it is at the limits of the calculation. However, the anionic gold clusters bound within the nitrogen base pair manifest almost the same level of stability (similar total energy) as the other isomers. This means that gold anionic clusters may dissociate the adenine–uracil base pair so that the conventional hydrogen bonds will be absolutely modified.

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Supporting Information Available: A figure with the adenine–uracil-optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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