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Theoretical Study of Silver-Ion-Mediated Base Pairs: The Case of C−Ag−C and C−Ag−A Systems

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Ⓢ *Supporting Information*

ABSTRACT: Silver-mediated base pairs applied to DNA represent a new biomacromolecular nanomaterial useful for generating nanodevices as ion sensors. Reported herein is a full quantum chemical study devoted to give further knowledge on the electronic and energetic properties of C−Ag−C and mixed C−Ag−A mismatched base pairs. The B3LYP functional in conjunction with the dispersion effects (D3) has been applied. Single-point calculations have been also performed by using the M06-L functional. The investigation of their behavior has been extended to the duplex DNA modeled by the $(dC−Ag−dC)_2$ and $(dC−Ag−dA)_2$ more complex systems. The solvent effect has been taken into account by the conductor-like screening model, COSMO. In the case of mixed C−Ag−A and $(dC−Ag−dA)_2$ systems, both the Watson−Crick and Hoogsteen arrangements have been taken into account. Results show that for $(dC−Ag−dA)_2$ systems, the binding energies are almost double that of the corresponding values of C−Ag−A ones.
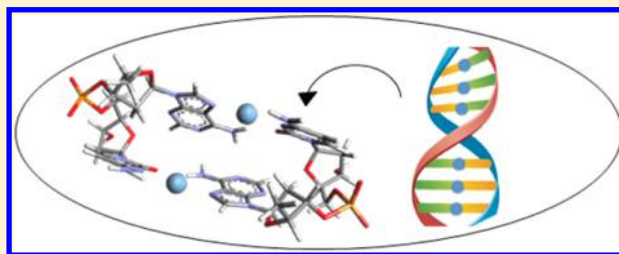
INTRODUCTION

In the past decade, interest in DNA duplexes containing metal-mediated natural mismatch base pairs has considerably grown due to their potential use in the development of new materials, (e.g., DNAzymes, logic gates, metal DNA wires, sensors able to detect different metal ions in aqueous environment, nanomaterials containing metals).[1−6] The basic idea into building up this kind of system is to replace the hydrogen atoms responsible for the H-bond in natural DNA with a metal ion having, possibly, coordination properties such to retain the DNA duplex structure. The presence of the metal ion often does not allow the formation of interbase hydrogen bonds (H-bonds) essentially due to noncomplementarity,[5] while in the Hoogsteen arrangement, the involvement of H-bonds has been observed.[5] Starting from the pioneering work of Tanaka and Shionoya in 1999,[7] numerous metal-mediated base pairs containing different metal ions, natural and artificial bases, and organic ligands have been synthesized and characterized.[4,5,8−21] Very recently, the Ono and Urata groups in a series of articles have reported that silver and mercury ions specifically stabilize the thymine-thymine (T-T) and cytosine-cytosine (C-C) mismatches in oligodeoxynucleotide (ODN) duplexes through the formation of the T−Hg−T, C−Ag−C, and C−Ag−A base pairs.[3,4,6,7,22,23]

Here, we report a theoretical analysis on the C−Ag−Cand C−Ag−A systems for which a series of experimental data are available.[4,8−10] Hoogsteen (H) geometries and energies compared to that corresponding Watson−Crick (WC) have been studied. In addition, we have considered the relative duplex forms $(dC−Ag−dC)_2$ and $(dC−Ag−dA)_2$.

COMPUTATIONAL METHOD

All the computations have been performed at the density functional theory level by using the long-range corrected hybrid B3LYP-D3 exchange−correlation potential[24,25] as implemented in TURBOMOLE code.[26,27] The choice to use dispersion-corrected density functional theory represents an accurate method to overcome the London dispersion problem of DFT that in these molecular systems plays a crucial role.[24,25] Aug-cc-pVDZ orbital basis sets have been employed for all atoms excepts for Ag, for which the Stuttgart pseudopotential (SDD) (including 28 core electrons) with the optimized valence basis set has been considered.[28] Full structure optimizations have been performed without geometrical constraints. The vibrational analysis has been carried out at the same level of theory in order to verify the minimum nature of the optimized structures as well as to compute the zero-point energy corrections.

The solvent effects have been considered by using the conductor-like screening model (COSMO)[29] as a continuum solvation model, on every examined system.

The Gibbs free energy has been obtained fixing the temperature at 298 K. The binding energies (BEs) have been computed following the equation $BE = G_{complex} − \sum G_{monomer}$.

NBO analysis[30] as implemented in the Gaussian03 code[31] has been performed by using the same basis set.
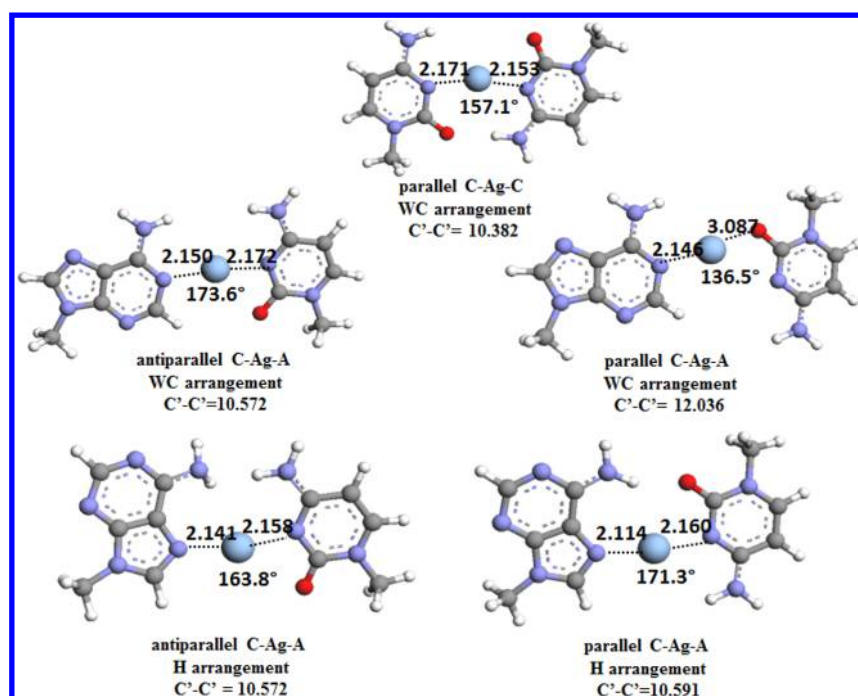
Figure 1. Optimized geometries of C−Ag−C and C−Ag−A monomers; distances are in Å, and angles are in degrees.

Because the calculation of BEs is subject to basis set superposition error (BSSE) when a finite basis set is used,[32] the counterpoise (CP) approach as implemented in the Gaussian03 code has been applied for calculating the BSSE by performing all of the calculations using the mixed basis sets, through introducing "ghost" atoms.

As carried out on similar systems,[33] the influence of another functional, M06-L,[34] on the energetic values has been taken into account by means of single-point energy calculations performed on the previously optimized geometries.

The Cartesian coordinates of all of the optimized species are given in the Supporting Information.

RESULTS AND DISCUSSION

In the first part of the work, we have considered the silver cation interacting with two naturally occurring cytosine and adenine nucleobases, generating mismatched base pairs (C−Ag−C, C−Ag−A) in the WC and Hoogsteen-like (H) arrangements and considering both the cis (antiparallel) and trans (parallel) conformations. The optimized structures are shown in Figure 1 along with the main geometrical parameters. Relative energy values and BEs, obtained in aqueous solution, for the investigated C−Ag−C and C−Ag−A systems are collected in Table 1. The C−Ag−C mismatched pair has been recently studied experimentally[4] owing to the fact that the C base selectively captures the Ag(I) ion in aqueous solution for generating the C−Ag−C base pair in the DNA duplex. In this system, only the WC coupling in both the trans and cis geometries is possible. Our computations show that the cis form collapses during the geometry optimization procedure into the trans one. In this last conformation, the vibrational analysis confirms the minimum nature of the obtained structure characterized by the Ag(I) linked to the N3 nitrogens of the bases by almost linear coordination geometries, as can be evinced by the valence angle value (157.1°). The two Ag(I)−N3′ distances have about the same value (2.153 versus 2.171 Å), and the presence of a H-bond of 2.125 Å between N−H

Table 1. Relative Energy Values (ΔΔG) and BEs in Water for the Investigated Base Pair Complexes

	H_2O phase				
	$\Delta\Delta G$	$BE_{B3LYP-D3}$	BE_{M06L}	$BE_{B3LYP-D3/BSSE}$	$BE_{M06L/BSSE}$
C−Ag−C					
trans		35.1	32.6	34.0	31.5
C−Ag−A					
WC					
cis	2.9	35.1	34.8	34.1	33.8
trans	6.0	30.7	30.2	29.8	29.3
Hoogsten					
cis	23.0	38.0	36.5	36.8	35.2
trans	0.0	41.3	39.4	40.0	38.1

and C−O groups of the two bases contributes to stabilize the system for which the computed BE is 34.0 and 31.5 kcal/mol at B3LYP-D3 and M06L, respectively (Table 1) . This value is lower than the BE previously found (42.9 kcal/mol), at almost the same level of theory (B3LYP-D3) but in a gas-phase environment, for the GC naturally occurring nucleobases that incorporate the silver ion.[35] The formation of this kind of WC structure has been observed experimentally also in the case of a silver ion interacting with artificial pyridine and imidazole.[36−38]

As far as the $(dC-Ag-dC)_2$ complex is concerned, the optimized structure depicted in Figure 2 shows a planar geometry on the upper base pair fragment, characterized by Ag−N distances of 2.169 and 2.147 Å with two H-bonds involving the C=O and H_2N groups equal to 3.062 and 3.497 Å. In the lower base pair, the distances between the silver ion and the cytosine nitrogens are slightly larger than the corresponding values in the upper base pair (2.204 and 2.194 Å). This layer shows a significant deviation from the planarity, as evidenced by the value of the propeller twist angle of 78.3° and by the loss of one H-bond (4.619 Å). The Ag−Ag interlayer length is 3.921 Å and falls in the range of values proposed experimentally on similar systems (~4 Å).[39] The
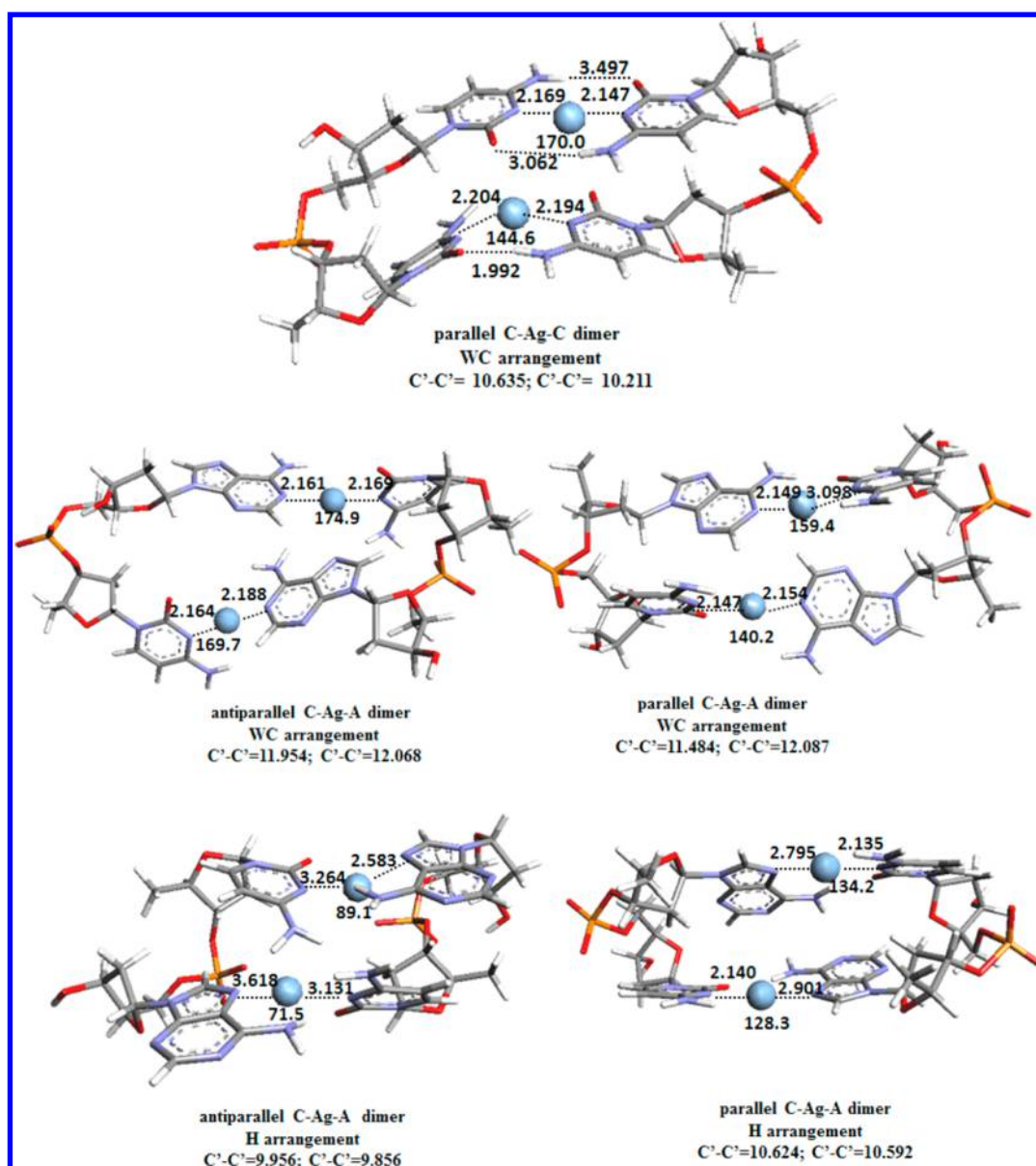
Figure 2. Optimized geometries of $(dC-Ag-dC)_2$ and $(dC-Ag-dA)_2$. Distances are in Å, and angles are in degrees.

computed BE (BE = 73.0 and 66.3 kcal/mol at B3LYP-D3 and M06L, respectively) is slightly higher than that obtained by addition of the BE found for the C−Ag−C species at both the B3LYP-D3 (68.0 kcal/mol) and M06L (63.0 kcal/mol) levels of theory and accounts for different factors, including the constraints of the phosphate and the sugar ring linkages and the Ag^+-Ag^+ and cytosine ring $\pi-\pi$ interactions other than the electrophilicity of the metal center.

Natural bond order (NBO) analysis shows that the positive charge is located on the silver cation with a value of about 0.71 |e| for the C−Ag−C system and 0.76 and 0.72 |e| for the two Ag^+ ions in the $(dC-Ag-dC)_2$ complex. The negative charge assumes almost the same value as the positive ones and is concentrated on the N3 nitrogen atoms. In the C−Ag−C system, the nitrogen reaches a net charge of −0.73 |e|, while that involved in the two interactions present in the $(dC-Ag-dC)_2$ have net charges of −0.74 and −0.75 |e|, respectively. Second-order perturbation analysis always indicates that the bond is electrostatic in nature.

In the C−Ag−A model system, the WC and Hoogsteen couplings in both the parallel (trans) and antiparallel (cis) arrangements are possible. Relative energies reported in Table 1 show that these four isomers are very close in energy, with the trans-Hoogsteen and the cis-Hoogsteen species being the absolute minimum and the low-lying one, respectively. In the most stable isomer, the BEs are 40.0 (B3LYP-D3) and 38.1 kcal/mol (M06L), and the Ag−N distances are 2.160 and 2.114 Å for cytosine and adenine, respectively. Only one H-bond between the cytosine C=O group and the adenine NH_2 one (2.033 Å) contributes to stabilize this structure. The two WC arrangements are less stable in energy also because of the lack of any kind of H-bonds (see Figure 1). The obtained value in the antiparallel arrangement in the WC base pair (34.1 kcal/mol at B3LYP-D3 level) is slightly higher than the BE previously calculated (42.9 kcal/mol), at almost the same level of theory, for the naturally occurring G−Ag−C system.[35] Also in this case, the previous computed value does not take into account the solvent effect. If we compare the present gas-phase

value of 42.4 kcal/mol (B3LYP-D3) with the value reported in ref 35, we note that the substitution of G with an adenine does not affect significantly the BE value. M06-L values propose a stability trend similar to that obtained at B3LYP-D3.

The corresponding $(dC-Ag-dA)_2$ system also prefers the Hoogsteen-type coupling over the WC one, with the trans isomer more stable than the cis one by only 1.2 kcal/mol. The WC base pair structures appear very different from the corresponding Hoogsteen ones. In fact, in the former, the two base pairs interacting with the Ag ion lie in two perpendicular planes, and the Ag–Ag distances are 5.040 and 7.180 Å for the trans and cis positions, respectively. In the Hoogsteen arrangement, the Ag ion lies at the center of a planar layer, and the distances between the metal ions are 5.180 (cis form) and 3.911 Å (trans form). In the cis conformer, the structure presents an interaction between the silver cation and the oxygen atom of the phosphate moiety (2.108 Å) that is absent in the trans arrangement, making the trans arrangement a structure more similar to that of regular DNA. The presence of the sugar and phosphate moieties imposes a constraint such that the driving force during the optimization procedure is represented by the metal–base pair attractions and by the ion–ion distance that minimizes the effect of the plane's distortion.

From the examination of the BEs (Table 2) emerges that B3LYP-D3 proposes the $(dC-Ag-dA)_2$ Hoogsteen pair in the

Table 2. Relative Energy Values ($\Delta\Delta G$) and BEs in Water for the $(dC-Ag-dC)_2$ and $(dC-Ag-dA)_2$ Complexes

	H_2O phase				
	$\Delta\Delta G$	$BE_{B3LYP-D3}$	BE_{M06L}	$BE_{B3LYP-D3/BSSE}$	$BE_{M06L/BSSE}$
$(dC-Ag-dC)_2$					
trans		75.6	68.9	73.0	66.3
$(dC-Ag-dA)_2$					
WC					
cis	11.2	65.8	60.2	63.5	57.8
trans	10.7	75.0	70.6	72.6	68.2
Hoogsten					
cis	1.2	80.2	67.1	74.9	61.8
trans	0.0	78.0	58.3	72.6	53.0

antiparallel arrangement as the system having the highest BE, while M06-L suggests the $(dC-Ag-dA)_2$ WC pair in the parallel conformation. Although this result is different, both functionals provide, as favored, the molecular system having similar geometry as far as the Ag^+-Ag^+ distance is concerned (about 5 Å), which represents a "measure" of the metallophilic attraction typically found in the nucleic acids complexed with metal ions.[21,33]

For both Hoogsteen and WC arrangements, NBO analysis indicates that the concentration of the net positive charge is on the silver cation (about 0.7 |e|) and that the negative one is on the nitrogen atoms (about −0.7 |e|). The charge on the two silver cations in $(dC-Ag-dA)_2$ has almost the same values (0.85 versus 0.86 |e| in the most stable Hoogsteen trans isomer). As observed in the previously examined cases, from the NBO analysis also in these systems, no evidence for the presence of a covalent bond between the metal ions and the nitrogen atoms occurs.

■ CONCLUSIONS

The structures of silver-mediated natural mismatch base pairs C–Ag–C, C–Ag–A, $(dC-Ag-dC)_2$, and $(dC-Ag-dA)_2$ have

been studied by means of density functional theory, including the long-range interactions. Results show that in the mixed C–Ag–A and $(dC-Ag-dA)_2$ systems, the Hoogsteen arrangement is preferred over the WC ones at the B3LYP-D3 level of theory; the BE of the $(dC-Ag-dC)_2$ and $(dC-Ag-dA)_2$ is about two times that of the corresponding C–Ag–C and C–Ag–A monomers, showing the additivity of the BE; and natural bond analysis indicates that in all cases the nature of the metal–ligand interactions are prevalently electrostatic in nature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Cartesian coordinates of all of the optimized geometries of the investigated species are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ ABBREVIATIONS

BE, binding energy; COSMO, conductor-like screening model; BSSE, basis set superposition error

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