Stabilization of an Unusual Tautomer of Guanine: Photoionization of Al−Guanine and Al−Guanine−$(NH_3)_n$

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Photoionization efficiency spectra of gas-phase Al−guanine−$(NH_3)_n$, $0 \leq n \leq 2$, have been measured in the 210−270 nm range. Within error the ionization energies, 4.65 ± 0.08, 4.6 ± 0.1, and 4.5 ± 0.2 eV for $n =$ 0, 1, and 2, respectively, are equivalent. This result is explained in terms of molecular geometries in which NH_3 associates with the guanine constituent of Al−guanine specifically. The onset of signal in the Al−guanine photoionization efficiency spectrum is found to shift from 5.6 ± 0.1 to 4.65 ± 0.08 eV upon introduction of NH_3 to the He carrier gas. The shift is indicative of formation of vastly different amounts of distinct isomers of Al−guanine in the presence or absence of NH_3. The geometries, ionization energies, and heats of formation of the isomers have been determined using DFT calculations benchmarked against the experimental ionization energies. The most stable isomer is one of an Al atom complexed to an unusual tautomer of guanine in which, effectively, a proton has been transferred from the six-membered ring to the five-membered ring. To our knowledge, this is the first demonstration of the existence of this tautomer of guanine.

1. Introduction

Studies of metal−DNA base complexes provide valuable thermodynamic and structural information relevant to discussions of metal effects on biological processes involving DNA. For example, the potential of some metals to disrupt DNA replication processes has been related to the ability of metals to stabilize tautomers of the DNA bases incompatible with formation of Watson−Crick[1] DNA base pairs.[2−4] With addition of metal the acidities of H-containing functional groups of the bases are altered, thus changing the energetics of tautomerization.[4] Typically, in these studies, the metal associates with nitrogen and there is an affinity of metal cations for the N7 (see Figure 1) site of guanine, claimed to be the best metal-binding site of the DNA bases.[4,5]

In light of this postulate, most theoretical studies of metal−DNA base interactions have focused on guanine complexes in which metal cations are bound to N7.[6−8] Little is known about the energetics or properties of other isomers of metal−guanine complexes in which the metal is bound to sites other than N7. It is not clear whether an analogous affinity for N7 applies to neutral metals, the focus of our experiments.

Extrapolation of gas-phase results to more biologically relevant solution-phase media requires an understanding of the effect of solvent. The importance of solvent in these systems is reflected by the large difference in the relative stabilities of the various tautomeric forms of metal-free DNA bases in aqueous versus gas-phase environments. In the gas phase, both keto and enol forms of guanine are present in significant amounts.[9] A similar result is found for guanine in solid Ar matrixes.[10,11] Theoretical work predicts that the heat of formation of four of the tautomers (two enol and two keto) are effectively equal.[9,12,13] In the solution phase the keto tautomers are 0.3−0.5 eV more stable than the enol forms.[14] The energy of solvation is 1 eV,[15] which is significantly larger than the energy difference between the different tautomers, suggesting that the relative abundance of the tautomers in solution is determined primarily by intermolecular solvent−base interactions; intramolecular interactions are much less important.

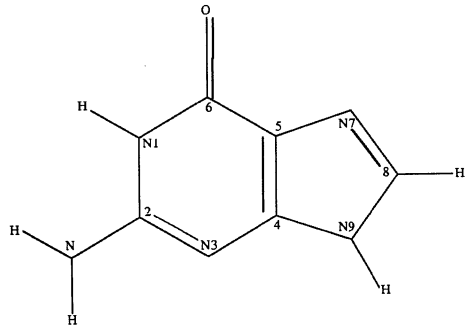

Figure 1. Numbering scheme for guanine.

Interactions of solvent with a metal−DNA base complex can be thought of in terms of two components: (1) direct interactions between the complex and solvent molecules in the first solvation shell; (2) endothermic interactions due to disruption of the H-bonding network of the solvent (solvent−solvent interactions).[16] The impact of the addition of a metal center to guanine on its solvation energy therefore depends on how the metal

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interacts with solvent directly and on how the metal affects the geometric arrangement of solvent molecules about the DNA base, primarily in the first solvation shell. Microsolvation of metal centers is well studied[17] and includes a study of Al−ammonia complexes.[18] This study has established the ionization energies of Al−$(NH_3)_n$ complexes as a function of n and the binding energy of select clusters. Overall, a near-monotonic decreasing trend in the ionization energies is observed with the exception of $n = 1$ or 2. For these clusters the drop in ionization energy manifested by addition of NH_3 is more drastic, amounting to 1 eV per NH_3. The binding energy of Al to NH_3 is found to be less than 0.4 eV. These studies provide thermodynamic values that quantify the Al−NH_3 interaction energy and make possible a comparison of the absolute magnitude of the metal−solvent interaction with that of the metal−DNA base and solvent−solvent interactions so that the relative importance of each in the solvation process can be determined. To our knowledge, analogous data for guanine−NH_3 interactions are not available.

In this paper we present a study of gas-phase Al−guanine complexes and a study of microsolvation of Al−guanine in NH_3. Photoionization efficiency spectra are collected and used to determine ionization energies of the gas-phase Al−guanine−$(NH_3)_n$, $0 \leq n \leq 2$, complexes as well as of Al−*o*-methylguanine (Al adduct of 2-amino-6-methoxypurine). No significant change in the ionization energy is observed to accompany the addition of one or two NH_3 molecules to Al−guanine. This result is interpreted in terms of an Al−NH_3 interaction much weaker than the hydrogen-bonding (H-bonding) interactions between NH_3 and guanine. We find evidence that with a change in the laser-ablation source conditions, two different isomers of Al−guanine are formed. Density functional theory (DFT) studies are used to determine the geometries of each isomer and of their tautomers. There is good agreement between the predicted ionization energies of the two isomers and those measured experimentally. Our most significant result is that the most stable isomer is one in which both of the nitrogen atoms in the five-membered ring of guanine are bound to H. To our knowledge, there is no prior experimental or theoretical observation of such isomers of guanine.

2. Experimental Section

The laser ablation/photoionization mass detection apparatus has been described previously.[19] The only significant difference in the present experiments was the use of pressed powder rods. Al (Fisher Scientific, 20 mesh and finer) and guanine (Aldrich, 98% pure) or *o*-methylguanine (Aldrich, 98% pure) powders were mixed together, in an approximately 70:30 volume ratio, and placed into a 6 mm diameter cylinder into which a 6 mm piston was forced by applying a pressure of 2500 psi (1.7×10^7 Pa). Pressure was maintained for approximately 2 min, after which the pressed rod was removed and placed in the ablation chamber of the apparatus. Ablation of the rod with less than 1 mJ pulse^{-1} of 355 nm laser (Lumonics YM200) light, focused onto an 1 mm^2 spot, synchronous with a He pulse of 20 μs duration (piezoelectric valve with a 50 psi (3×10^5 Pa) backing pressure) passed over the rod, generated Al_n−guanine$_m$ (or Al_n−*o*-methylguanine$_m$) species entrained in He. Source conditions were adjusted to maximize the Al−guanine (or Al_n−*o*-methylguanine$_m$) signal intensity. These species then underwent expansion into the 10^{-6} Torr (10^{-4} Pa) vacuum of the first chamber. In the second chamber the species were ionized using unfocused laser light of varying wavelength. Ionization laser fluences were measured using OPHIR/NOVA and Gentec Duo/ED-500 power meters. Solvation studies were performed by seeding NH_3 (<0.05%) into the He carrier gas.

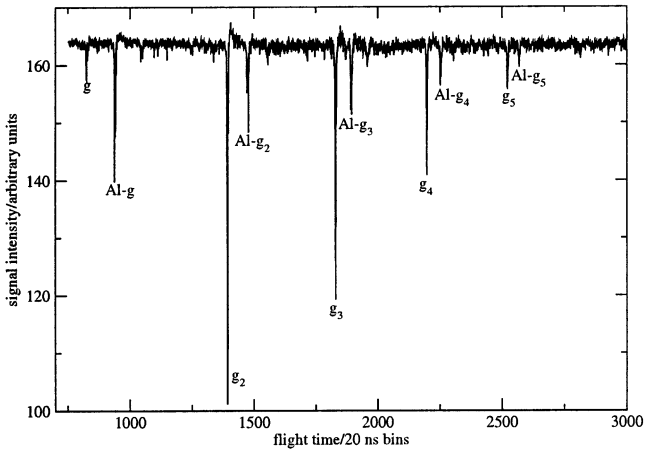

Figure 2. Section of the mass spectrum of laser-ablated Al−guanine. The abscissa corresponds to the flight time of the species in the time-of-flight mass spectrometer. g denotes guanine in the peak labels. Species were ionized with 157 nm (<1 mJ pulse^{-1}) laser light.

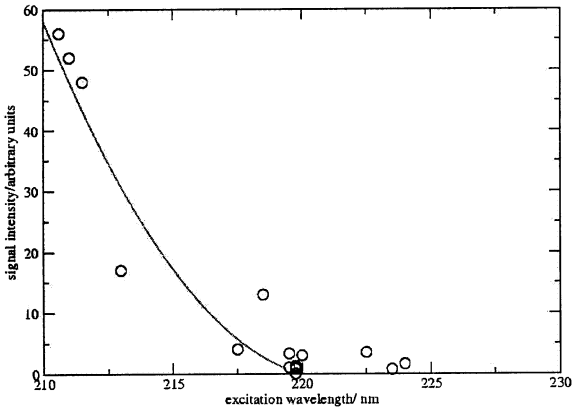

Figure 3. Al−guanine mass spectral signal intensity as a function of excitation wavelength. Data are shown as circles. A quadratic fit of the data is shown as a solid line as a guide to the eye. Ionization laser energies were kept below 200 μJ pulse^{-1}.

3. Results

Ablation of Al−guanine rods in the presence of pulsed He resulted in formation of complexes of the form Al−guanine$_m$ as seen in the section of the mass spectrum shown in Figure 2. Weak features positioned at slightly higher mass of each Al−guanine$_m$ peak correspond to Al_2−guanine$_m$. At higher magnification peaks corresponding to dehydrogenated Al−guanine$_m$ are also observable in the spectrum. The process responsible for dehydrogenation has been discussed in a previous publication.[20] To the left (lower mass) of the section of the mass spectrum shown, weak features corresponding to unidentified fragments of Al−guanine or guanine are present. These features are small in the mass spectrum, indicating that, despite the relatively harsh conditions expected of laser ablation, formation of Al−guanine$_m$ is the dominant process. This observation is consistent with the notion that laser ablation of pressed powder rods constitutes a useful method of introducing metal−biomolecule adducts to the gas phase.[20]

Tuning the ionization laser to longer wavelengths, the mass spectral feature associated with Al−guanine decreased in intensity as seen in Figure 3. By 220 ± 2 nm (5.6 ± 0.1 eV) the signal intensity is negligible. The 5.6 ± 0.1 eV value

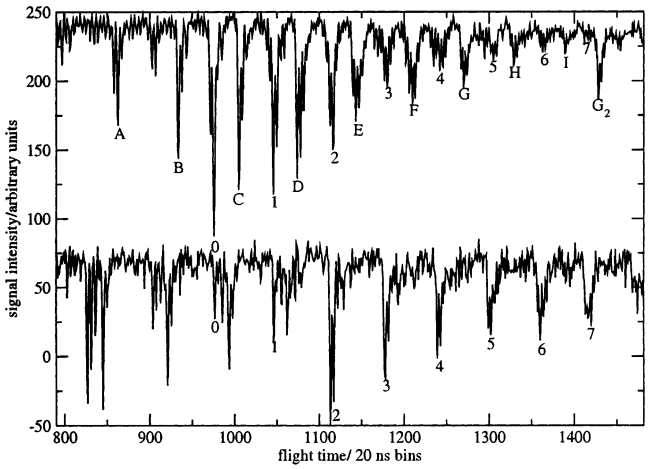

Figure 4. Section of the mass spectrum of species formed via laser ablation of an Al−guanine pressed powder rod with NH_3 seeded in the He carrier gas. The series A, B, C, ..., I corresponds to guanine−$(NH_3)_n$, where A is guanine. The series 0, 1, 2, ..., 7 corresponds to Al−guanine−$(NH_3)_n$, $n \geq 0$. G_2 is the guanine dimer. In the upper spectrum 157 nm laser light of <1 mJ pulse^{-1} was used to ionize these species. In the lower spectrum, 267 nm laser light of 67 μJ pulse^{-1} was used. The spectra are offset vertically for clarity. Other peaks (unlabeled) in the spectrum can be assigned to species of the forms $Al(NH_3)_n$ and $AlH(NH_3)_n$ as have been observed in previous studies.[18,21,22]

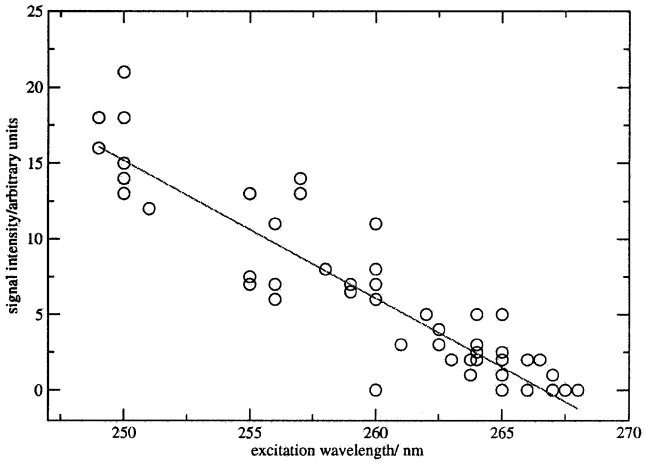

Figure 5. Al−guanine mass spectral signal intensity as a function of excitation wavelength. These data, shown as open circles, were collected with NH_3 (<0.05%) present in the He carrier gas. Ionization laser energies were kept at 70 μJ pulse^{-1} at all wavelengths. The straight line is a linear regression fit of the data, the *x*-intercept of which is taken as the ionization energy of this isomer of Al−guanine (see the text for details).

corresponds to the onset of signal and can be associated with the ionization energy of the complex, as discussed below.

With the introduction of NH_3 (<0.05%) to the He carrier gas, species of the form Al−guanine$_m$−$(NH_3)_n$ and guanine$_m$−$(NH_3)_n$ were formed. A sample mass spectrum is shown in Figure 4. A series of peaks with mass corresponding to Al−guanine−$(NH_3)_n$, with $0 \leq n \leq 10$, was observed. When 267 nm light was used to ionize, the spectrum shown as the lower trace in Figure 4 was collected. At this wavelength, guanine$_m$−$(NH_3)_n$ species were no longer observed but peaks corresponding to the Al−guanine$_m$−$(NH_3)_n$ species were still present. Less than 67 μJ pulse^{-1} of unfocused (cross-sectional area of 0.8 cm^2) 267 nm (4.64 eV) laser light was used to ionize the species observed: conditions under which multiphoton contributions to the observed signal should be negligible. The Al−guanine$_m$−$(NH_3)_n$ species observed are assumed to have ionization energies below 4.64 eV, accordingly, while the guanine$_m$−$(NH_3)_n$ do not. That is, guanine$_m$−$(NH_3)_n$ have ionization energies between 4.64 (267 nm) and 7.9 (157 nm) eV. Comparing with Figure 3, the presence of NH_3 therefore manifests an effective decrease in the ionization energy of Al−guanine to values nearly 1 eV lower than the 5.6 ± 0.1 eV value measured in the absence of NH_3.

Accordingly, in the presence of NH_3 the photoionization efficiency spectrum of Al−guanine is found to change such that the onset of signal occurs at much lower energy. In Figure 5 a near-linear decrease in mass spectral signal intensity of Al−guanine is observed in the 245−267 nm region, wavelengths well above the onset of signal observed in Figure 3. A straight line fit of the data in Figure 5 yields an intercept of 267 ± 5 nm (4.65 ± 0.08 eV). This onset is the lowest energy required to photoionize Al−guanine. Other features associated with higher energy processes resulting in formation of Al−guanine cations, such as ionization of other isomers of Al−guanine with higher ionization energies, were not discernible in the spectrum. However, this observation does not preclude the presence of such processes whose spectral features may be masked by those associated with the lower energy ionization process.

4. Discussion

4.1. The Two Isomers of Al−Guanine. The profound change in the photoionization efficiency spectrum observed upon introduction of NH_3 to the He carrier gas will be shown to be compatible with the formation of very different amounts of distinct isomers of Al−guanine in the presence or absence of NH_3. In the absence of NH_3, the onset of signal in the photoionization efficiency spectrum occurs at 220 ± 2 nm (5.6 ± 0.1 eV), as seen in Figure 3. This value is comparable to the 5.16 ± 0.01 eV ionization energy measured previously for a gas-phase Al−cytosine association complex.[20] The similarity suggests that the onset of signal observed in Figure 3 corresponds to the ionization energy of an Al−guanine association complex. For such complexes ionization energies near 5 eV are expected as, to first order, ionization is thought to manifest removal of an electron from Al, specifically.[20] The ionization energies are therefore near that of an Al atom (5.984 eV),[23] but slightly lower due to stabilization of the charge by interaction with the DNA base.

Using the BP86 functional,[24,25] full geometry optimizations without any symmetry constraints were performed using the Gaussian 98 program suite.[26] Several initial geometries were employed in an effort to locate different local minima. Starting geometries considered included those with Al bound to N7 or N3, with Al inserted into the N1−H bond, and with Al bridging the N3 and N9 positions, as well as various tautomers of each of these isomers. More details of these calculations are in an accompanying paper.[27] The most stable structure, **A**, shown in Figure 6, is predicted to have an ionization energy of 5.65 eV. The difference between this value and the experimental one (5.6 ± 0.1 eV) is within the 0.2−0.4 eV (5−10 kcal mol^{-1}) accuracy expected of such calculations. The good agreement suggests that the DFT structure is that of the Al−guanine species present in the experiment. As seen in Figure 6 the DFT geometry is that of an association complex as expected. The Al is bound to O and N1, suggesting that the Al−guanine bonding primarily involves interaction with the lone pairs. The geometry is very similar to that of the Al−cytosine association complex.[20] As seen in Figure 6, the calculations predict a significant change in the geometries of both isomers upon ionzation. From the DFT,[27] the ground state of the neutral complexes are ap-

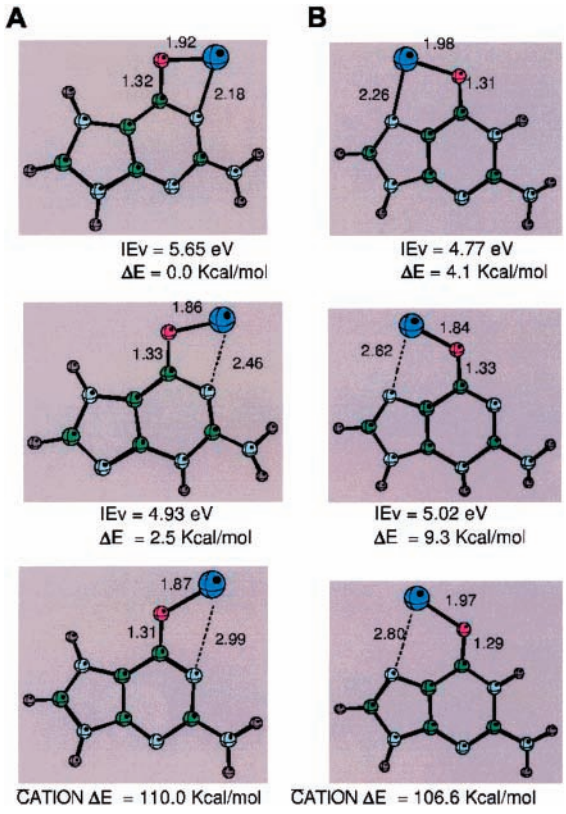

Figure 6. Structures of Al−guanine complexes predicted by DFT. **A** and **B** are the most stable isomers. The vertical ionization energy, IE_v, of each is given as is the heat of formation, ΔE, relative to the most stable structure **A**. Below **A** and **B** are the next most stable tautomers of each. Below these the ground-state geometries of the cationic forms of **A** and **B** are shown. ΔE for the cation equals the adiabatic ionization energy.

proximately guanine anions bound to Al cations. Upon removal of an electron, the complex no longer resembles an ion pair and a significant change in the Al−guanine bonding geometry results.

In the presence of NH_3, the onset of signal in the photoionization efficiency spectrum of Al−guanine occurs at much longer wavelengths. As seen in Figure 5, the onset of signal occurs at 266.7 ± 0.6 nm (4.65 ± 0.08 eV), as defined by the *x*-intercept of the linear fit shown. That is, the energetic requirement for formation of the Al−guanine cation has dropped approximately 1 eV from the 5.6 ± 0.1 eV value observed in the absence of NH_3. There are two plausible reasons for this drop, the first of which involves photoinduced dissociation−ionization of an Al−guanine−NH_3 complex. In this case, bonding interactions with NH_3 significantly distort the geometric and/or electronic structure of the Al−guanine. Loss of NH_3 during the photoexcitation−ionization event results in formation of electronically excited (or geometrically distorted) Al−guanine, the ionization energy of which is significantly lower than that of the ground state (or geometrically relaxed form) of Al−guanine. A prerequisite for this mechanism is that the heat of formation of Al−guanine−NH_3 must be significantly greater than that of Al−guanine + NH_3. That is, the association of NH_3 with Al−guanine must be endothermic. For Al, however, association with NH_3 is an exothermic process.[18] Similarly, NH_3 association with hydroxyquinoline, which has a heterocyclic aromatic ring and OH constituents, similar to those of guanine, is exothermic.[28] Endothermic association of NH_3 with Al−guanine therefore seems unlikely. Preliminary DFT studies find a near-nonbonding interaction between NH_3 and Al−guanine.

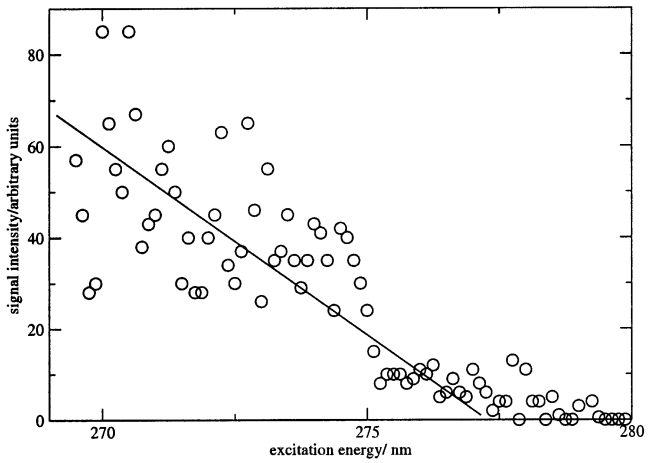

Figure 7. Photoionization efficiency spectrum of Al−*o*-methylguanine. Ionization laser energies were kept at 100 μJ pulse^{-1} at all wavelengths. The straight line is drawn as a guide to the eye. The *x*-intercept of the line is taken as the ionization energy of Al−*o*-methylguanine (see the text for details).

To further test photoinduced dissociation−ionization as a mechanism for formation of the Al−guanine cation, photoionization studies of Al−*o*-methylguanine were undertaken. In Figure 7 the photoionization efficiency spectrum is shown. As seen, the onset of signal in the spectrum occurs at 277.2 ± 0.2 nm (4.47 ± 0.01 eV). This value is comparable to the 4.65 ± 0.08 eV value observed for Al−guanine in the presence of NH_3 (Figure 5). The comparable ionization energies suggest that the two complexes have similar geometric structures and are evidence that 4.6 ± 0.1 eV is enough energy to ionize an Al−guanine-type complex, in the absence of NH_3. This is strong evidence that photoinduced dissociation−ionization is not the mechanism responsible for ionization of Al−guanine.

The second plausible reason that the energetic requirement for formation of the Al−guanine cation has dropped approximately 1 eV when NH_3 is present is that the ammonia facilitates formation of another isomer of Al−guanine which has a lower ionization energy. From DFT studies, the second most stable isomer of Al−guanine, **B**, with geometry shown in Figure 6, has an ionization energy of 4.77 eV. This value is comparable to the 4.65 ± 0.08 eV value where onset of signal is observed in the photoionization efficiency spectrum (Figure 5) for Al−guanine in the presence of NH_3. Accordingly, the 4.65 ± 0.08 eV value is taken to correspond to the ionization energy of the **B** isomer of Al−guanine. In this isomer Al is bound to O and N7 in a bridging arrangement similar to that of **A**. The formation of O−Al−N bridges in both **A** and **B** isomers of Al−guanine as well as in Al−cytosine[20] suggests that this geometry is characteristic of neutral metal−DNA base complexes.

The mechanisms responsible for formation of negligible and abundant amounts of isomer **B** of Al−guanine, in the absence or presence of NH_3, respectively, are not well understood due to the ill-defined conditions of the plasma/supersonic expansion source. There are literature examples of changes in the relative abundances of tautomers present in a molecular beam upon changes in the backing pressure.[29] The introduction of NH_3 may have a similar effect. A second possibility is that NH_3 facilitates formation of isomer **B** by acting as a catalyst. Energetic barriers between tautomers of guanine are predicted to lie in the 1.5−2.4 eV range but may decrease upon solvation.[30] Solvation of 6,8-dithioguanine by water, for example, is predicted to decrease the energetic barrier to tautomerization by 0.9−1.3 eV to a value

of 0.4 eV.[31] Although, in light of the various possible mechanisms, it is feasible that the introduction of NH_3 can manifest significant changes in the relative amounts of **A** and **B**, the mechanism at work in the laser ablation source is effectively unknowable. The occurrence of ionization, excitation, relaxation, recombination, dissociation, reneutralization, and quenching processes in the plasma source and the presence of anions, cations, electronically excited species, radicals, and neutrals in the plasma make it nearly impossible to determine *how* the **A** and **B** isomers are formed. Through interpretation of the photoionization data, however, it is possible to determine *what* species are formed.

The thermodynamics associated with the formation of tautomers of Al−guanine are distinct from those of metal-free guanine. For bare guanine at least three tautomers are present in significant amounts in both molecular beam[9,32] and solid rare-gas matrix[10,11,33] experiments. The heats of formation of the enol−amino and keto−amino tautomers are nearly equivalent, predicted to lie within 0.05 eV of each other.[13,34,35] The addition of Al, however, stabilizes the keto form (no H bound to O) of guanine specifically. In Figure 6, the four lowest energy tautomers of **A** and **B** isomers of Al−guanine are shown, and all are keto forms. Other tautomeric forms are found by DFT to have much greater, more than 10 kcal mol^{-1} (0.4 eV) larger, heats of formation. A similar result was obtained for Al−cytosine.[20] The binding of metal ions to DNA bases is known to affect the relative stabilities of the keto and enol isomers.[3,4] From the Al−guanine and Al−cytosine results it is now clear that neutral metals affect the energetics of tautomer formation as well.

The **A** isomer of Al−guanine is an Al atom complex of a previously unobserved, experimentally or theoretically, isomer of guanine and thus represents a significant discovery. Thermodynamically this species is the most stable form of Al−guanine in the gas phase. The chemical properties of **A** can be expected to differ significantly from those of **B**-type isomers. The much higher ionization energy of **A**, 5.6 ± 0.1 eV versus 4.65 ± 0.08 eV for **B**, is characteristic of a species with a much higher oxidative potential. The isomer is unusual in that both N7 and N9 are protonated, effectively amounting to transfer of a proton from the six-membered to the five-membered ring of guanine. Not a single reference to tautomers of this type could be found in the literature discussing the relative energies of tautomers of guanine or metal−guanine complexes.[3−5,9,13,14,32,35−46] Part of the reason for neglecting these isomers of guanine may be that, in the context of Kekule structures, isomer **A** has a formal charge in the five-membered ring which would render the isomer relatively unstable. In the Al−guanine complex, however, the charge can be resonance stabilized, as aromaticity is preserved. DFT predicts the bond lengths of the ring-constituent atoms in **A** to differ by less than 0.02 Å, consistent with an aromatic compound. A second reason may be associated with the fact that N9 is bound to the ribose sugar in DNA, and the formation of isomers such as **A** from DNA and/or their incorporation into DNA is impossible without cleaving the sugar−base bond. Nonetheless, these isomers may be biologically relevant in other contexts. For example, species such as **A** may be incompatible with the DNA base salvage machinery (hypoxanthine−guanine phosphoribosyltransferase (HGPRT)) responsible for binding sugar and base together.

4.2. Solvation Effects. Typically, solvation in a polar solvent manifests a significant lowering of the ionization energy of a complex. Strong interactions between polar solvents and charge tend to stabilize the ion relative to the neutral. The ionization energies of $Al(NH_3)_n$ complexes, for example, are 5.986, 4.908 ± 0.001, and 3.86 ± 0.13 eV for n equal to 0, 1, and 2, respectively.[18,23] By analogy for Al−guanine, where ionization is known to result in significant (+0.6 from our DFT calculations) charge localized on Al, association of NH_3 with the Al can be expected to manifest a lowering of the ionization energy of Al−guanine−$(NH_3)_n$ relative to that of Al−guanine.

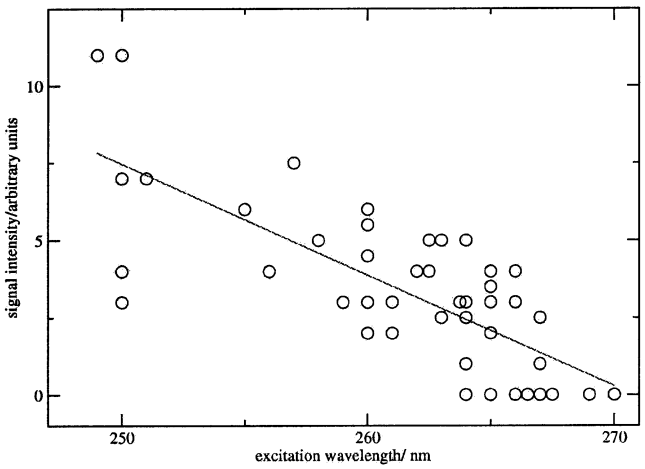

Figure 8. Al−guanine−$(NH_3)_2$ mass spectral signal intensity as a function of excitation wavelength. These data, shown as open circles, were collected with NH_3 (<0.05%) present in the He carrier gas. Ionization laser energies were kept at 70 μJ $pulse^{-1}$ at all wavelengths. The straight line is a linear regression fit of the data, the x-intercept of which is taken as the ionization energy of the Al−guanine−$(NH_3)_2$ complex (see the text for details).

In Figure 8, the photoionization efficiency spectrum of Al−guanine−$(NH_3)_2$ is shown. As described above for Al−guanine, the onset of signal in the spectrum corresponds to the ionization energy of the complex. From the x-intercept of the straight line shown, the ionization energy of the complex is 271 ± 5 nm (4.6 ± 0.1 eV). Via the same approach, data not shown, the ionization energy of Al−guanine−NH_3 is found to be 274 ± 8 nm (4.5 ± 0.2 eV). Within error, the ionization energies of the **B** isomer of Al−guanine (4.65 ± 0.08 eV), Al−guanine−NH_3 (4.5 ± 0.2 eV), and Al−guanine−$(NH_3)_2$ (4.6 ± 0.1 eV) are equivalent.

The noneffect of the addition of one or two NH_3 molecules to Al−guanine, on the ionization energy, indicates that the NH_3 molecules are bound sufficiently distant from Al as to have little interaction with the charge centered on Al in $(Al-guanine-(NH_3)_n)^+$. Accordingly, the molecules must bind to guanine. The presence of $guanine_m-(NH_3)_n$ species in Figure 4 constitutes evidence in support of the formation of guanine-bound ammonia molecules. The affinity of ammonia for guanine likely stems from favorable H-bonding interactions between NH_3 and the carbonyl, N, NH, and NH_2 functional groups of guanine. Analogous H-bonding interactions are found in guanine−$(H_2O)_n$ complexes.[14] H-bonds of this type have strengths on the order of 0.2 eV,[47,48] and the formation of two such bonds between NH_3 and guanine would manifest a total interaction energy of 0.4 eV. Considering that the binding energy of Al−NH_3 is less than 0.4 eV,[18,19] it is very likely that association of NH_3 with the guanine component of Al−guanine is energetically favored over its association with the Al part, consistent with the noneffect of NH_3 on the ionization energy observed.

For Al, covalent and acceptor−donor-type interactions with NH_3 solvent are expected to play a minor role in the solvation of Al−guanine. The Al−NH_3 interaction appears to be relatively weak and less significant than guanine−NH_3 H-bonding interac-

tions. Accordingly, the Al−NH_3 interaction energy likely contributes little to the overall solute−first solvent shell interaction component of the solvation energy. More important are the guanine−solvent H-bonding interactions. In this context the ability of Al to affect functional group acidities[20] and the positioning of the various H atoms, due to changes in the relative energies of the various tautomers, is a more significant effect. These results indicate that this indirect action of the metal has the greatest impact on the solvation energetics. Accordingly, theoretical studies of model metal−base complexes which consider solvation of the metal exclusively, and ignore solvation of the base, may lead to erroneous results.

5. Summary and Conclusions

Through photoionization efficiency measurements and DFT calculations two distinct isomers of Al−guanine have been observed and characterized. In both, Al bridges N and O in geometries analogous to that of Al−cytosine.[20] Al−*o*-methylguanine likely has a similar structure as its ionization energy is found to be comparable to that of the **B** isomer of Al−guanine. Effects of the addition of Al to guanine include a significant decrease in ionization energy and a significant stabilization of keto forms of guanine. Study of microsolvation of Al−guanine reveals a noneffect of addition of one or two NH_3 molecules on the ionization energy. The likely explanation is that association of NH_3 with guanine is energetically favored over association with Al. The most significant finding is that the most stable isomer of Al−guanine is an Al adduct of an unusual tautomer of guanine in which three hydrogens are present on the five-membered ring. To our knowledge this is the first observation of this tautomer of guanine.

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