Acetamidine−X^+ and Guanidine−X^+ (X = Li, Na, Mg, Al) Complexes in the Gas-Phase. A Theoretical Study

Emmanuelle Leon,[†] Badia Amekraz,[†] Jeanine Tortajada,*[,†] Jean-Pierre Morizur,[†] Ana I. González,[‡] Otilia Mó,[‡] and Manuel Yáñez*[,‡]

Laboratoire de Chimie Organique Structural, Université Pierre et Marie Curie, Boite 45, CNRS URA 506, 4 Place Jussieu, 75252 Paris Cedex 05, France, and Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

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The structures, harmonic vibrational frequencies, amino rotational barriers and binding energies of complexes formed by Li^+, Na^+, Mg^+, and Al^+ association to guanidine and acetamidine have been investigated by means of the B3LYP density functional approach. Both neutrals are predicted to be stronger bases than ammonia when the reference acids are the aforementioned metal cations. The basicity enhancement with respect to Mg^+ and Al^+ is only slightly smaller than that reported before when the reference acid is H^+. Metal cation association leads to a significant increase in the corresponding amino rotational barriers and to sizeable shiftings of different vibrational modes, in particular those associated with the amino groups. For Li^+ and Na^+ complexes, the ion−neutral interactions are essentially electrostatic, while the bonds involving Al^+ have a significant covalent character. For this reason the Al^+ complexes closely resemble the corresponding protonated species. Mg^+ represents an intermediate situation between alkali cations and Al^+. The empty 3p orbitals of the metal cation play an important role in this respect.

Introduction

In the last few years we have focused our attention to the study of the intrinsic reactivity of bidentate bases.[1−7] A particular interesting subset of molecules which have two distinct basic sites are the imidines.[1−3,8−10] The experimental gas-phase basicities of two members of this family of compounds, namely guanidine (**1**) and acetamidine (**2**), have been reported for the first time very recently. Although guanidine (**1**) is one of the strong organic bases in solution,[11,12] its gas-phase basicity is only moderately high (233 kcal/mol),[1] since it is less than 30 kcal/mol higher than that of ammonia. This is somehow an unexpected result if one considers that guanidinium ion is a typical Y-conjugated system. Also significantly, guanidine (**1**) was found to be only 2.4 kcal/mol more basic than acetamidine (**2**), where one of the amino groups has been substituted by a methyl group. This behavior seems to reflect that resonance stabilization in guanidinium ion is significantly hindered by the torsion of the three amino groups. This seems to be also consistent with the fact that the guanidinium ion has an amino rotational barrier significantly lower than formamidinium and acetamidinium ions.

The aim of this paper is to investigate the behavior of both bases, guanidine (**1**) and acetamidine (**2**), when the reference acid is a metal monocation, where the acid−base interactions are essentially electrostatic rather than covalent as in the protonation processes. We will also study the influence of the metal monocation on the corresponding amino rotational barriers for both systems. This point may be of some relevance, since while the protonated species of acetamidine and guanidine are stabilized by resonance, the complexes with the aforementioned metal cations should not be significantly stabilized by resonance. We have considered it also of interest to investigate the frequency shiftings undergone by both neutrals upon association with the aforementioned cations, because this information may guide future experimental studies.

Recently we have studied[14] the performance of different density functional theory (DFT) approaches to describe complexes involving metal monocations, with G2(MP2) high-level ab initio calculations taken as a suitable reference. In that paper it was concluded that hybrid functionals, namely B3LYP, B3P86, and B3PW91, yield optimized geometries close to the MP2-optimized ones, while the B3LYP method yields the best agreement with QCISD-optimized structures. It was also found that these DFT approaches, when a G2-type 6-311+G(3df,2p) basis set is used, provide binding energies,[14] as well as proton affinities,[1,2,13] in fairly good agreement with those obtained at the G2(MP2) level.

Computational Details

The Li^+, Na^+, Mg^+, and Al^+ binding energies of guanidine (**1**) and acetamidine (**2**) as well as the amino rotational barriers of the corresponding complexes were obtained using DFT methods, which, as mentioned above, seem to be a good alternative to ab initio treatments. On the basis of the results reported in ref 14 for similar complexes, we have chosen the B3LYP method as a reliable tool to describe the aforementioned acetamidine and guanidine complexes. The B3LYP approach corresponds to Becke's three-parameter functional,[15] where the three parameters which give the contributions of Slater, Hartree−Fock, and Becke functionals were determined by fitting the atomization energies, ionization potentials, and proton affinities of a series of molecules from the G1 set. The correlation functional corresponds to the gradient-corrected functional of Lee, Yang, and Parr.[16]

The geometries of the neutrals and their metal monocation complexes will be optimized using a 6-31G* basis set. The corresponding harmonic vibrational frequencies as well as the zero point energies (ZPE) will be obtained at the same level. The final energies will be evaluated at the B3LYP/6-311+G(3df,2p) level using the B3LYP/6-31G*-optimized geometries.

[†] Université Pierre et Marie Curie.
[‡] Universidad Autónoma de Madrid.
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TABLE 1: Total Energies (*E* in Hartrees) and Thermal Corrections to the Enthalpy[a]

system	*E* [B3LYP/ 6-31G*]	thermal correction	*E* [B3LYP/ 6-311+G(3df,2p)]
1	−205.362 58	0.081 76	−205.460 52
2(*E*)	−189.320 58	0.092 62	−189.404 16
2(*Z*)	−189.319 28	0.092 35	−189.402 38
3	−189.299 84	0.092 69	−189.389 48
1ALi	−212.744 19	0.085 39	−212.835 37
1ANa	−367.513 68	0.084 80	−367.611 72
1AMg	−405.261 09	0.085 04	−405.364 96
1AAl	−447.612 64	0.085 02	−447.720 77
1CLi	−212.748 46	0.085 66	−212.835 67
1CNa	−367.516 65	0.085 08	−367.611 15
1CMg	−405.260 22	0.085 30	−405.360 89
1DLi	−212.722 00	0.085 67	−212.807 72
1DNa	−367.496 44	0.085 25	−367.589 95
1DMg	−405.229 41	0.085 16	−405.328 24
1DAl	−447.572 40	0.085 13	−447.675 51
2ALi	−196.698 69	0.096 67	−196.776 15
2ANa	−351.470 43	0.096 07	−351.553 96
2AMg	−389.214 32	0.096 40	−389.303 99
2AAl	−431.563 92	0.093 46	−431.658 11
2BLi	−196.701 00	0.096 58	−196.777 90
2BNa	−351.472 11	0.095 94	−351.555 06
2BMg	−389.219 28	0.092 35	−389.306 20
2BAl	−431.566 07	0.096 25	−431.660 22
2CLi	−196.696 52	0.096 64	−196.769 75
2CNa	−351.467 36	0.096 17	−351.547 88
2CMg	−389.206 29	0.096 13	−389.293 17
3DLi	−196.674 45	0.097 13	−196.750 76
3DNa	−351.445 19	0.096 55	−351.529 14
3DMg	−389.183 70	0.096 70	−389.273 07
3DAl	−431.525 85	0.096 56	−431.619 51
3ELi	−196.662 15	0.095 67	−196.743 19
3ENa	−351.436 56	0.095 27	−351.525 42
3EMg	−389.185 10	0.095 78	−389.278 91
3EAl	−431.532 70	0.095 90	−431.630 52
NH_3	−56.547 95	0.038 37	−56.586 72
NH_3−Li$^+$	−63.903 55	0.043 09	−63.936 22
NH_3−Na$^+$	−218.673 52	0.042 53	−218.719 59
NH_3−Mg$^+$	−256.406 03	0.042 65	−256.459 14
NH_3−Al$^+$	−298.761 36	0.042 42	−298.807 25

[a] Thermal corrections were obtained at the B3LYP/6-31G* level.

For some specific cases, which will be discussed later, these results are compared with those obtained in the framework of the G2(MP2) theory.[17] For Mg^+ complexes, which are open shell species, these calculations have been carried out using unrestricted formalisms. In this respect it must be mentioned that, according to the expectation values of S^2, in no case was the spin contamination significant.

The calculated binding energies were defined as the negative of the enthalpy for the reactions:

$$\text{Base} + X^+ \rightarrow \text{Complex} \qquad (1)$$

For this purpose the thermal corrections for a temperature of 298.2 K given in Table 1 were used. In reaction 1 the base is in its most stable conformation. As was already found for similar complexes,[14] basis set superposition errors (BSSE) are rather small when extended basis sets of the 6-311+G(3df,2p) quality are used. This was also the case for the complexes included in this study. The calculated BSSE corrections to the binding energies were always smaller than 0.6 kcal/mol. Furthermore, they were about the same for the different complexes, and they were not included in our calculated binding energies.

All these calculations have been carried out using the Gaussian-94 series of programs.[18]

The bonding characteristics of the systems included in this study will be discussed in terms of the topological characteristics of their electron charge densities by means of the atoms in molecules theory of Bader and co-workers.[19−21] In particular we will locate the bond critical points (bcps) associated with the linkages which involve the metal cation. The bcps correspond to critical points of the charge density, ρ, where ρ has two negative curvatures and a positive one, i.e., where the charge density is minimum along the bond path and maximum in the other two directions. The values of ρ and its Laplacian, $\nabla^2\rho$, at these points provide useful information on the characteristics of the corresponding bonds. These topological analyses were performed using the PROAIM series of programs.[22]

For the particular case of acetamidine (**2**), both the *E* and the *Z* isomers as well as its isomer 1,1-diaminoethylene (**3**) were considered. For the sake of consistency, and to have a suitable reference to discuss the intrinsic basicities of these compounds with respect to the metal monocations under consideration, we have also studied, at the same level, the corresponding complexes with ammonia.

The different kind of complexes which were found to be local minima of the corresponding potential energy surfaces are schematized in Figure 1. Complexes **A** and **B** correspond to the association to the imino nitrogen atom. It must be noticed that for the particular case of guanidine (**1**) both complexes are identical. Complexes **C** correspond to chelated structures where the metal cation interacts simultaneously with both the amino and the imino nitrogen atoms. For acetamidine, complexes **C** can only arise from the most stable *E* isomer. Complexes **D**, where the metal cation bridges between both amino groups are only possible for guanidine (**1**) and 1,1-diaminoethylene (**3**). For the latter, we have also considered the association to the methylene carbon atom which would yield **E**-type complexes. In order to make our discussion more systematic, the following nomenclature for the complexes included in this study will be adopted hereafter. After the number which identifies the neutral we have first added **A**, **B**, **C**, ... to indicate the kind of complex considered. This is followed by the chemical symbol of the corresponding metal monocation. Hence, **1AMg** will designate the complex where Mg^+ is attached to the imino nitrogen of guanidine (**1**). Similarly, **2CLi** will correspond to a chelated species where Li^+ bridges between the amino and the imino nitrogens of acetamidine (**2**).

Results and Discussion

Structures and Relative Stabilities. The optimized geometries of the different neutrals and their complexes are given as Supporting Information. The total energies are presented in Table 1. We shall discuss here only the most significant structural features. As it was reported previously in the literature, guanidine (**1**)[1,23] and acetamidine (**2**)[2] are predicted to have strongly pyramidal NH_2 groups. For the latter, the *E* isomer, in which the imino hydrogen is *trans* with respect to the amino group, is predicted to be only 0.7 kcal/mol more stable than the *cis* isomer, in good agreement with previous estimations obtained at the G2 level.[2] As shown by Gobbi and Frenking,[23] 1,1-diaminoethylene (**3**) has a C_s symmetry, while the C_{2v} planar structure is a saddle point of third order. This species is predicted to be 9.6 kcal/mol less stable than acetamidine (**2E**), again in fairly good agreement with G2 estimations.[2]

In all cases the ion−neutral interactions are essentially electrostatic. As illustrated in Table 2, the different linkages between the basic center of the neutrals and the metal cations are characterized by rather small charge densities and by positive values of the Laplacian at the bond critical points, which is typical of ionic bonds.

For the particular case of acetamidine (**2**) it was found that association with the less stable *Z* isomer is always more

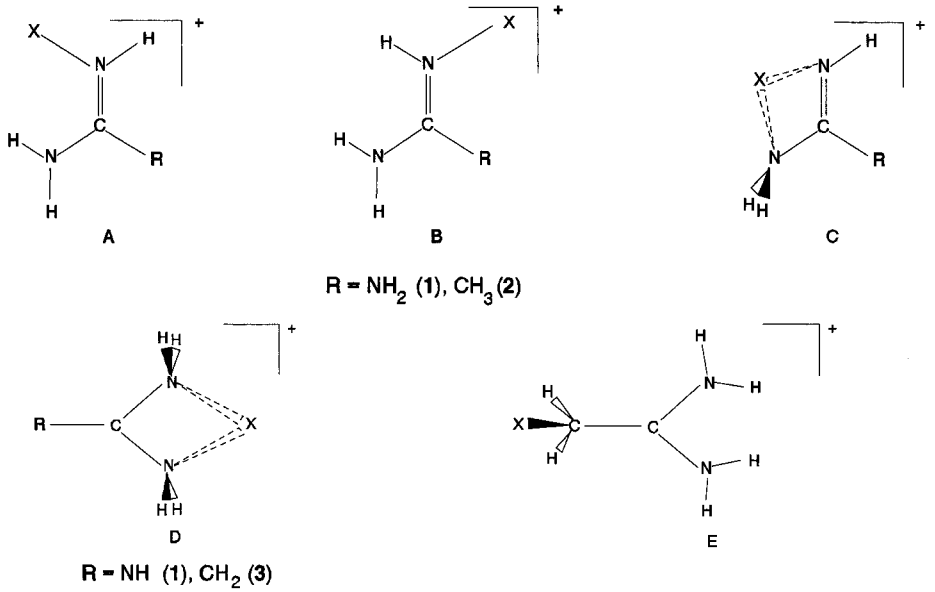

Figure 1. Schematic structures of the different complexes which can be formed by metal cation association with guanidine **1**, acetamidine **2**, and 1,1-diaminoethylene **3**.

TABLE 2: Bonding Characteristics of the N−X (X = Li, Na, Mg, Al) Linkages of the Guanidine−X^+ and Acetamidine−X^+ Complexes[a]

system	ρ	$\nabla^2\rho$
1ALi	0.040	0.279
1ANa	0.030	0.193
1AMg	0.045	0.298
1AAl	0.060	0.297
2ALi	0.038	0.267
2ANa	0.029	0.184
2AMg	0.043	0.283
2AAl	0.058	0.265
2BLi	0.039	0.272
2BNa	0.031	0.193
2BMg	0.044	0.286
2BAl	0.058	0.267
1CLi	0.033 (0.023)	0.234 (0.141)
1CNa	0.027 (0.016)	0.168 (0.082)
1CMg	0.039 (0.021)	0.244 (0.100)
2CLi	0.030 (0.023)	0.205 (0.145)
2CNa	0.025 (0.015)	0.153 (0.076)
2CMg	0.034 (0.023)	0.203 (0.100)
1DLi	0.025 (0.023)	0.158 (0.137)
1DNa	0.020 (0.015)	0.112 (0.078)
1DMg	0.028 (0.024)	0.138 (0.107)
1DAl	0.036 (0.028)	0.048 (0.021)
3DLi	0.027	0.167
3DNa	0.020	0.112
3DMg	0.039	0.163
3DAl	0.035	0.052
3ELi	0.032	0.160
3ENa	0.025	0.120
3EMg	0.029 (0.029)	0.144 (0.143)
3EAl	0.055	0.120

[a] When two nonequivalent N−X bonds exist, the values of ρ and $\nabla^2\rho$ for the second one are given within parentheses.

favorable than the association with the most stable *E* isomer. This can be explained if one takes into account that the *Z* isomer of acetamidine has a dipole moment about 0.6 D greater than that of the *E* isomer. Since, as mentioned above, the neutral−cation interactions in these complexes are essentially electrostatic and therefore dominated by the ion−dipole terms, a stronger ion−neutral stabilizing interaction should be expected with the former. In all cases association to the imino nitrogen of acetamidine (**2**) involves a flattening of the amino group which becomes almost strictly planar in **2A** complexes. In the **2B** global minima the methyl group, which in the neutral has one hydrogen atom lying in the plane defined by the heavy atoms, rotates to avoid the repulsion with the positive charge associated with the metal.

For guanidine these trends are similar although there are some specific differences. The formation of **1A** complexes implies a torsion of both amino groups. It is interesting to note that a similar torsion of the amino groups is found upon protonation. As shown before in the literature,[23] the guanidinium ion ($C(NH_2)_3^+$) is not a D_{3h} planar cation, since the three amino groups rotate about 15° and the corresponding equilibrium conformation has D_3 symmetry. Upon metal cation association, a similar effect appears. The amino group *trans* to the metal cation becomes almost planar and undergoes a torsion of about 10−12° with respect to the plane defined by the heavy atoms of the system. Neither the amino group which is *cis* to the metal cation nor the NHX group is strictly planar, due to the repulsive interaction between one of the hydrogen atoms of the former and the metal. Both groups also exhibit a noticeable torsion.

In the **1C** and **2C** species, the metal cation which bridges between the imino and the amino nitrogens is not located in a symmetric position, the distance to the imino nitrogen being always shorter than the distance to the amino one. This finding is consistent with the topology of ρ which shows (see Table 2) that the bonding charge density is always greater at the imino−X bond than that at the amino−X linkage. This difference is more pronounced for Mg^+ than for Li^+ or Na^+ complexes. For Al^+ these chelated species are not stationary points of the potential energy surface as they collapse, without activation barrier, to yield the imino-attached species **1AAl** and **2AAl**, respectively.

The fact that neither **1CAl** nor **2CAl** is stable reflects that, as it has been shown for other bases,[3,24−28] the interactions with Al^+ although essentially electrostatic have a non-negligible covalent character. Although Al^+ is a closed shell system as are Li^+ and Na^+, it has empty low-lying 3p orbitals which are accessible for a charge transfer from the base lone pair. Accordingly, to favor this charge-transfer process Al^+ locates preferentially in the direction of the imino lone pair, which explains that only **1AAl** and **2AAl** species are stable.

In complexes **1D** and **3D**, the four-membered ring formed upon cation association is significantly puckered, the X−C−R

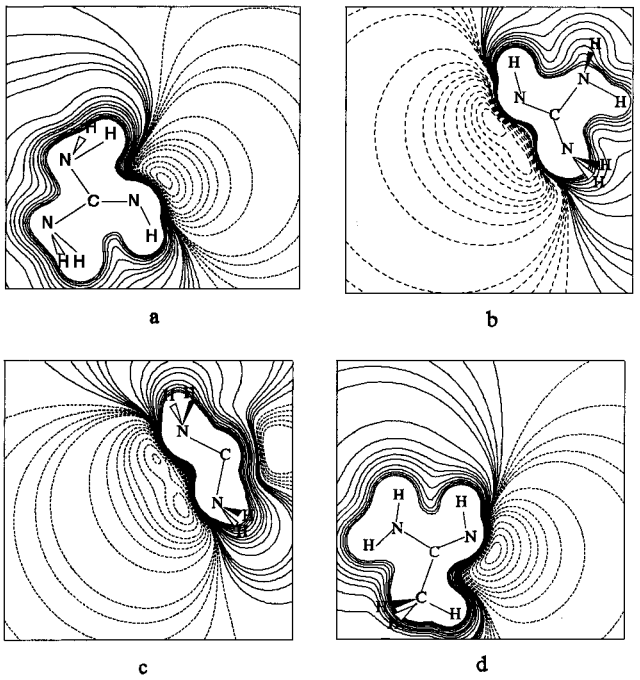

Figure 2. Molecular electrostatic potential map for (a) guanidine in its most stable conformation ($V_m = -75.0$), (b) guanidine when one of the amino groups becomes pyramidal ($V_m = -83.4$), (c) guanidine when both amino groups become pyramidal ($V_m = -66.5$), and (d) acetamidine in its *Z* conformation ($V_m = -76.1$). V_m stands for the value of the potential (in kcal/mol) at each local minimum. Positive and negative values of the potential are denoted by full and dashed lines, respectively. Contour values, in kcal/mol, are as follows: ±1, ±2, ±3, ±4, ±5, ±10, ±15, ±20, ±25, ±30, ±40, ±50, ...

angle being 130−140.° In complexes **3E** the two amino groups become strictly planar, while the methylene group becomes strongly pyramidalized. Actually, the H−C−H and the H−C−X bond angles of the CH_2X group in the complex are about 110 and 103,° respectively.

The relative stabilities of these species deserve a closer analysis. It is worth noting that at the B3LYP/6-31G* level the chelated species **1CLi** and **1CNa** are predicted to be more stable than the imino-attached species **1ALi** and **1ANa**. This situation changes however when the basis set is enlarged, and at the B3LYP/6-311+G(3df,2p) level species **1CLi** and **1ALi** become degenerate, while the **1ANa** complex is predicted to be 0.6 kcal/mol more stable than the **1CNa** one. Taking into account the nature of the interactions in these complexes, the analysis of their relative stabilities can be done in terms of the corresponding molecular electrostatic potential (MEP) maps, which are presented in Figure 2 for the particular case of guanidine. Figure 2a corresponds to the MEP of guanidine in its equilibrium conformation, while Figure 2b,c contains the MEP maps corresponding to the conformations where one or both amino groups are pyramidalized to yield **1C** and **1D** complexes, respectively. The first conspicuous fact is that the pyramidalization of one of the amino groups implies a reinforcement of the attractive potential, since there is an overlap between the attractive basins associated with both the imino and the amino lone pairs. Furthermore, polarization contributions also enhance the stability of complexes **1C**, since the metal cation can simultaneously polarize both lone pairs. According to these arguments the interaction energies in complexes **1C** should be greater than those in complexes **1A**. This is indeed the case for Li^+ and Na^+. According to our calculations the interaction between guanidine in its equilibrium conformation and the metal cation is about 15 kcal/mol smaller than the interaction when the amino group is pyramidalized. However, as we have mentioned above, complexes **1C** are slightly less stable than complexes **1A**. This can be explained by the high energetic cost (15.7 kcal/mol) involved in the pyramidalization of the amino group, which is almost equal to the aforementioned stabilization effect.

TABLE 3: Rotational Barriers (kcal/mol) for the Most Stable Complexes of Guanidine (1) and Acetamidine (2) with Li^+, Na^+, Mg^+, and Al^+[a]

system	rotational barrier	system	rotational barrier
1ALi	10.0	**2BLi**	16.5
1ANa	9.0	**2BNa**	14.8
1AMg	11.2	**2BMg**	18.1
1AAl	12.7	**2BAl**	20.2

[a] Values obtained at the B3LYP/6-311+G(3df,2p) level.

As mentioned before, neither complexes **1CAl** nor **2CAl** are stable since the interaction of Al^+ with the imino lone-pair is significantly favored. Mg^+ constitutes an intermediate case between Li^+ (or Na^+) and Al^+. For this metal monocation the covalent interactions are already sizeable, but smaller than those for Al^+. Consequently, both the **1CMg** and **2CMg** species are local minima of the potential energy surface, but 2.7 and 10.6 kcal/mol, respectively, less stable than **1AMg** and **2BMg**, where the metal cation interacts specifically with the imino lone pair (see Table 1).

The low stability of complexes **1D** can be also explained in terms of the corresponding MEP maps. A comparison of parts a and c of Figure 2 clearly indicates that the attractive potential around the two amino nitrogens is much shallower than that associated with the imino nitrogen. Furthermore, the pyramidalization of both amino groups to yield **1D**-type complexes also has a non-negligible energetic cost, which at the B3LYP/6-31G* level is estimated to be 11.0 kcal/mol. The lower stabilities of the N−X linkages in complexes **1D** as compared to those of complexes **1C** are also reflected in lower charge densities at the corresponding bond critical points. It should also be noticed that, as shown by the values in Table 2, the two N−X bonds are not strictly equivalent. The one which exhibits a greater charge density is always that which is in position *trans* with respect to the N−H group. Accordingly, this bond is also systematically shorter than the other one.

It is worth noting that, as far as 1,1-diaminoethylene is concerned, the chelated **3DLi** and **3DNa** complexes are found to be 3.8 and 1.5 kcal/mol, respectively, more stable than the carbon-attached complexes **3ELi** and **3ENa**. In contrast, for the Mg^+ and Al^+ the opposite situation is found. In this respect it should be mentioned that, for the particular case of the Mg^+ complexes, a G2(MP2) treatment predicts[14] both species to be nearly degenerate. To check whether a similar disagreement between the high-level ab initio calculation and the DFT results appears for the Al^+-containing species, we have studied complexes **3DAl** and **3EAl** using the G2(MP2) theory. These calculations show, contrarily to what was found for Mg^+ complexes, that the carbon-attached species **3EAl** is 2.4 kcal/mol more stable than the cyclic **3DAl** complex. This result seems to confirm the preference of Al^+ to yield interactions with sizeable covalent character. This is consistent with the strong distortion of the methylene group found in **3EAl** complexes.

Rotational Barriers. The amino rotational barriers for the global minima (complexes **1A** and **2B**) are summarized in Table 3. It can be observed that these rotational barriers are significantly higher than those previously reported[29] for the corresponding neutrals. At similar levels of accuracy the amino rotational barrier of acetamidine is 9.5 kcal/mol, while that of

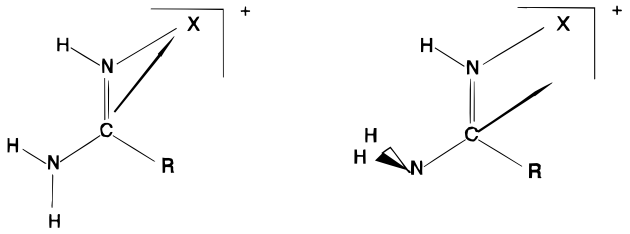

Figure 3. Schematic representation of the change in the direction of the dipole moment of the acetamidine and guanidine complexes when the amino group rotates.

guanidine is only 5.2 kcal/mol. An increase in the rotational barriers for both compounds is also observed upon protonation. Protonated acetamidine was predicted to have a rotational barrier of about 21 kcal/mol, while that of guanidinium ion is about 13 kcal/mol.[29] However, the origin of this increase is not exactly the same. Protonation enhances the resonance stabilization of the system, and accordingly, the energy required to rotate one of the amino groups of the corresponding molecular ion is greater than that needed to rotate the amino group of the neutral. Since in the complexes with metal monocations the interaction is essentially electrostatic, no significant changes in the electronic resonance of the system should be expected. In these cases the unexpected increase in the rotational barrier is due to a change in the direction of the dipole moment. In the global minimum the metal cation lies approximately in the direction of the dipole moment, to enhance the ion−dipole interactions. Upon rotation of the amino group there is a significant change in the dipole moment orientation, so that in the new conformation the amine dipole moment is no longer aimed in the direction of the metal cation (see Figure 3) and, accordingly, a significant decrease in the ion−dipole interaction and, as a consequence, in the stability of the system takes place. This effect can be roughly estimated if one takes into account that ion−dipole interaction energies are given by $E = -\mu q \cos \theta / r^2$ and assuming that only the value of θ changes. For instance, for **1ALi** complexes, the value of θ changes from 12° in the global minimum to 26° in the transition state. This implies a decrease in the ion−dipole interaction of about 3.9 kcal/mol which is rather similar to the calculated increase in the rotational barrier (4.8 kcal/mol) upon Li^+ association.

It is also interesting to note that the calculated rotational barriers increase in the sequence: $Al^+ > Mg^+ > Li^+ > Na^+$ for both acetamidine and guanidine complexes. This is also the sequence followed by the charge densities at the corresponding bond critical points (see Table 2), which indicates that the rotational barriers become higher in response to larger perturbations of the neutral system caused by the metal cation. In this respect it should be emphasized that for Al^+ complexes, where the covalent character of the bonding between the neutral and the metal is higher, the rotational barriers are only slightly smaller than those predicted for the corresponding protonated species.

Harmonic Vibrational Frequencies. The harmonic vibrational frequencies of the most stable **1A** and **2B** complexes are compared with those of the corresponding neutrals, guanidine (**1**) and acetamidine (**2**), in Tables 1 and 2 of the Supporting Information, respectively. For both families of complexes, significant frequency shiftings are predicted by our calculations. For instance, in all cases metal cation association induces a blue shifting of the NH_2 stretching frequencies, while the C−NH stretch is red-shifted. The influence on the NH_2 twisting and wagging modes is also quite important. The former appears shifted to much higher frequencies while the latter appears displaced to lower values. The consequence is that, while for the neutrals the wagging should be observed at higher frequencies than the twisting, in the metal complexes it is the other way around. Quite interestingly, in guanidine complexes the N−H stretch is also blue-shifted, while in acetamidine complexes it appears at lower frequencies than in the neutral. In acetamidine complexes both the C−H and the C−C stretching displacements are blue-shifted.

As expected the additional vibrational modes involving the metal cation are of low frequency. In all cases the N−X stretch should be observed in the 300−400 cm^{-1} region.

TABLE 4: Binding Energies (BE, kcal/mol) for the Different Complexes Included in This Study[a]

complex	BE	complex	BE
1ALi	55.6	**1DLi**	38.1
1ANa	39.5	**1DNa**	25.5
1AMg	59.1	**1DMg**	36.0
1AAl	59.0	**1DAl**	30.5
2ALi	53.6	**3DLi**	46.6
2ANa	38.3	**3DNa**	31.7
2AMg	58.51	**3DMg**	45.6
2AAl	56.5	**3DAl**	39.6
2BLi	54.7	**3ELi**	42.8
2BNa	39.1	**3ENa**	30.2
2BMg	59.9	**3EMg**	49.8
2BAl	56.1	**3EAl**	44.3
1CLi	55.6	NH_3−Li^+	39.0
1CNa	38.9	NH_3−Na^+	27.3
1CMg	56.4	NH_3−Mg^+	38.4
2CLi	49.6	NH_3−Al^+	33.5
2CNa	34.4		
2CMg	49.3		

[a] Values obtained at the B3LYP/6-311+G(3df,2p) level.

Binding Energies. The binding energies have been summarized in Table 4. This table also includes the corresponding binding energies for ammonia. Unfortunately there are no experimental values to compare with for acetamidine and guanidine. For ammonia we are only aware of the experimental value of the NH_3Na^+ complex,[30] which is quite close to our estimated value. For the remaining ammonia complexes, our estimated binding energies are also in very good agreement with the previously reported high-level ab initio values.[31,32]

The first important finding is that both guanidine and acetamidine are stronger bases than ammonia, also when the reference acid is not a proton. Table 4 shows, for instance, that Li^+, Na^+, Mg^+, and Al^+ binding energies to guanidine are 16.6, 12.2, 20.7, and 25.5 kcal/mol higher than the corresponding binding energies to ammonia. It should be recalled that guanidine was predicted[1] to have a proton affinity 29 kcal/mol greater than that of ammonia. Hence, as it should be expected from the essentially electrostatic nature of the interactions involving Li^+ and Na^+ complexes, the basicity enhancement for these two reference acids is smaller than that found for the proton, but still significant. Due to the much higher covalent character of the linkages involving Al^+, the basicity enhancement for these two metal cations is only about 4 kcal/mol smaller than that measured when the reference acid is the proton. Again Mg^+ is an intermediate case between alkali cations and Al^+.

Also interesting is the comparison between guanidine and acetamidine. The former was found[1] to be almost 3 kcal/mol more basic than the latter[2] in protonation processes. A similar difference is predicted when the reference acid is Al^+ and only slightly smaller when the reference acid is Mg^+. The differences between the intrinsic basicities become smaller than 1 kcal/mol for Li^+ and Na^+ complexes, but still guanidine is predicted to be more basic than acetamidine, even though the MEP map of acetamidine is slightly deeper than that of guanidine. This is consistent with the fact that the dipole moment of acetamidine

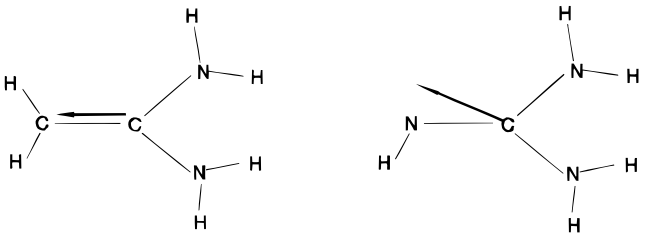

Figure 4. Schematic representation to show the different orientation of the dipole moment of 1,1-diaminoethylene with respect to guanidine.

is slightly greater than that of guanidine. Hence, in terms of electrostatic arguments one should expect acetamidine to be slightly more basic than guanidine with respect to Li^+ and Na^+. The fact that acetamidine$-Li^+$ and acetamidine$-Na^+$ binding energies are about 1 kcal/mol smaller than those of guanidine is related to the fact that in acetamidine, as we have mentioned above, the cation association involves the less stable isomer of the neutral, which is about 1 kcal/mol less stable than the global minimum.

It is also worth noting that the formation of **1D** complexes is significantly less exothermic than the formation of **3D** complexes. This implies that when R = NH the basicity of the system is significantly lower than when $R = CH_2$. Two factors may be responsible for this difference. In the first place, it must be taken into account that the NH_2 groups of 1,1-diaminoethylene should be more basic than those of guanidine, since in the latter the methylene group is replaced by a $-NH$ group which results in a poorer electron donor ability of the amino groups. This is clearly reflected in the fact that for **1D** complexes the lower binding energy corresponds to Al^+, where the electron donation component should dominate. On the other hand, the dipole moment of 1,1-diaminoethylene lies in the symmetry plane which bisects the NCN bond angle, while when the methylene group is replaced by a NH group, the direction of the dipole moment changes significantly (see Figure 4). Since in both **1D** and **3D** complexes the metal cation is practically in that plane, the ion$-$dipole interaction must be significantly greater in the latter.

Conclusions

Similar to what has been found in protonation processes,[1,2] both guanidine and acetamidine are predicted to have metal cation binding energies greater than ammonia. The basicity enhancement is particularly large for Al^+ and Mg^+ because the ion$-$molecule interaction has non-negligible covalent character, which arises from the charge transfer from the lone pairs of the base to the empty 3p orbitals of the metal. Very likely, the higher covalent character of the linkages involving Al^+ is responsible for the fact that for this metal cation the formation of the carbon-attached species to 1,1-diaminoethylene **3EAl** is preferred to the formation of **3DAl**, where the electrostatic interactions should be maximum. As it has been shown before in the literature, the charge transfer from the base lone pair to the empty 3p orbitals of Al^+ is the most important contributor to the covalent character of the bonds involving this metal cation. This seems to explain also why the chelated species **1CAl** and **2CAl** are not stationary points of the corresponding potential energy surfaces as they collapse, without activation barrier, to yield species **1AAl** and **2AAl**, where the metal cation locates in the direction of the imino nitrogen lone pair.

The stabilizing interactions when the reference acid is Li^+ or Na^+ are essentially electrostatic, and the basicity enhancement of guanidine and acetamidine with respect to ammonia is much smaller. For the same reason the chelated **3DLi** and **3DNa** species are predicted to be more stable than the carbon-attached species **3ELi** and **3ENa**, respectively. Mg^+ can be considered as an intermediate situation, where the covalent character becomes already sizeable, but quantitatively smaller than that found for Al^+. As a consequence, for this metal cation the carbon-attached species **3EMg** and the chelated **3DMg** structure are almost degenerate. Similarly, although the chelated species **1CMg** and **2CMg** are minima of the potential energy surface, they are much less stable than the corresponding global minima **1AMg** and **2BMg**.

Cation association involves a significant increase in the rotational barriers of both neutrals, due mainly to the change in the direction of the dipole moment of the system. This effect increases in the sequence $Li^+ < Na^+ < Mg^+ < Al^+$.

The effects on the harmonic vibrational frequencies are also sizeable. In particular, for the global minima, the NH_2 stretchings are systematically blue-shifted. The N$-$X stretch is predicted to be observed in the 300$-$400 cm^{-1} region.

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Supporting Information Available: Tables of B3LYP/6-31G* harmonic vibrational frequencies of the guanidine, guanidine$-X^+$, acetamidine, and acetamidine$-X^+$ complexes (2 pages). Ordering information is given on any current masthead page.

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