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Coordination Chemistry of Silver Cations

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Abstract: While in pure solvents Ag^+ is known to be tetrahedrally coordinated, in the presence of ligands such as ammonia it forms linear complexes, usually explained by the ion's tendency toward sd-hybridization. To explore this disparity, we have investigated the reaction of ammoniated silver cations $Ag^+(NH_3)_n$, $n = 11-23$, with H_2O as well as the complementary process, the reaction of $Ag^+(H_2O)_n$, $n = 25-45$, with NH_3 by means of FT-ICR mass spectrometry. In both cases, ligand exchange reactions take place, leading to clusters with a limited number of NH_3 ligands. The former reaction proceeds very rapidly until only three NH_3 ligands are left, followed by a much slower loss of an additional ligand to form $Ag^+(NH_3)_2(H_2O)_m$ clusters. In the complementary process, the reaction of $Ag^+(H_2O)_n$ with NH_3 five ammonia ligands are very rapidly taken up by the clusters, with a much less efficient uptake of a sixth one. The accompanying DFT calculations reveal a delicate balance between competing effects where not only the preference of Ag^+ for sd-hybridization, but also its ability to polarize the ligands and thus affect the strength of their hydrogen bonding, as well as the ability of the solvent to form extended hydrogen-bonded networks are important.

Introduction

Ammonia is the most common nitrogen-containing donor ligand in aqueous chemistry, especially important in the aqueous chemistry of silver. It is well-known that if NH_3 is added to an aqueous solution of a silver salt, the extremely stable linearly coordinated $[Ag(NH_3)_2]^+$ complex ion is formed. Because of its high stability, even an AgCl precipitate can be dissolved simply by the addition of NH_3.

The very stable linearly coordinated silver (I) complexes, AgL_2^+, are well-known in both solid and liquid phase, a fact explained by the electronic structure of Ag^+. By forming a hybrid orbital from 5s and $4d_{z^2}$, electron density is shifted from the lobes of the d_{z^2} orbital to the ring. This results in regions of reduced electron density along the *z*-axis, which are occupied by the lone-pairs of the two ligands.[1,2] However, it has been demonstrated that in highly concentrated aqueous ammonia solutions a triammine complex $[Ag(NH_3)_3]^+$ forms.[3] Moreover, if a silver salt is dissolved in pure water or liquid ammonia solvents, tetrahedral $Ag(L)_4^+$ ions are formed.[4-9] These observations seem to be contradictory. Why is the coordination different in pure and mixed solvent systems? Why does the sd-hybridization not lead to linear complexes in pure solvents? A promising approach to address these questions would seem to be the investigation of the silver cation coordination chemistry on a molecular level, in gas-phase clusters.

The investigation of ligand exchange reactions is important for the understanding of many chemical phenomena, for example the substitution of ligands close to a central ion proceeding in cluster ions in the atmosphere[10,11] or the dynamics of ligand exchange reactions in solutions of electrolytes.[12] Furthermore, studies of ligand exchange reactions can yield information about their relative binding energies[13-19] or provide new insights into catalytic processes proceeding on metal surfaces.[20,21]

Using the FT-ICR technique with an efficient external ion source one can study solution chemistry in finite clusters and

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gain a microscopic, molecular-scale understanding. In several studies, we have shown that water clusters are very simple model systems for aqueous solutions. We have for instance been able to show that HCl will dissolve ionically in finite clusters just as it does in bulk water,[22,23] redox or neutralization reactions leading to salts can take place,[24−27] organic base- or acid-catalyzed reactions proceed as they do in bulk,[28] and even an analogue to precipitation reactions can be observed.[29] Recently, we have shown[30] that the versatile laser vaporization source developed in our laboratory can, besides hydrated clusters, equally well produce ions solvated by other ligands, including ammonia. To gain insight into the coordination chemistry of silver cations in mixed solvent systems, we examine here the reactions and ligand exchange of hydrated silver cations $Ag^+(H_2O)_n$ with NH_3, as well as the complementary process, the reaction of large ammoniated silver cations $Ag^+(NH_3)_n$ with H_2O. To get a more detailed insight into the structure and energetics of solvated silver cations, we have complemented the experimental studies by DFT calculations on a number of smaller clusters.

Computational Details

The computations were carried out on a Pentium III-based Linux system using the Gaussian98[31(a)] program package. Results were visiualized with Molden[31b] and Molekel.[31c,d] The three-parameter hybrid Hartree−Fock/density functional (B3LYP) method described by Becke[32−34] with the Lee−Yang−Parr correlation functional[35] as incorporated in Gaussian98 was used throughout. For the geometry optimizations and frequency calculations, the 6-31G(d,p) basis set was used for H, N, and O, and also thermal corrections were taken from this level of theory. Single-point energy calculations were performed employing the larger Gaussian98 6-311++G(3df,3pd) basis set, treating explicitly all electrons, with two diffuse and four polarization functions on all atoms. For Ag, the pseudorelativistic effective core basis set of the Stuttgart/Dresden group[36] as implemented in Gaussian98 was used in every case.

Experimental Details

The experiments discussed here were performed on a modified Spectrospin CMS47X mass spectrometer described in detail elsewhere.[37] The cluster ions were generated in a pulsed supersonic expansion source using 10 bar of helium carrier gas seeded with about 30 mbar of either water vapor or ammonia. Metal cations were produced by laser vaporization of a solid silver disk (Chempur, 99.995%+), using a Nd:YAG laser Continuum Surelite II operating at 10 Hz and a pulse energy of typically 5 mJ. The plasma produced was entrained in a carrier gas pulse and cooled by flowing through a confining channel with the clustering and solvation of the ions taking place in the subsequent supersonic expansion into high vacuum. The cluster ions produced in the source were transferred through several stages of differential pumping into the high-field region of the superconducting magnet and stored inside the ICR cell. The reactant gases, NH_3 and H_2O, were introduced into the ultrahigh vacuum region via a needle valve. The pressure in the cell region after introducing the reactant gas was around 1×10^{-7} mbar, corresponding to some 10 collisional encounters every second. After accumulating the ions in the ICR cell, the mass spectra of the trapped ions and their products were taken after varying reaction delays.

Computational Results

We investigated several small clusters $Ag^+(NH_3)_n(H_2O)_m$, $n,m = 1−3$, $n + m \leq 4$, by means of density functional theory (B3LYP) to get a more detailed insight into the structure and energetics of silver cations coordinated by both kinds of solvent molecules. We chose B3LYP because it gives reliable results at moderate computational costs. To the best of our knowledge, the mixed clusters are studied theoretically for the first time. Pure hydrated and ammoniated silver cations have been investigated before. Feller et al.[38] used RHF, MP2, and CCSD(T) with different basis sets to determine the structures and energetics of $Ag^+(H_2O)_{1-4}$. More recently, Widmer-Cooper et al.[39] studied $Ag^+(H_2O)_{1-2}$ and $Ag^+(NH_3)_{1-2}$ using density functional and CCSD(T) electronic structure methods with different basis sets. Shoeib et al.[44] optimized structures of $Ag^+(NH_3)_{1-6}$ at the B3LYP/DZVP level of theory. Since we wanted to compare our results for the mixed clusters to $Ag^+(NH_3)_n$ or $Ag^+(H_2O)_m$, we have also reinvestigated the structures of these pure clusters by means of B3LYP and with the same basis sets. Some of these structures, which seemed relevant for the question of linear two-fold coordination of the core ion, have not been previously reported.

Pure Silver−Water Clusters $Ag^+(H_2O)_n$, $n = 1−4$. Optimized geometries of $Ag^+(H_2O)_n$, $n = 1−4$, are displayed

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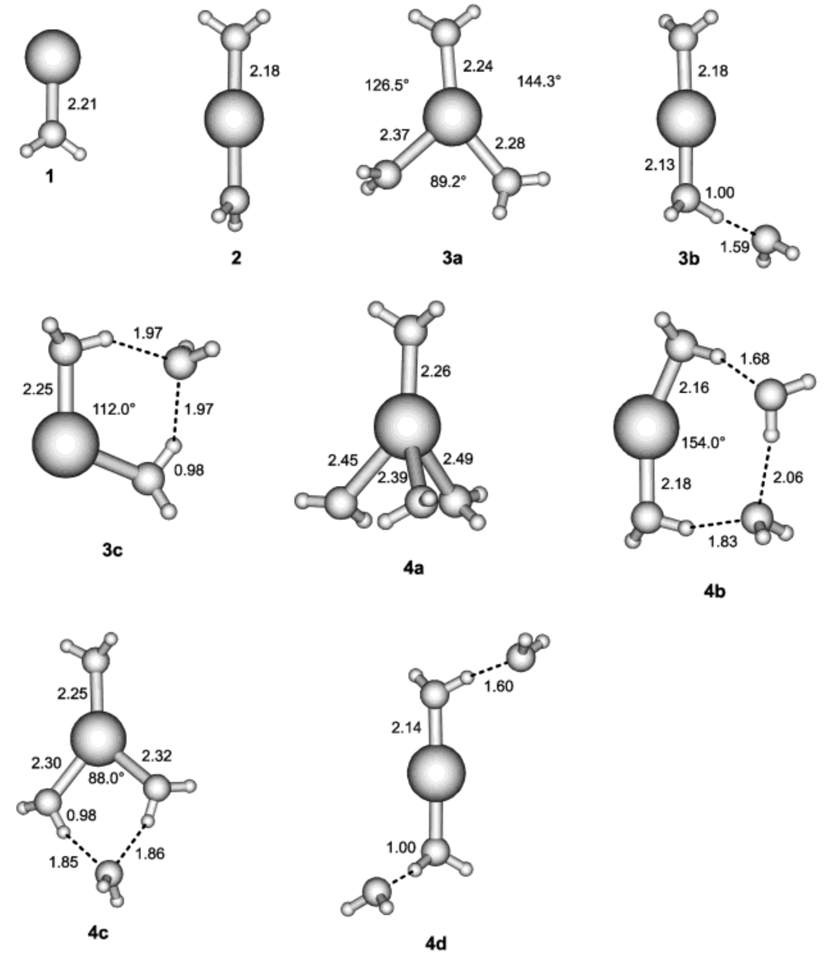

Figure 1. Fully optimized structures of $Ag^+(H_2O)_n$, $n = 1-4$, at the B3LYP level of theory. Bond lengths are in Å. All O−H bonds, except where otherwise noted, are 0.97 Å.

in Figure 1, together with the key structural parameters. The geometry and bond lengths of $Ag^+(H_2O)$ (**1**) and $Ag^+(H_2O)_2$ (**2**) agree very well with the previous quantum chemical studies by Feller et al.[38] and Widmer-Cooper et al.[39] For the following discussion, we will use the notation suggested by Feller et al.,[38] a tag of the form ($m + n$) where m equals the number of ligands directly coordinated to the central ion and n equals the number of ligands in the second solvation shell.

Table 1. Relative Energies of the Isomers of $Ag^+(H_2O)_n$, $n = 3, 4$, Calculated at the B3LYP/6-311++(3df,3pd) Level of Theory Referred to the Lowest-Energy Structure[a]

structure	3a	3b	3c	4a	4b	4c	4d
ΔH_{298K} [kJ/mol]	7.9	0	32.5	24.9	24.2	10.4	0

[a] Structure numbering refers to Figure 1.

For $Ag^+(H_2O)_3$ we have investigated one (3 + 0) configuration and two different (2 + 1) structures. Starting from the highly symmetric (3 + 0) structure with three equal Ag−O bond lengths and O−Ag−O angles of 120° the geometry converges fast to the asymmetric, nearly planar structure **3a** shown in Figure 1. It is interesting to note that while two of the Ag−O bond lengths are nearly identical, the third one is much longer. This, together with the large 144.3° angle between the first two ligands, indicates that these try to achieve a linear arrangement. In addition, one can note an interaction between two of the water ligands coordinated at an 89.2° angle. For (2 + 1) coordination, we have investigated an open structure (**3b**) and a ring structure (**3c**). The open structure contains a linearly coordinated Ag^+ cation. Binding of the second shell water ligand results in a decreased Ag−O bond length due to the additional polarization caused by the hydrogen bond. The ring structure exhibits C_s symmetry, with the comparably long length of the hydrogen bonds, indicating that these are rather weak. As can be seen in Table 1, the open, linearly coordinated (2 + 1) structure **3b** is lowest in energy with **3a** being about 7.9 kJ higher. The ring structure **3c** is significantly higher, with a difference of 32.5 kJ/mol, although the additional H-bond might be expected to decrease the energy. The energy difference and the bond lengths of **3b** and **3c** clearly show that the water ligand in the second solvation shell is more strongly bound if the silver cation is linearly coordinated. The energy difference between **3a** and **3b** lies within the accuracy of the method, suggesting that direct coordination of the third water ligand is energetically almost equivalent to placing it in the second solvation shell. However, as structure **3c** shows, this is only valid if the first ligands are linearly coordinated, in which case the silver cation seems to polarize the linearly coordinated water ligands very effectively. Somewhat different results were obtained by Feller et al.[38] They found at the RHF/6-31+G*/ECP+f level of theory that the global minimum is a $D_3(3 + 0)$ configuration, whereas a $C_1(2 + 1)$ and a $C_s(2 + 1)$ structure are both 7.6 kJ/mol higher in energy. At the MP2/6-31+G*/ECP+f level of theory the lowest energy structure is a $C_2(3 + 0)$ configuration and the energy difference to the corresponding (2 + 1) structure is less

Table 2. Experimental and Calculated Binding Energies of $Ag^+(H_2O)_n$, $n = 1-4^a$

	$\Delta H_{1,0}$ [kJ/mol]	$\Delta H_{2,1}$ [kJ/mol]	$\Delta H_{3,2}$ [kJ/mol]	$\Delta H_{4,3}$ [kJ/mol]
expt^b	−139.3	−106.3	−62.8	−62.3
calcd	−118.3	−116.1	−58.9	−55.6

[a] The energetically lowest lying isomers were chosen for the calculation. [b] Reference 45a.

than 1 kJ/mol. The lowest-energy structure is a transition state with a low-frequency mode (-30 cm^{-1}), which Feller et al. attribute to numerical inaccuracies in the ECP gradients. Unfortunately, they did not study a ring configuration. For $Na^+(H_2O)_3$ and $K^+(H_2O)_3$, however, quite different results have been obtained, for example, by Feller et al.[40] at the MP2 level of theory. In these cases, structures corresponding to **3a** and **3c** are energetically almost equal ($\Delta E \approx 7-8$ kJ/mol) while the configuration corresponding to **3b** is higher in energy ($\Delta E \approx 12-16$ kJ/mol).

The optimized structures we obtained for $Ag^+(H_2O)_4$, are displayed in Figure 1 as **4a**−**4d**. The four-fold tetrahedrally coordinated configuration converges to the distorted structure **4a** with remarkably long Ag−O bonds. **4c** represents a (3 + 1) ring structure, while **4d** and **4b** are open-chain and ring (2 + 2) structures, respectively. Again, the open-chain structure with the silver ion linearly coordinated is the one with lowest energy (see Table 1). Still of comparable energy with a difference of +10.4 kJ/mol is **4c**. The other configurations are more than 20 kJ/mol higher in energy. Thus, the lowest-energy configurations are those obtained by adding an additional water ligand to **3a** and **3b**.

The incremental binding energies obtained by using the H_{298K} values are summarized and compared with the experimental values in Table 2. This table suggests that the calculated binding energy of the first ligand, $\Delta H_{0,1}$, is underestimated by 21.0 kJ/mol while $\Delta H_{2,1}$ is overestimated by 9.8 kJ/mol. These deviations are probably not caused by too-small basis sets, since this usually results in overestimating the binding energies. Quantitatively very similar results were obtained by Widmer-Cooper et al.[39] at both the CCSD(T)/aVDZ(f) and the B3LYP/aVTZ(f) level of theory. The results of Feller et al.[38] show the same tendency. However, if the combined experimental errors and the accuracy of the calculations are taken into account, the values agree reasonably well. The calculated $\Delta H_{3,2}$ and $\Delta H_{4,3}$ values, on the other hand, agree perfectly well with those determined experimentally. Interestingly, the binding energy of a water ligand in the second solvation shell to one which is directly coordinated, that is, for example $\Delta H_{3,2} = -58.9$ kJ/mol, is much higher than the binding energy of the water dimer (22.6 kJ/mol[41−43]) which reflects the strong influence of the polarizing Ag^+ central ion on the hydrogen bond.

Pure Silver−Ammonia Clusters $Ag^+(NH_3)_n$, $n = 1-4$. Figure 2 displays our optimized structures of $Ag^+(NH_3)_n$, $n = 1-4$, together with some key geometry parameters. The structures found for $Ag^+(NH_3)$ (**5**) and $Ag^+(NH_3)_2$ (**6**) agree very well with those computed by Widmer-Cooper et al.[39] at the CCSD(T)/aVDZ(f) level of theory. The bond lengths we find are 0.1 Å shorter than those obtained by Shoeib et al.[44] at the B3LYP/DZVP level of theory. These differences may be due to the fact that in this study the small DZVP basis set was also used for Ag instead of the SECP basis set[36] used in the other investigations. The (3 + 0) and (2 + 1) configurations we have investigated for $Ag^+(NH_3)_3$ converged to the structures **7a** and **7b**, respectively. **7b** shows as **3b** does a shortened Ag−N distance for the NH_3 which has the third ligand attached, again undoubtedly due to the enhanced polarization of the ammonia molecule. Structure **7b** is computed to be lower in energy, but the difference, 2.4 kJ/mol, is probably within the accuracy of the computations. In fact, with the 6-31G(d,p) basis set which we used for the geometry optimization, **7a** becomes the global minimum with a difference of 1.5 kJ/mol. Within the accuracy of our computations there is little difference between directly coordinating the third ammonia ligand and placing it into the second solvation shell. This differs from the study of Shoeib et al.[44] who find the **7a** (3 + 0) configuration to be 17.3 kJ/mol lower in energy. Our results probably again reflect energy-lowering of the (2 + 1) structure due to the strong polarizing effect of the central Ag^+ ion on the hydrogen bonds.

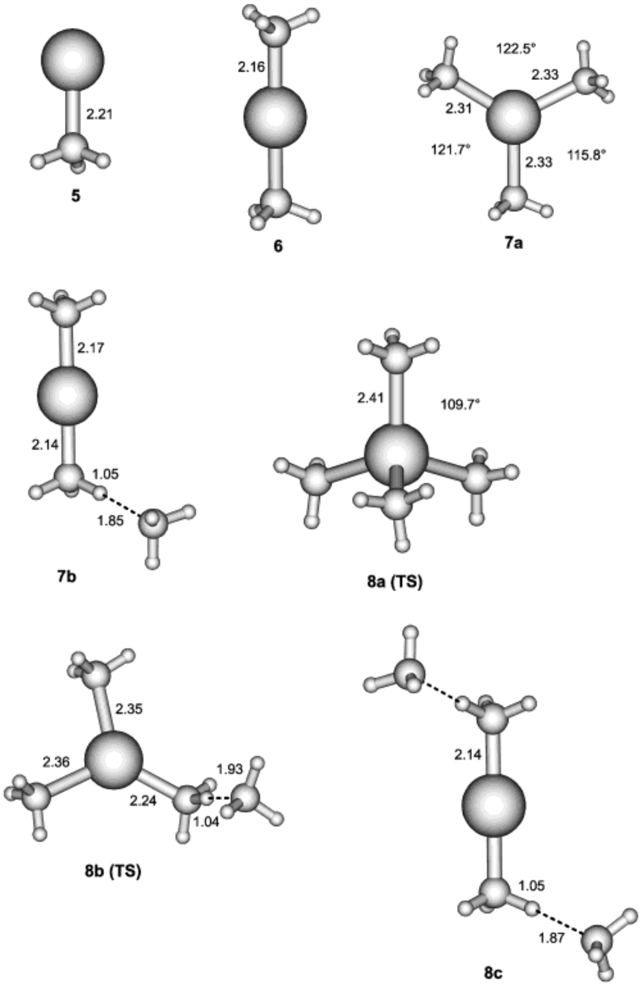

Figure 2. Fully optimized structures of $Ag^+(NH_3)_n$, $n = 1-4$, at the B3LYP level of theory. Bond lengths are in angstroms. All N−H bonds, except where otherwise noted, are 1.02 Å. Structures marked with TS are transition states with a low imaginary frequency mode representing internal rotations of the NH_3 groups.

For $Ag^+(NH_3)_4$ we have considered three different configurations. The (4 + 0) structure converged to **8a**, an almost perfect tetrahedron with four comparably long Ag−N bonds. The normal-mode analysis produced one low (-28 cm^{-1}) imaginary frequency for this complex, which essentially corresponds to an internal rotation of two of the ammonia ligands. Several

Table 3. Relative Energies of the Isomers of $Ag^+(NH_3)_n$, $n = 3, 4$, Calculated at the B3LYP/6-311++(3df,3pd) Level of Theory Referred to the Lowest-Energy Structure[a]

structure	**7a**	**7b**	**8a**	**8b**	**8c**
ΔH_{298K} [kJ/mol]	2.4	0	7.5	8.6	0

[a] Structure numbering refers to Figure 2.

Table 4. Experimental and Calculated Binding Energies of $Ag^+(NH_3)_n$, $n = 1-4$

	$\Delta H_{1,0}$ [kJ/mol]	$\Delta H_{2,1}$ [kJ/mol]	$\Delta H_{3,2}$ [kJ/mol]	$\Delta H_{4,3}$ [kJ/mol]
expt	-203.8^b	-154.4^c	-61.1^c	-54.4^c
calcd	−183	−177.3	−45.1	−46.5

[a] The energetically lowest-lying isomers were chosen for the calculation. [b] Reference 13. [c] Reference 45a.

attempts to find the minimum with the CalcFC option failed. Since the potential surface is very flat as indicated by the low frequency, the energy difference and the difference in geometry between this transition state and the minimum is negligible. The (3 + 1) structure converged to **8b**, which is nominally also a transition state with an even lower imaginary frequency (-7 cm^{-1}). Lowest in energy turned out to be the linear (2 + 2) configuration **8c**. Again, the energy difference between the structures is found to be small, with **8a** and **8b** being only 7.5 and 8.6.kJ/mol, respectively, higher in energy, as listed in Table 3.

The calculated sequential ligand binding energies summarized and compared with experimental values in Table 4 exhibit the same trends as the hydrated silver cations. The binding energy of the first ligand, $\Delta H_{0,1}$ underestimates the experimental value by 21 kJ/mol, while that for the second ligand, $\Delta H_{1,2}$, is overestimated by ~23 kJ/mol. For the former value the agreement with the experiment is acceptable if one considers the experimental error of about 16 kJ/mol,[13] but the latter deviation is well outside the stated ±3.4 kJ/mol accuracy of the experiment.[45a] Widmer-Cooper et al.[39] who used in their study much larger basis sets for N and H atoms get a maximum deviation of ~16 kJ/mol for these energies. The calculated values for the next two incremental binding energies, $\Delta H_{2,3}$ and $\Delta H_{3,4}$ both underestimate slightly the experimental values, with the differences being probably within the combined uncertainties of the experiment and the calculation.

Mixed Silver−Water−Ammonia Clusters $Ag^+(NH_3)_n(H_2O)_m$, $n,m = 1-3$, $n + m \leq 4$. The optimized geometries we have obtained for clusters with mixed water and ammonia ligands are presented in Figure 3. For $Ag^+(NH_3)(H_2O)$, the calculated structure **9** is again a transition state with a low imaginary frequency mode (-22 cm^{-1}) corresponding to an internal rotation of the H_2O group against the NH_3 group. As in the ammonia cluster above, the energy and geometry differences between this structure and the global minimum are negligible. The Ag−O and Ag−N bond lengths are similar to the corresponding distances in the homogeneous $Ag^+(H_2O)_2$ and $Ag^+(NH_3)_2$ clusters. For clusters with more than two ligands we failed to find any stable (n + 0) configurations, with all of them converging rapidly to one of the structures shown in the figure. Thus, both $Ag^+(NH_3)_2(H_2O)$ (**10**) and $Ag^+(NH_3)(H_2O)_2$ (**11**) converge to the linear (2 + 1) type structure, even when starting from a (3 + 0) configuration. The optimized structure **10** indicates that direct coordination of ammonia to silver is energetically favored and water prefers to be in the hydrogen-bonded network around it. As observed for the homogeneous clusters, binding of a ligand in the second coordination shell again shortens the Ag−X bond. Interestingly, the N−H−O hydrogen bond angle in **10** is less than 180°, probably reflecting a weak interaction between the oxygen lone pair and the silver cation. For the same reason, similar slight distortions of the hydrogen bonds are also found in the open (2 + 2) structure **12a** of $Ag^+(NH_3)_2(H_2O)_2$. Interestingly, in contrast to the hydrated silver cations, the ring structure **12b** is only 2.9 kJ/mol higher in energy, which may be connected to the almost linear N−Ag−N angle of 170.3°. Again, it was not possible to eliminate the remaining imaginary frequency (-31.7 cm^{-1}). Three different structures were found for $Ag^+(NH_3)_3(H_2O)$ with the linear configuration **13b** being the absolute minimum. As can be seen in Table 5, the geometry **13a** is only slightly higher (+4.8 kJ/mol) suggesting that also in the case of mixed complexes the structures with two and three directly coordinated ammonia ligands exhibit comparable stabilities. Interestingly, in contrast to **12b**, **13c** is more than 11.7 kJ/mol higher in energy, despite having one more hydrogen bond than **13b**. Apparently, the strong preference for a linear N−Ag−N configuration results in unusually long and weak hydrogen bonds, so that the one additional hydrogen bond cannot compensate for the overall increase in the complex energy. In the case of **12b**, the additional hydrogen bond might be much stronger because it is formed between two water molecules and may thus compensate for the energy increase due to the nonlinear arrangement.

Table 5. Relative Energies of the Isomers of $Ag^+(NH_3)_2(H_2O)_2$ and $Ag^+(NH_3)_3(H_2O)$ Calculated at the B3LYP/6-311++(3df,3pd) Level of Theory Referred to the Lowest-Energy Structure[a]

structure	**12a**	**12b**	**13a**	**13b**	**13c**
ΔH_{298K} [kJ/mol]	0	2.9	4.8	0	11.7

[a] Structure numbering refers to Figure 3.

Discussion of the DFT Results

An analysis of the molecular orbital coefficients in the $Ag(NH_3)_2^+$ calculation reveals that indeed sd-hybridization takes place, while the 5p orbitals do not contribute at all. Our DFT calculation is fully consistent with the empirical picture developed by Orgel in 1958,[2] that the two-fold linear coordination is caused by an sd_{z^2} hybrid orbital, which reduces the electron density along the z-axis. To visualize this effect, we have plotted an sd_{z^2} orbital and the electron density of an sd_{z^2} hybridized Ag^+ ion as isodensity surfaces in Figure 4. The area of reduced electron density, which accommodates the NH_3 lone pair, is clearly visible.

The calculations reveal that clusters with three ligands directly coordinated to the silver cation and those with only two ligands linearly coordinated to the central ion and the third one located in the second solvation shell are energetically almost equal. This finding seems to be contradictory to the well-known pronounced preference of Ag^+ for two-fold linear coordination, but it is instructive and may indeed provide the key to a refined understanding of its coordination chemistry. Undoubtedly, the desire of Ag^+ to be linearly coordinated is reflected in the computational results; most structures contain the AgL_2^+ center,

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(45) (a) Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195−4205. (b) Poisson, L.; Lepetit, F.; Mestdagh, J.-M.; Visticot, J.-P. *J. Phys. Chem. A* **2002**, *106*, 5455−5462.

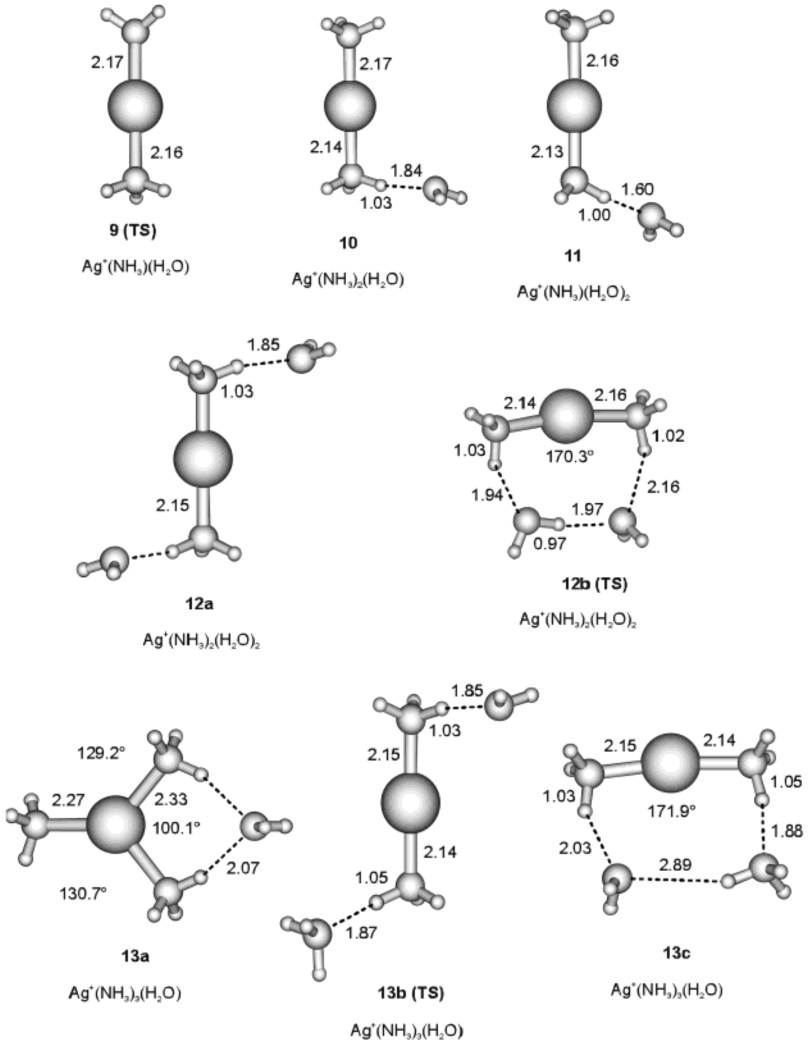

Figure 3. Fully optimized structures of Ag$^+$(NH$_3$)$_n$(H$_2$O)$_m$, $n,m = 1-3$, $n + m \leq 4$, at the B3LYP level of theory. Bond lengths are in Å. All N−H bonds and O−H bonds, except where otherwise noted, are 1.02 and 0.97 Å, respectively. Structures marked with TS are transition states with a low imaginary frequency mode representing an internal rotation of the NH$_3$ groups.

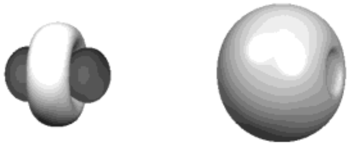

Figure 4. Isosurfaces of the wave function of the 5s4d$_{z2}$-hybrid orbital $1/2\psi_{5s} + \sqrt{3}/2\psi_{4d_{z2}}$ (left) and of the total electron density of sd-hybridized Ag$^+$ (right). Coefficients were chosen to reflect the degree of hybridization in the Ag(NH$_3$)$_2$$^+$ silver diammine complex. Hybridization shifts electron density from the lobes of the d$_{z^2}$ orbital to the ring, thereby generating two areas of reduced electron density along the z-axis. These areas are taken by the ammonia lone pairs, which can come closer to the Ag$^+$ and interact with a partially unshielded silver core.

with additional hydrogen-bonded ligands. The sd-hybridization, however, is energetically costly, and the net gain after coordinating two ligands is so small that it can be compensated by placing a third ligand in the first solvation shell. An example is **7a**, where Ag$^+$ acts as spherically symmetric core ion.

A ligand like NH$_3$ coordinating into such a hole in the d-shell interacts with a higher than +1 charge on the metal, since the core is no longer homogeneously shielded. The additional polarization of the NH$_3$ strengthens the hydrogen bond between the first and the second solvation shell. This secondary effect contributes to the stability of linear coordination and may in fact be crucial for the slight preference of **3b**, **4d**, **7b**, **8c**, and **13b** over the other isomers, which lie within 10 kJ/mol of these minima. Since the energy differences are smaller than the energy of a single hydrogen bond, typically 20 kJ/mol, the number of hydrogen bonds should be of equal importance for the finally exhibited structure in bulk solution. The ability of the central structure to integrate into an existing hydrogen-bonded network seems to be of equal importance.

Since in the clusters investigated here different isomers are very close in energy, kinetic effects should also be taken into account, and molecular dynamics studies should be interesting and desirable. They could provide information about the "real" geometries of the clusters, although the lower level of theory introduces a different source of errors. High-level Car−Parrinello molecular dynamics simulations would probably be the method of choice. The small energy differences of two or three isomers indicate that a mixture of different isomers can be present in the experiment, as recently reported by Poisson et al.[45b] in CID experiments of Au(H$_2$O)$_n$$^+$, $n \leq 10$.

Altogether disturbing is the deviation of experimental and theoretical binding energies of the first and second ligand, both for H$_2$O and NH$_3$, Tables 2 and 4, respectively. Interestingly, the errors in $\Delta H_{1,0}$ and $\Delta H_{2,1}$ almost exactly compensate, which means that most probably only the AgL^+ energy is either not calculated or measured correctly. These deviations seem to occur consistently for different theoretical methods. One reason for both DFT and Post-Hartree–Fock methods with large basis sets yielding similar errors for AgH_2O^+ and $AgNH_3^+$ only could be the inclusion of the 3d electrons in the effective core potentials. In the AgL_2^+ species, the ligands are closer to the Ag^+ than in AgL^+, indicating different dominant interactions. While two ligands are sufficient to induce sd-hybridization and at the same time are unable to efficiently polarize the metal center in a linear geometry, the more distant single ligand seems to interact predominantly via polarization. The absent 3d electrons may contribute significantly to core polarization, while they do not play a part in the 5s4d-hybridization. This would explain the systematic error for AgL^+ species only. To finally settle this question, an additional experimental assessment of the AgL^+ binding energy with a different method would be highly desirable, for example collision-induced dissociation threshold experiments in a guided ion beam apparatus. On the theory side, relativistic effective core potential basis sets with explicit treatment of the 3d electrons might be helpful.

Experimental Results and Discussion

Reaction of $Ag^+(NH_3)_n$ with H_2O. The reaction of ammoniated silver cations $Ag^+(NH_3)_n$, $n = 11-23$, with H_2O corresponds to the conditions in aqueous solution in the sense that it proceeds with a large excess of water, so that exchange of ammonia ligands for water, but not of water for ammonia, was possible. To keep the collision rate sufficiently high, a pressure of about 9×10^{-8} mbar was maintained in the ICR cell during the experiment. Figure 5a shows part of a typical mass spectrum in the range of clusters with 8–11 ligands after a nominal reaction time of 0 s. Since the reaction already proceeds while the clusters formed in 20 vaporization cycles are being accumulated in the ICR cell, some products are already present at this “zero” time. The interpretation of the mass spectra is somewhat complicated by the presence of two silver isotopes, $^{107}Ag^+$ and $^{109}Ag^+$ in comparable abundances (51.839 and 48.161%), as well as by the fact that each exchange of an ammonia ligand for water, that is, reaction of $Ag^+(NH_3)_n(H_2O)_m$ to $Ag^+(NH_3)_{n-1}(H_2O)_{m+1}$ increases the nominal mass of the cluster by one amu. As can be seen in Figure 5a, the reaction takes place remarkably fast, with up to eight water molecules having already been taken up during the cell filling cycle, at a nominal time $t = 0$. Even at this short time, the most abundant products retain only four of the originally present ammonia ligands. On the basis of the estimated collision rate, almost every collision must be reactive, with the ligand exchange proceeding according to the following reaction scheme:

$$Ag^+(NH_3)_n + H_2O \rightarrow Ag^+(NH_3)_{n-x}(H_2O) + xNH_3$$

More than one ammonia molecule can be set free, that is x may be larger than one, since in addition to the binding energy also the collision energy can be released as heat in the cluster and the value will also depend on the size of the cluster. The exact number of ammonia molecules released in a single collision cannot be determined accurately, since the ligand exchange proceeds concurrently with collisional and blackbody radiation-induced fragmentation. Due to these processes, the clusters rapidly lose ligands and shrink, so that after 7 s in Figure 5b the distribution maximum has shifted to $n + m = 3$. Despite the long reaction time, and despite the fast initial exchange of ammonia for water, the most abundant remaining clusters (marked with hollow circles in Figure 5b) still retain three ammonia molecules. Much less abundant are clusters $Ag^+(NH_3)_2(H_2O)_m$, that is with only two ammonia ligands remaining, and this does not change appreciably even after longer reaction delays or in experiments employing a still higher water pressure (3×10^{-7} mbar). The smallest cluster observed in small quantity after a long time is $n = 2$, $m = 0$, and products containing fewer than two ammonia ligands were not observed in any case.

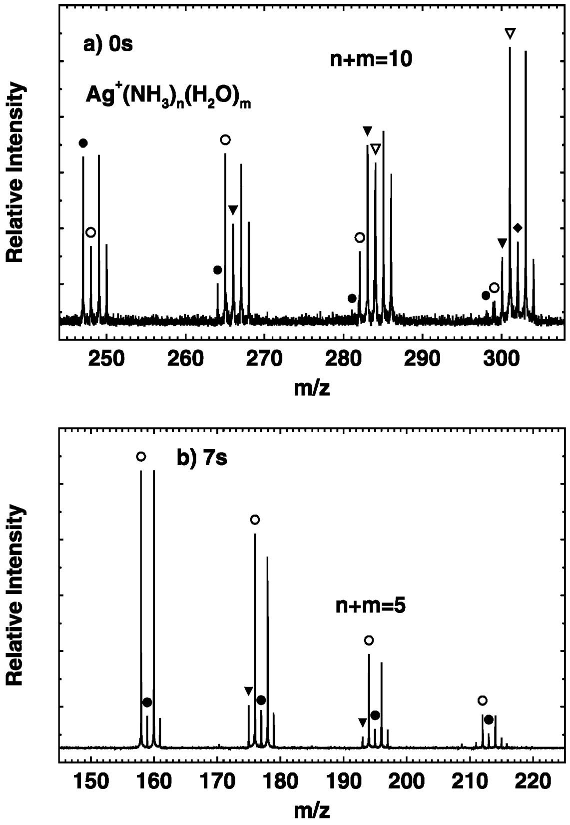

Figure 5. Typical parts of the mass spectrum of the reaction of ammoniated silver cations $Ag^+(NH_3)_n$, $n = 11-23$, with H_2O with a reaction delay of (a) 0 s and (b) 7 s. Panel (a) shows the remarkably high rate of this reaction. The labeled peaks represent clusters that correspond to a composition $^{107}Ag^+(NH_3)_n(H_2O)_m$, the remaining peaks belong to clusters containing the heavier isotope ^{109}Ag. Clusters $^{107}Ag^+(NH_3)_m(H_2O)_n$ and clusters $^{109}Ag^+(NH_3)_{m+2}(H_2O)_{n-2}$ have very similar masses ($m = 0.03$ amu) which are physically resolved but not displayed as two peaks due to the data set size limit of 128 kW. The different cluster species are labeled as follows: (●) $Ag^+(NH_3)_n(H_2O)_4$; (○) $Ag^+(NH_3)_n(H_2O)_5$; (▼) $Ag^+(NH_3)_n(H_2O)_6$; (▽) $Ag^+(NH_3)_n(H_2O)_7$; (◆) $Ag^+(NH_3)_n(H_2O)_8$ The most dominant products after 7 s can be seen in panel (b). These are cluster species of (○) $Ag^+(NH_3)_3(H_2O)_m$ composition. The hydrated silver diammine complex, (●) $Ag^+(NH_3)_2(H_2O)_m$, as well as (▼) $Ag^+(NH_3)_4(H_2O)_m$ clusters, are present in lesser amounts.

The ratio of $Ag^+(NH_3)_2(H_2O)_m$ to $Ag^+(NH_3)_3(H_2O)_m$ clusters increases with increasing numbers of water molecules in Figure 5b. This might provide some experimental justification for the hypothesis that the water networks stabilize the $n = 2$ structures, allow a more facile ligand exchange, and lead to an easier ejection of the third ammonia ligand. However, alternative explanations for this relative intensity pattern are possible. Under the experimental conditions, fragmentation and ligand exchange compete. If an $n = 3$ cluster collides with water, it may undergo ligand exchange to $n = 2$ and remain in the peak group, or fragment by losing a water molecule. This effect alone is capable of enriching $n = 2$ in the bigger clusters.

The results thus suggest that the ammonia ligands are easily and efficiently exchanged against water, with the exception of the last three. It also is possible, but apparently energetically not very favorable, to exchange one additional ammonia ligand, but then the reaction stops. Since ligand exchange reactions proceed at roughly collision rate as long as they are exothermic, this should indicate that replacing an ammonia by a water ligand is exothermic if more than three ammonia ligands are bound to the cluster. Exchanging an ammonia ligand if only three of them remain would then appear to be slightly endothermic, that is it can happen if collisionally or blackbody radiation activated, but it is not very favorable. For $Ag^+(NH_3)_2(H_2O)_m$ species, the exchange of an ammonia ligand for water is apparently too endothermic to be activated either by collisions or by blackbody radiation. To verify these conclusions, we have calculated the enthalpies and Gibbs free energies of several ligand exchange reactions by using the values obtained in our DFT calculations:

$$Ag^+(NH_3)_2 + H_2O \rightarrow Ag^+(NH_3)(H_2O) + NH_3 \qquad (1)$$

$$\Delta H = +59.4 \text{ kJ/mol}$$
$$\Delta G = +61.2 \text{ kJ/mol}$$

$$Ag^+(NH_3)_2(H_2O) + H_2O \rightarrow Ag^+(NH_3)(H_2O)_2 + NH_3 \qquad (2)$$

$$\Delta H = +42.1 \text{ kJ/mol}$$
$$\Delta G = +36.9 \text{ kJ/mol}$$

$$Ag^+(NH_3)_3 + H_2O \rightarrow Ag^+(NH_3)_2(H_2O) + NH_3 \qquad (3)$$

$$\Delta H = +7.6 \text{ kJ/mol}$$
$$\Delta G = +7.5 \text{ kJ/mol}$$

$$Ag^+(NH_3)_3(H_2O) + H_2O \rightarrow Ag^+(NH_3)_2(H_2O)_2 + NH_3 \qquad (4)$$

$$\Delta H = +7.3 \text{ kJ/mol}$$
$$\Delta G = +1.1 \text{ kJ/mol}$$

$$Ag^+(NH_3)_4 + H_2O \rightarrow Ag^+(NH_3)_3(H_2O) + NH_3 \qquad (5)$$

$$\Delta H = +11.9 \text{ kJ/mol}$$
$$\Delta G = +8.2 \text{ kJ/mol}$$

The enthalpies of reactions 1 and 2 clearly confirm that these are too endothermic for an exchange of an ammonia ligand for water to occur under our experimental conditions, if only two NH_3 ligands remain in the cluster, and consistently, no products with less than two ammonia ligands are observed. Again consistent with the experiment, the reactions 3 and 4 show slightly endothermic values, verifying that replacing an ammonia ligand in clusters with three ammonia ligands can be collisionally or blackbody radiation activated. Somewhat surprisingly, the reaction 5, that is the exchange of an ammonia molecule in a cluster with four NH_3 ligands is found to be more endothermic than the reactions 3 and 4. This might indicate that the investigated structures for the mixed cluster $Ag^+(NH_3)_3(H_2O)$ which can have a lot of isomers did not include the global minimum. A more likely reason, however, is that the reaction is more favorable in an extended hydrogen-bonded network, where the role of water as both donor and double acceptor, that is, its greater ability to participate in extended networks than ammonia, gets more important.

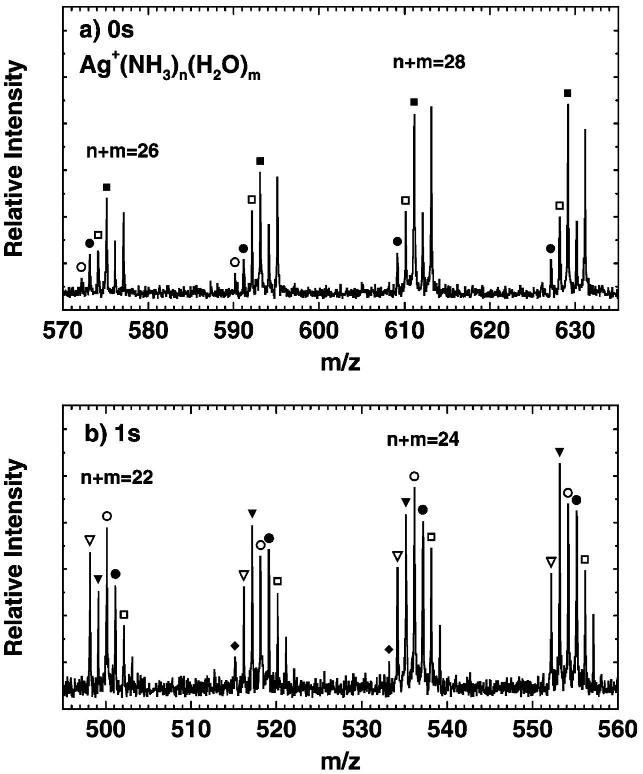

Figure 6. Typical parts of the mass spectrum of the reaction of large hydrated silver cations $Ag^+(H_2O)_n$, $n = 25-45$, with NH_3 with a reaction delay of (a) 0 s and (b) 1 s. The clusters are labeled in the following way: (■) $Ag^+(H_2O)_m$, (□) $Ag^+(NH_3)(H_2O)_m$, (●) $Ag^+(NH_3)_2(H_2O)_m$, (○) $Ag^+(NH_3)_3(H_2O)_m$, (▼) $Ag^+(NH_3)_4(H_2O)_m$, (▽) $Ag^+(NH_3)_5(H_2O)_m$, (◆) $Ag^+(NH_3)_6(H_2O)_m$ The spectra show that up to five ammonia molecules are taken up with high efficiency, a sixth one less efficiently.

As already mentioned above, this reaction is the gas-phase analogue of the formation of $[Ag(NH_3)_2]^+$ in aqueous solution because both proceed with a large excess of water. The observation that $Ag^+(NH_3)_3(H_2O)_m$ clusters are the dominant products and that additional exchange resulting in $Ag^+(NH_3)_2(H_2O)_m$ appears inefficient seems to be at odds with the bulk solution observations, where the linear $Ag^+(NH_3)_2$ cluster ions seem to dominate. In a bulk liquid, however, the number of collisions is many orders of magnitude larger than in our experiments, which may make the reaction proceed efficiently to $n = 2$. In addition, the presence of a more extensive hydrogen-bonded network may shift the energetics in favor of the $Ag^+(NH_3)_2$ cations.

Reaction of $Ag^+(H_2O)_n$ with NH_3. The complementary reaction of hydrated silver cations with NH_3 has been studied under similar conditions. Figure 6a shows a section of a typical mass spectrum resulting from the reaction of large hydrated silver cations $Ag^+(H_2O)_n$, $n = 25-45$, with NH_3 after a nominal 0 s delay. As can be seen in Figure 6a, the reaction again proceeds fast, and first products have already been formed, with up to three ammonia molecules having been taken up during the filling process by some of the clusters. No unreacted $Ag^+(H_2O)_n$ clusters remain after a 1 s delay in Figure 6b, and clusters with five or even six ammonia ligands are now present. This efficient exchange of water for ammonia is in agreement with the previous investigations on smaller hydrated clusters, $H^+(H_2O)_n$, $n = 2-11$, and $Na^+(H_2O)_n$, $n = 1-3$.[14,46]

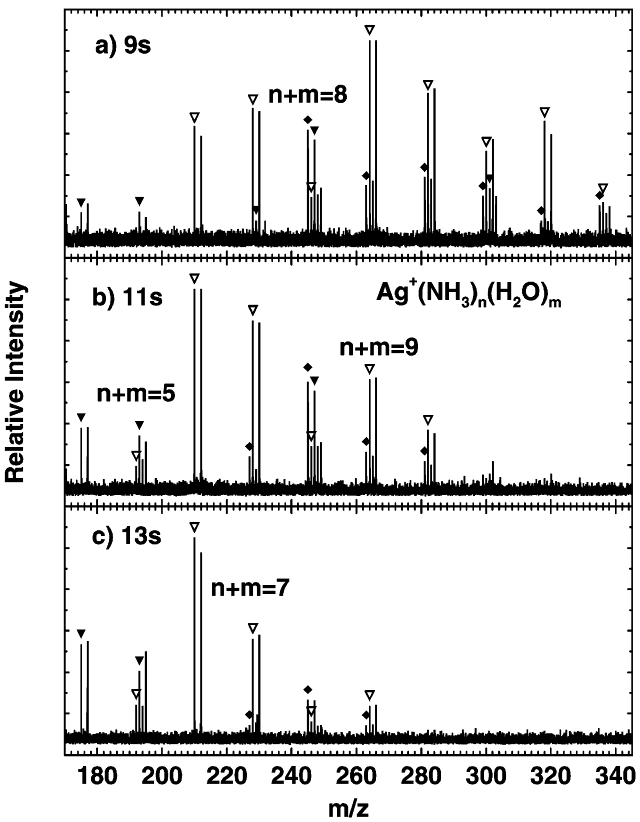

Figure 7. Typical parts of the mass spectrum of the reaction of large hydrated silver cations $Ag^+(H_2O)_n$, $n = 25-45$, with NH_3 with a reaction delay of (a) 9 s, (b) 11 s, and (c) 13 s. (Cluster labeling is similar to Figure 5: (▼) $Ag^+(NH_3)_4(H_2O)_m$, (▽) $Ag^+(NH_3)_5(H_2O)_m$, (◆) $Ag^+(NH_3)_6(H_2O)_m$). Even after these longer reaction delays, not more than six ammonia molecules are taken up by the clusters.

Superficially, the available data would seem to suggest that for all the hydrated cations a uniformly efficient and rapid ligand exchange is taking place:

$$Ag^+(H_2O)_n(NH_3)_m + NH_3 \rightarrow Ag^+(H_2O)_{n-x}(NH_3)_{m+1} + x(H_2O)$$

However, a closer examination of the large cluster reactions reveals a more complex behavior. As can be seen in Figure 7, at even longer reaction delays the clusters with five ammonia molecules, $Ag^+(NH_3)_5(H_2O)_m$, become dominant, but the uptake of a sixth ligand is obviously much less efficient, and in no case products with more than six ammonia ligands were observed. To verify that the limit on the number of ammonia ligands that can be taken up is not a function of the cluster size, we have repeated the experiments with various initial $Ag^+(H_2O)_n$ distributions. We found that the rapid exchange of five ligands, but a more hesitant uptake of a sixth one is a common feature of for instance two experiments with $n = 25-45$ and $n = 7-15$ initial cluster size ranges, respectively, and in neither experiment any uptake of more than six ammonia molecules was observed.

To gain some more insight into these observations and ligand exchange processes, it is instructive to examine the results of our DFT computations compiled in Tables 1−5. Comparison of Tables 2 and 4 immediately reveals an interesting result: while the first two ammonia ligands exhibit appreciably stronger bonds to Ag^+ than water molecules, the situation is reversed in larger clusters. Already the third and fourth ammonia are found to be weaker bound then their water counterparts, a result confirmed also by the experimental results of Holland and Castleman[45a] and Deng and Kebarle.[13] While a direct bond to the metal favors ammonia, in a larger solvation shell water with its two electron lone pairs can produce more stable structures than ammonia, which can typically form only a single acceptor hydrogen bond. It is the result of the ability of H_2O to form extended hydrogen-bonded networks, which is also reflected in the much higher boiling point and lower vapor pressure of bulk water, when compared with ammonia. If one takes the properties of the two ligands into consideration, it is therefore not surprising that the ligand exchange is initially very efficient, but stops at a certain number of ammonia ligands.

An exception to the observed preference for structures with five ammonia ligands is the $Ag^+(NH_3)_6(H_2O)_2$, $n + m = 8$, cluster ion, which is consistently more intense than the $Ag^+(NH_3)_5(H_2O)_3$ and $Ag^+(NH_3)_4(H_2O)_4$ species, and also exhibits higher intensities than its $n + m = 9$ and 7 neighbors, $Ag^+(NH_3)_6(H_2O)_3$ and $Ag^+(NH_3)_6(H_2O)$. Clearly, a complex ion with six ammonia and two water ligands appears to be particularly stable. On the other hand, panel (a) of Figure 7 shows that $Ag^+(NH_3)_6(H_2O)_6$ is very weak compared to $Ag^+(NH_3)_6(H_2O)_5$ and $Ag^+(NH_3)_6(H_2O)_7$, suggesting that the structure of this particular composition is especially unfavorable, and it probably fragments efficiently to form either $Ag^+(NH_3)_5(H_2O)_6$ or $Ag^+(NH_3)_6(H_2O)_5$.

The weakly bound nature of a sixth ammonia ligand is also evident by examining the later stages of cluster fragmentation in Figure 7. The particularly stable $Ag^+(NH_3)_6(H_2O)_2$ cluster ion fragments predominantly by the loss of the sixth ammonia. The very small amount of $Ag^+(NH_3)_6(H_2O)$ formed fragments in the very next step with a loss of NH_3, so that the sixth ammonia always evaporates before the last water ligand, with the $n + m = 6$ cluster having a unique composition of $Ag^+(NH_3)_5(H_2O)$. The fact that the sixth ammonia ligand always evaporates before the last water ligand is due to the ability of water to form two acceptor hydrogen bonds, which leads to a higher binding energy. The $Ag^+(NH_3)_5(H_2O)$ cluster fragments preferentially by the loss of an ammonia ligand, but approximately one-third of these clusters fragment by losing a water ligand, suggesting that the binding energy of the fifth NH_3 and the last H_2O ligand are comparable. In the next step, both possible fragmentation products, $Ag^+(NH_3)_4(H_2O)$ and $Ag^+(NH_3)_5$, then fragment by forming $Ag^+(NH_3)_4$, indicating that the binding energy of the fifth ammonia ligand in $Ag^+(NH_3)_5$ and the binding energy of the water ligand in $Ag^+(NH_3)_4(H_2O)$ are similar.

In view of the well-known fact that silver salts form in aqueous solutions very stable $[Ag(NH_3)_2]^+$ cations it might at first appear surprising that more than two ammonia ligands can be taken up by the clusters. However, investigations in highly concentrated aqueous ammonia have suggested that here three NH_3 ligands may be bound to the silver cations.[3] The difference in the FT-ICR study is that here ammonia is present in excess as reaction gas, so unlike that in aqueous solution, the exchange can only proceed in one direction. To gain some more insight

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(46) Viggiano, A. A.; Dale, F.; Paulson, J. F. *J. Chem. Phys.* **1988**, *88*, 2469−2477.

into the energetics of the ligand exchange reactions, we have used our DFT calculation results to obtain the enthalpies and Gibbs free energies of some relevant reactions:

$$Ag^+(H_2O) + NH_3 \rightarrow Ag^+(NH_3) + H_2O \qquad (6)$$

$$\Delta H = -64.7\ \text{kJ/mol}$$
$$\Delta G = -58.4\ \text{kJ/mol}$$

$$Ag^+(NH_3)(H_2O) + NH_3 \rightarrow Ag^+(NH_3)_2 + H_2O \qquad (7)$$

$$\Delta H = -59.4\ \text{kJ/mol}$$
$$\Delta G = -61.2\ \text{kJ/mol}$$

$$Ag^+(NH_3)_2(H_2O) + NH_3 \rightarrow Ag^+(NH_3)_3 + H_2O \qquad (8)$$

$$\Delta H = -7.6\ \text{kJ/mol}$$
$$\Delta G = -7.5\ \text{kJ/mol}$$

$$Ag^+(NH_3)_2(H_2O)_2 + NH_3 \rightarrow Ag^+(NH_3)_3(H_2O) + H_2O \qquad (9)$$

$$\Delta H = -7.3\ \text{kJ/mol}$$
$$\Delta G = -1.1\ \text{kJ/mol}$$

$$Ag^+(NH_3)_3(H_2O) + NH_3 \rightarrow Ag^+(NH_3)_4 + H_2O \qquad (10)$$

$$\Delta H = -11.9\ \text{kJ/mol}$$
$$\Delta G = -8.2\ \text{kJ/mol}$$

The results are clearly in good agreement with the experimental observations. The reactions 6 and 7 show that taking up the first and second NH_3 molecule is a strongly exothermic process, and will probably lead to evaporation of more than one water molecule. The exchanges of a third and fourth ligand are found to be also exothermic by a much smaller amount but probably outside the uncertainty of the computations. Unfortunately, the computations for larger clusters are getting progressively more tedious and time-consuming due to the drastically increasing number of isomers, and with $n + m = 4$ ions we have reached the limit of what is feasible for us with the available computing time. It would, of course be very interesting to extend the calculations to still larger species. On the basis of the experimental results, one might expect also the exchange of the fifth ligand to be exothermic. The reluctance of the clusters to accept a sixth one probably indicates that this step is slightly endothermic, and occurs as a result of thermal or collisional activation. Also computations of species which appear to be particularly stable, such as $Ag^+(NH_3)_6(H_2O)_2$ or $Ag^+(NH_3)_5(H_2O)$ would surely be of interest.

Comparison with Bulk Behavior. The DFT calculations and the results of the gas-phase reactions did not reveal a clear preference for linear coordination of Ag^+ cations as it is known from the bulk. What is different in aqueous solution? To address this question, it is instructive to compare the energetics of reactions 3 and 4:

$$Ag^+(NH_3)_3 + H_2O \rightarrow Ag^+(NH_3)_2(H_2O) + NH_3 \qquad (3)$$

$$\Delta H = +7.6\ \text{kJ/mol}$$
$$\Delta G = +7.5\ \text{kJ/mol}$$

$$Ag^+(NH_3)_3(H_2O) + H_2O \rightarrow Ag^+(NH_3)_2(H_2O)_2 + NH_3 \qquad (4)$$

$$\Delta H = +7.3\ \text{kJ/mol}$$
$$\Delta G = +1.1\ \text{kJ/mol}$$

These two reactions show the effect of stepwise hydration of the silver complex. Considering the enthalpy, the additional water ligand has almost no effect. Quite different is the situation if one takes entropy into account and looks at the Gibbs free energy. In this case, adding a water ligand favors the formation of the diammine complex.

Trying to transfer these observations to solution phase, it seems obvious, that freeing an NH_3 from the complex into solution considerably increases the entropy of the system and thus shifts the free energy in the desired direction. To quantify this effect, we modify reactions 3 and 4 by adding reaction 11, which leads to reactions (3′) and (4′) where bulk behavior is at least reflected on the ligand side:[47]

$$NH_3(g) + H_2O(l) \rightarrow NH_3(aq) + H_2O(g) \qquad (11)$$

$$\Delta H = +9.8\ \text{kJ/mol}$$
$$\Delta G = -1.5\ \text{kJ/mol}$$

$$Ag^+(NH_3)_3(g) + H_2O(l) \rightarrow Ag^+(NH_3)_2(H_2O)(g) + NH_3(aq) \qquad (3')$$

$$\Delta H = +17.4\ \text{kJ/mol}$$
$$\Delta G = +6.0\ \text{kJ/mol}$$

$$Ag^+(NH_3)_3(g) + H_2O(l) \rightarrow Ag^+(NH_3)_2(H_2O)(g) + NH_3(aq) \qquad (4')$$

$$\Delta H = +17.1\ \text{kJ/mol}$$
$$\Delta G = -0.4\ \text{kJ/mol}$$

Surprisingly, reaction 11 is only slightly exoergic. This means that the entropy increase due to the hydration of the ammonia molecules is almost exactly compensated by the loss of enthalpy due to the weaker interaction of NH_3 with the water network. Consequently, the entropy increase due to dissolving ammonia in water does not seem to be responsible for the formation of the diammine complex. The key thermochemical parameter probably is the solvent interaction of $Ag^+(NH_3)_3$ versus $Ag^+(NH_3)_2(H_2O)$. Adding solvent to these gas-phase species in the calculations by going from 3′ to 4′ shifts ΔG in the desired direction, which supports the idea that solvent effects promote the formation of the diammine complex. With increasing ammonia concentration, formation of the triammine complex has been observed by Bjerrum.[3] The interaction with the solvent environment seems to determine whether the diammine or triammine complex is formed.

Conclusions

The reaction of the gas-phase $Ag^+(NH_3)_{10-26}$ cluster ions with water vapor is the analogue to the well-known formation of the diammine silver complex $[Ag(NH_3)_2]^+$ in aqueous solutions, since both proceed in a large excess of H_2O. In the gas phase, the dominant products are species with three remaining NH_3 ligands, $Ag^+(NH_3)_3(H_2O)_m$, but at longer times cluster ions with only two ammonia ligands are also present. The reluctance of the third ammonia to be exchanged may be due to a slight change of the relative energies of the solvated ions in the cluster and in bulk solutions, or may reflect a high activation barrier for the exchange process, which is overcome in the large number of collisions in the bulk. Overall, the gas-phase reaction is in accordance to the bulk aqueous solutions, where depending on

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(47) Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, Melbourne, Tokyo, 2001.

the ammonia concentration either $Ag^+(NH_3)_2$ or $Ag^+(NH_3)_3$ seems to prevail.

In the complementary process, the reaction of hydrated silver cations $Ag^+(H_2O)_{25-45}$ with NH_3, again a ligand exchange reaction takes place, with first five ammonia molecules being very efficiently exchanged for water, and with a sixth one being taken up much more reluctantly. This rapid exchange confirms the results of our DFT computations that the NH_3 ligands are more strongly bound to the cation as long as they are in its immediate proximity. The limit of six NH_3 ligands, and the lack of exchange of more remote ligands reflects the weaker interactions between NH_3 molecules, the much higher volatility of ammonia, and its reduced ability to form extended hydrogen-bonded networks when compared with water.

The experiments show that in mixed clusters the first and second ammonia ligand, however, are much more strongly bound than water because they cannot be exchanged. The third ammonia ligand is also more strongly bound since it can only be replaced by water if the clusters are additionally activated by collisions or blackbody radiation. The binding energy of the fifth and fourth ammonia ligand is comparable to the binding energy of the respective water ligands because ligand exchange proceeds efficiently in both directions. The sixth NH_3 ligand, however, is much more weakly bound than a water ligand. It is taken up very reluctantly even in the reaction with 100% excess of NH_3 and very quickly replaced by water in the complementary reaction. This gradual transition of the relative water/ammonia binding energies is responsible for the observed coordination numbers.

The accompanying DFT calculations of small hydrated silver cations, $Ag^+(H_2O)_n$, $n = 1-4$, ammoniated silver cations, $Ag^+(NH_3)_n$, $n = 1-4$, and silver cations solvated by mixed ligands, $Ag^+(NH_3)_n(H_2O)_m$, $n,m = 1-3$, $n + m \leq 4$, clearly show that the coordination chemistry of silver is characterized by subtle differences in the binding energies between the first and second solvation shell. Cooperative effects in the surrounding solvent have to be taken into account to fully describe the observed effects. The coordination chemistry of silver cations is much more complex than the simple textbook picture of a linear, two-fold coordination would suggest.

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Supporting Information Available: *Z*-matrixes and thermochemical values of all calculated species (RTF). This material is available free of charge via the Internet at http://pubs.acs.org.

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