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A study of complexes $Mg(NH_3)_n^{+\cdot}$ and $Ag(NH_3)_n^{+}$, where n = 1–8: Competition between direct coordination and solvation through hydrogen bonding

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Abstract

Density functional calculations at B3LYP/6-31+G(d) and B3LYP/DZVP are reported for $Mg(NH_3)_n^{+\cdot}$, where n = 1–6 and for some solvated ions $Mg(NH_3)_n^{+\cdot} \ldots NH_3$ (n = 1–3, 6). After correction for basis set superposition errors, the enthalpies for sequential addition of NH_3 to $Mg^{+\cdot}$ resulting from direct coordination to the metal are 38.1, 26.6, 21.2, 13.7, 12.1, and 11.3 kcal mol^{-1}. The free energies for these same addition reactions are all negative, although for complexes with $n \geq 4$ the values are very small. Attempts at optimising structures with higher coordination numbers all resulted in the formation of solvated octahedral complexes. Enthalpies for solvation through hydrogen bonding to one of the ligated NH_3 molecules are all less than 16 kcal mol^{-1} and decrease rapidly as the number of ligated NH_3 molecules increases. Molecular orbital calculations at B3LYP/DZVP have been used to optimise structures for ions $Ag(NH_3)_n^{+}$, where n = 1–6. The five-coordinate and six-coordinate structures have very small binding enthalpies (4.3 and 2.6 kcal mol^{-1}) and the free energies for formation of these ions are positive. The binding energies for the addition of the first and second NH_3 molecules added to Ag^{+} are 40.1 and 36.1 kcal mol^{-1}, while those for the third and fourth additions are much smaller (15.1 and 11.0 kcal mol^{-1}). Adducts up to n = 3 have been detected in electrospray experiments. The first three adducts of Ag^{+} with NH_3 have been formed in the selected ion flow tube apparatus and multicollision induced dissociation experiments show $Ag(NH_3)_3^{+}$ to have a lower binding enthalpy than both $Ag(NH_3)_2^{+}$ and $Ag(NH_3)^{+}$. (Int J Mass Spectrom 201 (2000) 87–100) © 2000 Elsevier Science B.V.

Keywords: Density functional theory; Coordination numbers; Selected-ion flow tube; Electrospray; Collision-induced dissociation; Binding enthalpies

1. Introduction

In the gas phase, metal ions react with ligands such as amines, alcohols and carbonyl-containing compounds to form adducts in which the bonding is electrostatic [1–6]. In this type of bonding, in contrast with changes induced by formation of a covalent bond, the geometry of the ligand is often almost identical to that in the free ligand. Binding energies for monoadducts of singly charged ions are generally in the range 20–45 kcal mol^{-1} [5,7,8].

Our interests in the gas phase chemistry of metal ions have led us to study two very different ions;

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$Mg^{+\cdot}$ and Ag^+. $Mg^{+\cdot}$ is a radical cation with only one electron in the valence shell, while Ag^+ has a closed shell electronic configuration with a valence shell that is d^{10} and hence is closer to being valence saturated. Nevertheless, Ag^+ is considerably larger than $Mg^{+\cdot}$ and on steric grounds might be expected to accommodate a larger number of ligands. Preliminary experimental results on these ions suggested that this is not the situation and for this reason we have carried out a study to compare the coordination chemistries of these two metal ions. Ammonia, a powerful σ donor, has been selected as the ligand.

As a part of systematic experimental studies of the gas-phase chemistry of $Mg^{+\cdot}$, we have observed ions $Mg(NH_3)_n^{+\cdot}$, where $n = 1–5$ [9]. $Mg(NH_3)_5^{+\cdot}$ was only found in small amounts relative to the fourth adduct at high NH_3 flow rates and, if all five ammonia molecules are directly coordinated to the metal, then formally there are 11 valence electrons around the magnesium. Also our collision induced dissociation spectra provided some indication that there are two isomers of $Mg(NH_3)_4^{+\cdot}$ and we tentatively assigned these structures as a four coordinate isomer and a three coordinate isomer in which an additional ammonia is attached to one of the ligated ammonias through a hydrogen bond. By contrast, in electrospray mass spectrometry experiments we have observed only ions $Ag(NH_3)_n^+$, where $n = 1–3$. The higher coordination number of the smaller ion, $Mg^{+\cdot}$, and the apparent inability of Ag^+ to accept more coordinating ammonia molecules despite its "softness," led us to carry out a theoretical study of the NH_3 adducts of these two metal ions.

There have been several theoretical studies of $Mg^{+\cdot}$ ligated by small bases [4–8], but only three have involved NH_3. In the earliest study only the monoadduct, $Mg(NH_3)^{+\cdot}$, was reported and the binding energy was found to be 37.7 kcal mol^{-1} [5]. In a subsequent publication by the same authors the binding energy of the monoadduct was reported to be 39.0 kcal mol^{-1} [7], and most recently we have used MP4SDTQ(fc)/6-311++G(2df, p) calculations to obtain a value of 39.7 kcal mol^{-1} [9]. Addition of a second NH_3 molecule to form the adduct $Mg(NH_3)_2^{+\cdot}$ has been calculated to be exothermic by ~30 kcal mol^{-1} [7,9] and addition of a further NH_3 is considerably less exothermic. There are two literature values for the addition of the third NH_3, 24.2 [7] and 22.3 kcal mol^{-1} [9], and one for the fourth addition, 15.5 kcal mol^{-1} [9]. We are unaware of any experimental binding energies, although our multicollision induced dissociation (multi-CID) experiments indicate that the fourth adduct is rather weakly bound and that the energy for removal of NH_3 molecules increases as n decreases in $Mg(NH_3)_n^{+\cdot}$ [9].

Two-coordinate linear complexes of Ag^+ with NH_3 [10] and with imidazole [11] have been characterised by x-ray crystallography and four-coordinate tetrahedral complexes containing ligands such as acetonitrile [12] and pyridines [13–15] are known in the solid state. In a wide variety of neat solvents (water, pyridine, acetonitrile, trimethylphosphate, N,N-dimethylformamide, 1,1,3,3-tetramethylurea, dimethylsulfoxide, *n*-alkylamines and ethylenediamine) the structures of solvated Ag^+ is always four coordinate [16]. No higher coordination numbers have been observed experimentally, but molecular orbital calculations have shown that formation of trigonal bipyramidal $Ag(RCN)_5^+$ ($R = H, CH_3$) and octahedral $Ag(HCN)_6^+$ complexes are weakly exothermic [16].

The earliest quantitative study of complexes of Ag^+ in the gas phase involved use of high pressure mass spectrometry to give van't Hoff plots for the formation of complexes $Ag(H_2O)_n^+$ (where $n = 1–6$) and $Ag(NH_3)_n^+$ (where $n = 2–5$) [17]. For the reaction in Eq. (1) these measurements yielded binding enthalpies (in kcal mol^{-1}) of 36.9 ± 0.8 for $n = 2$, 14.6 ± 0.1 for $n = 3$, 13.0 ± 0.1 for $n = 4$, and 12.8 ± 0.2 for $n = 5$

$$Ag(NH_3)_n^+ + NH_3 \rightarrow Ag(NH_3)_{(n+1)}^+ \qquad (1)$$

In a subsequent high pressure mass spectrometry study Deng and Kebarle measured the energies for formation of diadducts AgL_2^+ (where L is water, primary alcohols, alkyl bromides, benzene, methyl acetate, alkyl ketones, ammonia, methyl cyanide, dimethyl sulfide and dimethyl sulfoxide), and reported that reaction of Ag^+ with two NH_3 molecules is exothermic by 85.6 kcal mol^{-1} [18]. Combining

Table 1
Total energies, unscaled zero-point and thermal energies and entropies at B3LYP/6-31+G(d) and B3LYP/DZVP

	B3LYP/6-31+G(d)				B3LYP/DZVP			
Molecule (**Structure Number**)	Energy (hartrees)	ZPE (kcal mol^{-1})	Thermal[a] (kcal mol^{-1})	Entropy (cal K^{-1} mol^{-1})	Energy (hartrees)	ZPE (kcal mol^{-1})	Thermal (kcal mol^{-1})	Entropy (cal K^{-1} mol^{-1})
$Mg(NH_3)^{+\cdot}$ (**1**)	−256.419 00	24.0	2.2	60.9	−256.408 66	23.9	2.2	61.0
$Mg(NH_3)_2^{+\cdot}$ (**2**)	−313.025 86	48.0	4.2	81.7	−313.022 70	47.8	4.3	82.8
$Mg(NH_3)_3^{+\cdot}$ (**3**)	−369.622 98	72.1	6.1	95.6	−369.626 80	71.8	6.2	96.6
$Mg(NH_3)_4^{+\cdot}$ (**4**)	−426.205 90	94.0	8.0	112.8	−426.208 07	92.9	8.5	113.2
$Mg(NH_3)_5^{+\cdot}$ (**5**)	−482.790 08	118.2	9.7	125.1	−482.795 37	116.6	10.3	124.6
$Mg(NH_3)_6^{+\cdot}$ (**6**)	−539.372 10	141.6	11.9	139.6	−539.380 63	140.4	11.9	139.8
$Mg(NH_3)^{+\cdot} \ldots NH_3$ (**1-1S**)	−313.003 91	47.7	4.1	81.0				
$Mg(NH_3)_2^{+\cdot} \ldots NH_3$ (**2-1S**)	−369.607 03	71.6	6.2	101.4				
$Mg(NH_3)_3^{+\cdot} \ldots NH_3$ (**3-1S**)	−426.199 97	95.6	8.2	117.1				
$Mg(NH_3)_6^{+\cdot} \ldots NH_3$ (**6-1S**)	−595.946 53	165.2	14.3	160.3	−595.960 65	163.7	14.1	160.1
$Mg(NH_3)_6^{+\cdot} \ldots 2NH_3$ (**6-2S**)	−652.519 90	189.3	16.2	181.6	−652.539 17	187.0	16.4	181.1
$Mg^{+\cdot}$	−199.795 55	—	0.89	36.8	−199.778 89	—	0.89	36.8
NH_3	−56.556 99	21.7	1.8	48.1	−56.564 04	21.7	1.8	48.2

[a] Sum of rotational, translational, and vibrational energies required to correct from 0 to 298 K.

this result with Holland and Castleman's exothermicity for the second addition gives a value of 48.7 kcal mol^{-1} for the formation of the first adduct, $Ag(NH_3)^+$.

We are unaware of any theoretical studies of $Ag(NH_3)_n^+$ complexes, although there has been a recent publication on monoadducts AgL^+ (where L = benzene, acetone, 2-pentene, and isoprene) in which theory and gas phase experimental chemistry using radiative association kinetics have been successfully combined [8].

2. Computational methods

All molecular orbital calculations were performed using GAUSSIAN 98 [19]. Structure optimisations were carried out using the density functional theory hybrid method at B3LYP [20–23]. The 6-31+G(d,) basis set [24–27] was used for structure optimisations on all the ions containing magnesium. As a check on the reproducibility of structural parameters, these optimisations were repeated using the double zeta valence polarization (DZVP) basis set [28], and this latter basis set was then used for optimisation of the $Ag(NH_3)_n^+$ complexes. All critical points were characterised by harmonic frequency calculations [29]. Calculated energies and entropies are given in Tables 1 and 2.

3. Experimental methods

Experiments using electrospray mass spectrometry were performed on a triple quadrupole SCIEX TAGA 6000E instrument. A solution of 5 mM silver nitrate in 5% ammonia/water was continuously infused into the electrospray probe at a flow rate of 2 μL min^{-1}. A Q1 scan revealed the presence of ions $Ag(NH_3)_n^+$, where $n = 0$–3; the $Ag(NH_3)_2^+$ ion was mass selected and a multi-CID was performed on this ion in q2 using argon as the collision gas, and at thickness [30] of 1.1×10^{15} atoms cm^{-2}; Q3 was then scanned to record the product ion spectrum.

A combination of an inductively coupled plasma (ICP) source, used to generate Ag^+, and a selected-

Table 2
Total energies, unscaled zero-point and thermal energies and entropies at B3LYP/DZVP

Molecule (**Structure Number**)	Energy (hartrees)	ZPE (kcal mol^{-1})	Thermal[a] (kcal mol^{-1})	Entropy (cal K^{-1} mol^{-1})
$Ag(NH_3)^+$ (**7**)	−5255.831 23	24.1	2.2	64.0
$Ag(NH_3)_2^+$ (**8**)	−5312.459 93	48.5	4.2	83.2
$Ag(NH_3)_3^+$ (**9**)	−5369.053 68	71.6	6.7	108.2
$Ag(NH_3)_4^+$ (**10**)	−5425.640 42	94.6	9.2	127.1
$Ag(NH_3)_5^+$ (**11**)	−5482.212 91	116.8	12.1	153.1
$Ag(NH_3)_6^+$ (**12**)	−5538.782 41	138.5	15.3	176.6
$Ag(NH_3)^+ \ldots NH_3$ (**7-1S**)	−5312.421 37	47.8	4.2	84.4
$Ag(NH_3)_2^+ \ldots NH_3$ (**8-1S**)	−5369.047 10	72.1	6.2	102.0
$Ag(NH_3)_3^+ \ldots NH_3$ (**9-1S**)	−5425.636 66	95.1	8.8	128.8
$Ag(NH_3)_4^+ \ldots NH_3$ (**10-1S**)	−5482.220 35	117.9	11.5	151.4
$Ag(NH_3)_4^+ \ldots (NH_3)_4$ (**11-4S**)	−5651.954 70	188.4	18.1	208.9
Ag^+	−5199.198 15	—	0.89	39.9

[a] Sum of rotational, translational, and vibrational energies required to correct from 0 to 298 K.

ion flow tube (SIFT), used to follow the addition of NH_3 and subsequent multicollision-induced dissociation, enabled us to study ions $Ag(NH_3)_n^+$, where $n = 1–3$. The SIFT has been described in detail elsewhere [31,32], and the initial report of using an ICP as the ion source is currently in press [33]. Briefly, Ag^+ was generated from a 5 ppm silver nitrate solution in 2% nitric acid sprayed into the ICP torch by argon. The Ag^+ ions were selected for study in the SIFT and these plasma ions were allowed to thermalise by collisions with the SIFT buffer gas (helium at 0.35 ± 0.01 Torr) prior to reaction with NH_3. The tube temperature was 296 ± 2 K.

4. Results and discussion

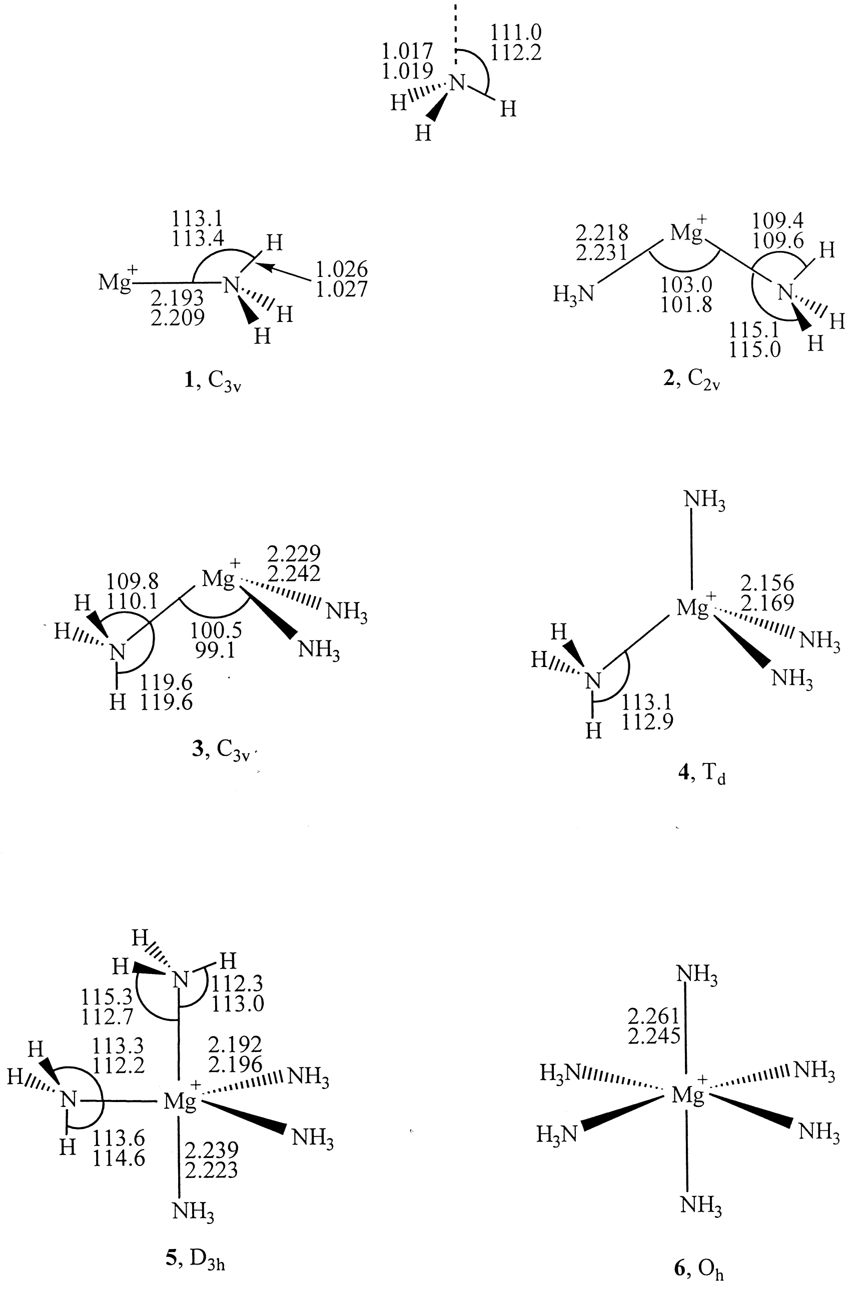
4.1. Structural features

4.1.1. Directly coordinated complexes, $Mg(NH_3)_n^{+\cdot}$

The structures of $Mg(NH_3)_n^{+\cdot}$ ($n = 1–6$) complexes in which NH_3 is directly coordinated to magnesium are given in Fig. 1. All these structures were optimised with two different basis sets: 6-31+G(d) and DZVP. The bond lengths from the 6-31+G(d) basis set calculations are consistently slightly smaller than those from the DZVP calculations, with the exception of the bonds in **5** (axial bonds only) and **6**. Overall, the optimised geometries from the different levels of theory are very similar and, consequently, in the remainder of the work we only optimised at one level. For simplicity, in the comparisons discussed below we use only parameters from the B3LYP/6-31+G(d) calculations; exactly the same patterns are followed using the DZVP results. Ions **1**, **2** and **3** have symmetries C_{3v}, C_{2v}, and C_{3v}, respectively, even when the hydrogen atoms are included; however, for **4**, **5** and **6** the symmetries given refer only to the locations of the nitrogen atoms.

Addition of NH_3 to a $Mg(NH_3)_n^{+\cdot}$ complex has minimal effect on the geometry of the added NH_3. For example, formation of $Mg(NH_3)^{+\cdot}$ results in elongation of the N–H bonds by only 0.009 Å and the Mg–N–H angle is 2° larger in the complex than the corresponding angle in NH_3. Similar changes occur in other complexes; consequently in Fig. 1 for simplicity we have included only angles that show larger changes.

The Mg–N distances increase with increases in n



1, C_{3v} **2**, C_{2v} **3**, C_{3v} **4**, T_d **5**, D_{3h} **6**, O_h

Fig. 1. Structures of $Mg(NH_3)_n^{+\cdot}$ for directly coordinated complexes as optimised at B3LYP/6-31+G(d) (upper numbers) and at B3LYP/DZVP (lower numbers). Bond lengths are in angstroms and the bond angles are in degrees.

on going from $Mg(NH_3)^{+\cdot}$, **1**, to $Mg(NH_3)_3^{+\cdot}$, **3**, consistent with a decrease in the binding energies. The most interesting geometric feature of these three complexes is that the N–Mg–N bond angle in **2** is 103.0° and that in **3** is 100.5°. $Mg^{+\cdot}$ has one unpaired electron in its valence shell and one explanation is that in $Mg(NH_3)^{+\cdot}$ this electron is polarised away from the Mg–N bond and the second NH_3 then approaches the opposite side from the unpaired electron [7]. An alternative explanation is that bonding occurs through donation from the lone pair on each nitrogen into the vacant *p* orbitals of magnesium, and there is a slight increase in the bond angle from the expected 90° due to steric interaction between the two ligands [9]. This type of bonding, where the unpaired electron essentially remains in the 3*s* orbital, can be attributed to the larger *s*-*p* gap that occurs in the second full row of the Periodic Table. This type of bonding would also lead to the three-coordinate ion, **3**, having small N–Mg–N angles and in fact the angles in **3** are smaller than that in **2**.

$Mg(NH_3)_4^{+\cdot}$ is tetrahedral with Mg–N distances that are the shortest in all the six complexes examined. This contrasts markedly with the structure calculated for $Mg(H_2O)_4^{+\cdot}$, where all four water molecules were found to be on the *same* side of the magnesium, essentially in a square planar arrangement with the $Mg^{+\cdot}$ sitting above the plane [6]. All attempts to optimise such a structure for $Mg(NH_3)_4^{+\cdot}$ resulted in the tetrahedral arrangement.

In $Mg(NH_3)_5^{+\cdot}$ the axial bonds are slightly longer (by 0.047 Å) than the equatorial ones, a situation that is usually attributed to the higher *d* character in the axial bonds. The axial bonds are unusually long (2.239 Å) and, of the complexes studied here, only the octahedral complex, **6**, has longer bond lengths.

4.1.2. Solvated complexes, $Mg(NH_3)_n^{+\cdot} \ldots NH_3$

Addition of a second NH_3 to $Mg(NH_3)^{+\cdot}$ can, in principle, occur through hydrogen bonding to the ligated NH_3 as in structure **1-1S**. This interaction delocalises some of the charge onto the solvating NH_3 and results in a shortening of the Mg–N distance (from 2.193 to 2.138 Å) and a lengthening (from 1.026 to 1.057 Å) of the N–H bond that is involved in the hydrogen bond.

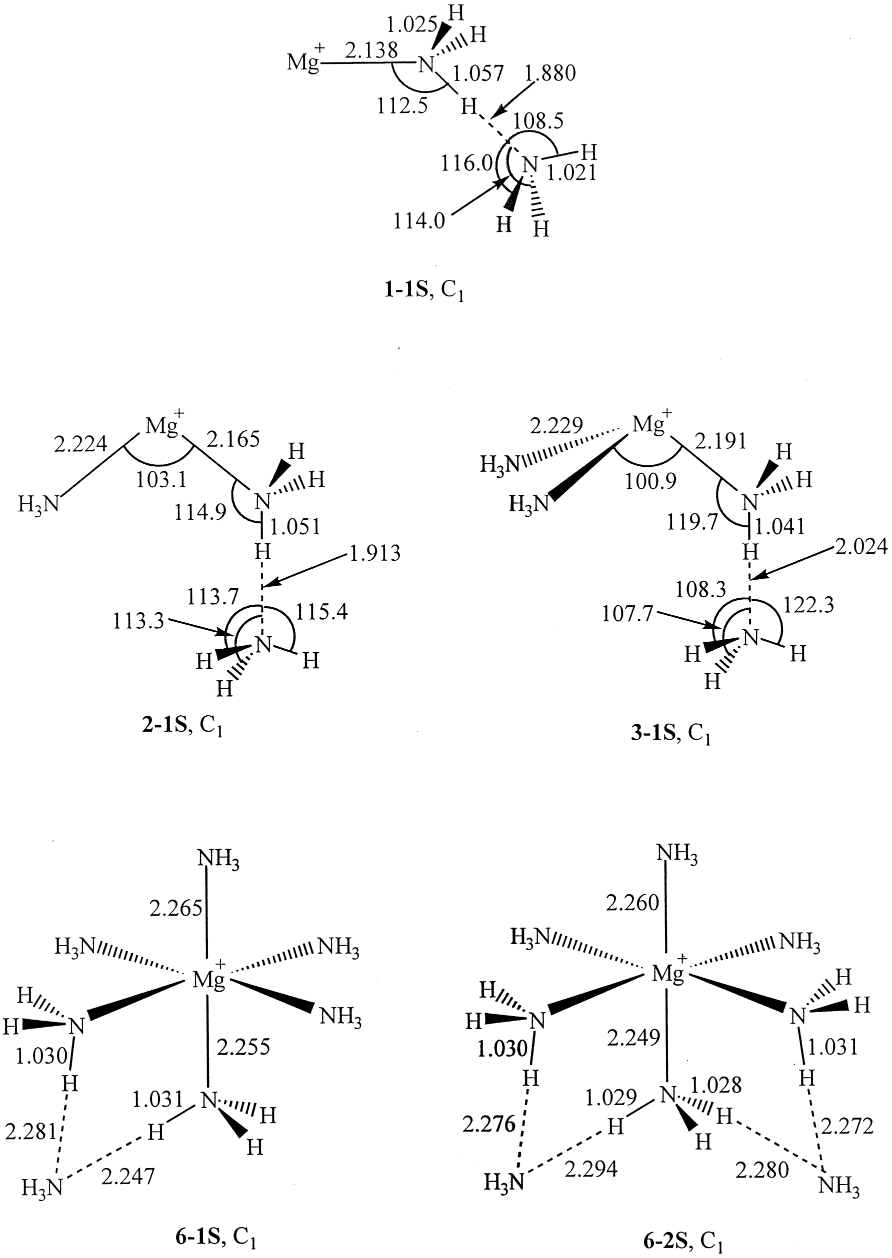
In Fig. 2 we present geometric parameters for ions $Mg(NH_3)_n^{+\cdot} \ldots NH_3$ where $n = 1$–3. These ions display a trend in which the N–H distance decreases from 1.057 Å in **1-1S** to 1.041 Å in **3-1S**, and H . . . N increases from 1.880 to 2.024 Å. These structural changes indicate that solvation through hydrogen bonding has the largest effect when $n = 1$ and the smallest when $n = 3$. Curiously the only experimental evidence that we obtained from our CID experiments was for the existence of a small amount of $Mg(NH_3)_3^{+\cdot} \ldots NH_3$.

In an attempt to obtain the highest possible coordination number for $Mg^{+\cdot}$ we tried to optimise structures with both seven and eight directly coordinated NH_3 molecules. Both of these optimisations collapsed into octahedral structures, ions **6-1S** and **6-2S**, in which the additional NH_3 molecules solvate the octahedral complex. Structures **6-1S** and **6-2S** are unusual in that the solvating NH_3 molecules are not directly hydrogen bonded to only one hydrogen atom of a coordinated NH_3, but are positioned between two NH_3 molecules. Effectively the nitrogen atoms in the solvating molecules are five coordinate. However, we did not pursue these structures in more detail because examination of the energetics revealed that the free energies for formation of the octahedral ion **6** and of the solvated ions **6-1S** and **6-2S** are close to zero and possibly positive.

4.1.3. Directly coordinated complexes, $Ag(NH_3)_n^+$

The structures of the $Ag(NH_3)_n^+$ complexes (n = 1–6), ions **7-12**, follow a predictable pattern (Fig. 3). As in the $Mg(NH_3)_n^{+\cdot}$ complexes, the structural parameters of the ligated NH_3 molecules are very similar to those of the free NH_3.

In solution and in the solid state Ag^+ frequently is dicoordinate with an angle of 180° between the ligands and this is the geometry found for the $Ag(NH_3)_2^+$ ion **8**. Complex $Ag(NH_3)_3^+$ ion **9** has essentially a trigonal pyramidal structure and ions **10**, **11**, and **12** are tetrahedral, trigonal bipyramidal, and octahedral when the positions of only the nitrogen atoms are considered. In structure **11** the axial bonds differ by 0.014 Å due to the orientation of the NH_3 molecules. Both axial bonds are more than 0.13 Å longer than the equatorial bonds, a much larger difference than in the Mg–N distances in $Mg(NH_3)_5^{+\cdot}$. As the number of ligands increases, the Ag–N distances also systematically increase, with one notable exception, ion **8**, where the Ag–N distance is the shortest found in any of these complexes. The differ-



1-1S, C_1

2-1S, C_1

3-1S, C_1

6-1S, C_1

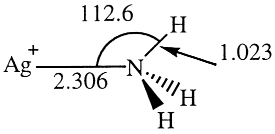
6-2S, C_1

Fig. 2. Structures of $Mg(NH_3)_n^{+\cdot}$ complexes solvated by NH_3 molecules as optimised at B3LYP/6-31+G(d). Bond lengths are in angstroms and the bond angles are in degrees.

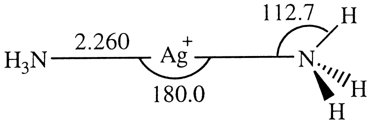
ence in the Ag–N distances vary from 2.260 to 2.668 Å, a range of over 0.4 Å; this contrasts with a difference of only 0.105 Å in the $Mg(NH_3)_n^{+\cdot}$ complexes.

4.1.4. *Solvated complexes, $Ag(NH_3)_n^+ \ldots NH_3$*

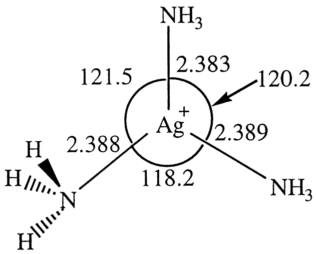
Solvating a directly coordinated NH_3 by attaching another NH_3 molecule through a hydrogen bond results in a decrease in the Ag–N distance for the



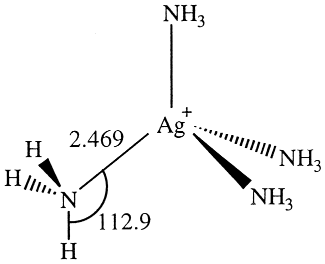
7, C_{3v}



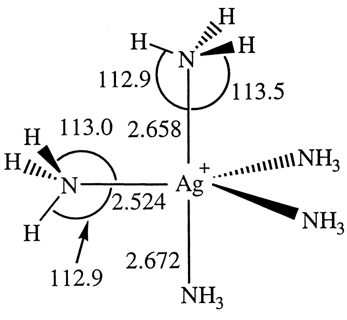
8, C_{3v}



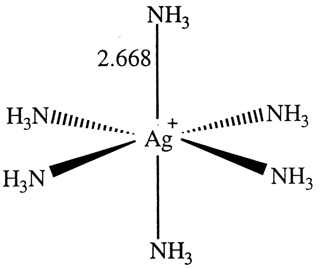
9, C_1



10, T_d



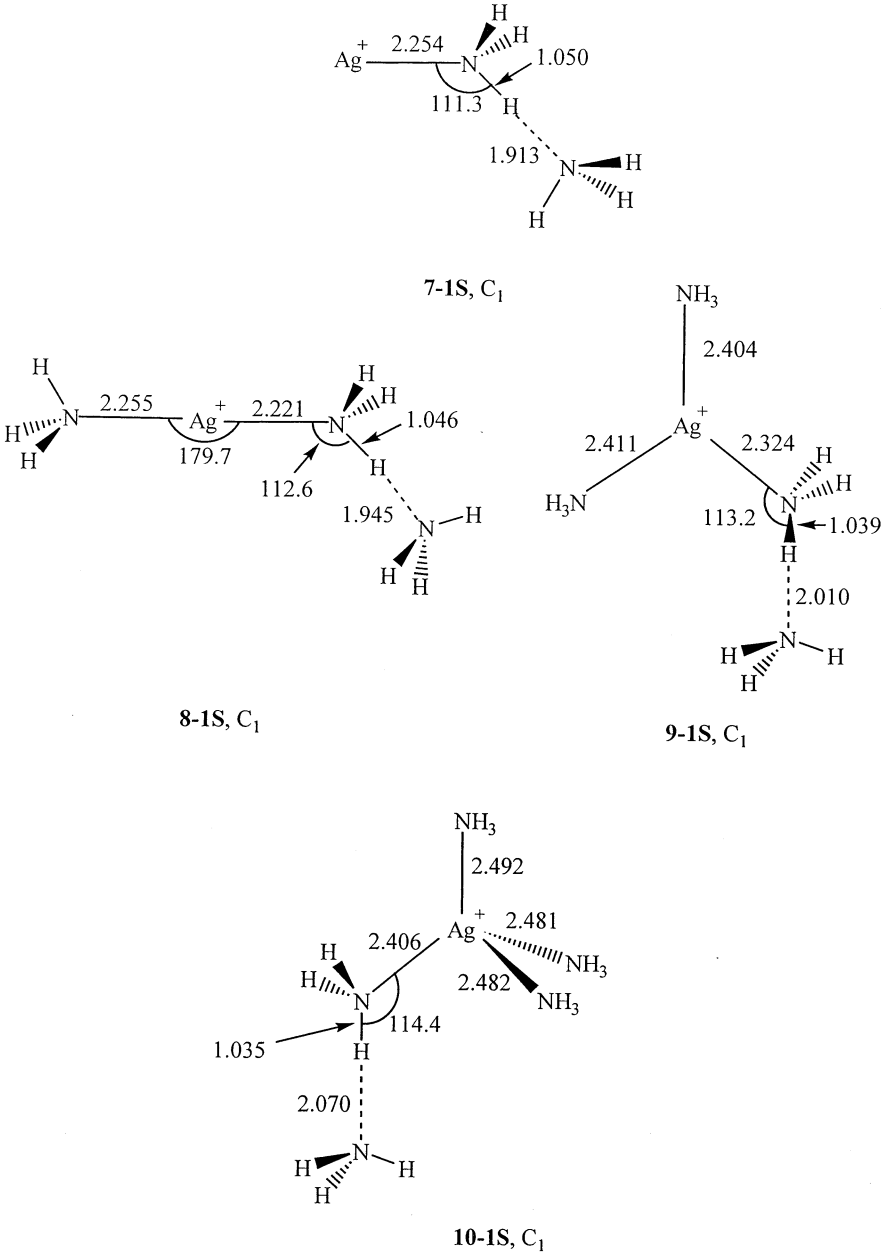
11, C_1



12, O_h

Fig. 3. Structures of $Ag(NH_3)_n^+$ for directly coordinated complexes as optimised at B3LYP/DZVP. Bond lengths are in angstroms and the bond angles are in degrees.

ligated molecule (Fig. 4). Curiously this change increases with n and reaches a maximum of 0.063 Å when **10-1S** is formed from **10**. The same type of geometric trends, as noted in the solvation of the $Mg(NH_3)^{+\cdot}$ ions, also occurs in the $Ag(NH_3)_n^+ \ldots NH_3$ ions, namely for the bonds around the hydrogen atom involved in the hydrogen bonding, the N–H distances decrease and the N . . . H distances increase as the number of NH_3 molecules attached to the metal increases. In $Ag(NH_3)^+ \ldots NH_3$, ion **7-1S**, the N–H distance is 1.050 Å and this decreases monotonically as n increases to 1.035 Å in $Ag(NH_3)_4^+ \ldots NH_3$, **10-1S**. Over this same range of four complexes, the N . . . H distances increase monotonically from 1.913 Å in **7-1S** to 2.070 Å in **10-1S**. These geometric changes indicate that the hydrogen bonding interaction is becoming weaker as the number of ligating NH_3 molecules increases.



7-1S, C_1

8-1S, C_1

9-1S, C_1

10-1S, C_1

Fig. 4. Structures of $Ag(NH_3)_n^+$ complexes solvated by NH_3 molecules as optimised at B3LYP/DZVP. Bond lengths are in angstroms and the bond angles are in degrees.

4.2. Energetics

4.2.1. Magnesium complexes

Bonding enthalpies for direct coordination of NH_3 molecules with $Mg^{+\cdot}$ are given in Table 3. There is good agreement between the two levels of theory except for the formation of $Mg(NH_3)^{+\cdot}$, where the DZVP result is anomalously low. In all molecular orbital calculations on dissociation reactions, deficiencies in the basis sets result in the adduct being

Table 3
Enthalpies and free energies for reactions $Mg(NH_3)_n^{+\cdot} + NH_3 \rightarrow Mg(NH_3)_{(n+1)}^{+\cdot}$ [a,b]

	B3LYP/6-31+G(d)				B3LYP/DZVP	
Product	$\Delta H_{un}(298)$[d]	BSSE	$\Delta H_{cor}(298)$	$\Delta G_{cor}(298)$	$\Delta H_{un}(298)$	$\Delta G_{un}(298)$
1	−40.5	2.4	−38.1	−30.9	−40.1	−32.0
2	−29.4	2.8	−26.6	−18.4	−28.9	−21.0
3	−23.3	2.2	−21.1	−10.9	−22.7	−12.5
4	−16.6	2.9	−13.7	−4.5	−10.9	−1.5
5	−15.3	3.2	−12.1	−1.4	−12.6	−1.6
6	−14.2	2.9	−11.3	−1.3	−11.4	−1.6
1-1S	−15.4	—	—	−7.1[c]		
2-1S	−13.1	—	—	−4.6[c]		
3-1S	−8.4	1.2	−7.2	+0.7		
6-1S	−8.4	—	—	−0.3[c]		
6-2S	−17.4	—	—	−1.2[c]		

[a] All energies are in kcal mol^{-1}.

[b] The subscripts un on $\Delta H_{un}(298)$ and on $\Delta G_{un}(298)$ indicate *no* correction for BSSE; $\Delta H_{cor}(298)$ and $\Delta G_{cor}(298)$ have been corrected.

[c] Not corrected for BSSE.

[d] These numbers are slightly different from those in [9] because of an incorrect value previously used for the zero-point energy of NH_3.

described more fully than the dissociation products. Counterpoise method calculations, in which ghost orbitals are added to the basis sets for the dissociation products at the geometry of the adduct, provide a means of assessing this basis set superposition error (BSSE) [34]. We have performed BSSE calculations on all the directly coordinated ions at B3LYP/6-31+G(d) and find the correction to be between 2.2 and 3.2 kcal mol^{-1}. The net effect of these corrections is to reduce the binding enthalpies, but the overall pattern remains the same with the first adduct having a binding enthalpy of 38.1 kcal mol^{-1}, the second 26.6 kcal mol^{-1}, and the third 21.1 kcal mol^{-1}. The next three adducts have almost identical binding enthalpies, ranging from 13.7 to 11.3 kcal mol^{-1}. Combination of these enthalpies with entropies give $\Delta G(298)$ values for the formation reactions that are negative, but the values for formation of the fourth, fifth and sixth adducts, ions **4**, **5** and **6**, are all very small. From our experimental data [9] we obtained upper estimates of $\Delta G°(298)$ for the reactions in Eqs. (2) and (3)

$$Mg(NH_3)_2^{+\cdot} + NH_3 \rightarrow Mg(NH_3)_3^{+\cdot} \qquad (2)$$

$$Mg(NH_3)_3^{+\cdot} + NH_3 \rightarrow Mg(NH_3)_4^{+\cdot} \qquad (3)$$

The experimental value for reaction (2) is ≤ -8.8 kcal mol^{-1} and this compares with the calculated value of -10.9 kcal mol^{-1}; for reaction (3) experiment gives ≤ -6.4 kcal mol^{-1} compared with the calculated value of -4.5 kcal mol^{-1}.

Dissociation of solvated ions involves only the breaking of a long bond and calculations of this type of dissociation are less susceptible to basis set superposition errors. We calculated the BSSE correction for **3-1S** to be 1.2 kcal mol^{-1} and this compares with a value of 2.9 kcal mol^{-1} for the isomeric ion **4**. Inclusion of the BSSE correction for **3-1S** resulted in a $\Delta G(298)$ value of $+0.7$ kcal mol^{-1}; this compares with a $\Delta G(298)$ value of -4.5 kcal mol^{-1} for formation of **4**. It is difficult to estimate the error in these computed numbers, possibly ±2 kcal mol^{-1}, and any small change in ΔG could make formation of **3-1S** exoergic. On the basis of CID results on $Mg(NH_3)_3^+$, we have argued previously that two isomers exist in the SIFT experiments and that the sterically less hindered solvated ion $Mg(NH_3)_2^+ \ldots NH_3$ is dominant [9]. Following this line of argument, if only one isomer of $Mg(NH_3)_4^+$ exists, as suggested by our previous experimental data [9], and it has a very low dissociation energy, then it probably is the solvated ion **3-1S**, formed by a sterically preferred exoergic or slightly endoergic solvation reaction at room temperature.

The uncorrected $\Delta G(298)$ values for reaction of

Table 4
Enthalpies and free energies for reactions $Ag(NH_3)_n^+ + NH_3 \rightarrow Ag(NH_3)_{(n+1)}^+$[a]

Product	$\Delta H_{un}(298)$	BSSE	$\Delta H_{cor}(298)$	Expt. $\Delta H(298)$[b]	$\Delta G_{cor}(298)$	Expt. $\Delta G(298)$[b]
7	−42.0	1.9	−40.1		−32.9	—
8	−38.3	2.3	−36.1	−36.9 ± 0.8	−27.5	−27.2
9	−17.1	2.0	−15.1	−14.6 ± 0.1	−8.2	−7.3
10	−12.9	1.9	−11.0	−13.0 ± 0.1	−2.3	−4.1
11	−4.3	—	—	−12.8 ± 0.2	+2.3[c]	−2.6
12	−2.6	—	—		+4.7[c]	
7-1S	−14.7	—	—		−6.5[c]	
8-1S	−12.4	—	—		−3.6[c]	
9-1S	−9.7	—	—		−1.5[c]	
10-1S	−8.4	—	—		−1.3[c]	
10-4S	−30.1	—	—		+2.9[c]	

[a] All energies are in kcal mol^{-1}.
[b] Reference [17].
[c] Not corrected for BSSE.

the solvated ions examined in Table 3 are all negative, but small. Inclusion of BSSE corrections for **6-1S** and **6-2S** would probably result in positive ΔG values.

4.2.2. Silver complexes

Two NH_3 molecules are tightly bound to Ag^+, with binding enthalpies calculated to be 40.1 and 36.1 kcal mol^{-1} (Table 4). The third and fourth NH_3 molecules are much more weakly bound, with binding enthalpies of 15.1 and 11.0 kcal mol^{-1}. The calculated ΔH and ΔG values for the reaction of $Ag(NH_3)^+$, $Ag(NH_3)_2^+$, and $Ag(NH_3)_3^+$ with NH_3 (reactions (1) with $n = 1$, 2, and 3) are all in excellent agreement with Holland and Castleman's experimental values [17].

Addition of a fifth NH_3 is calculated to be weakly exothermic (−4.3 kcal mol^{-1}) and it is estimated that inclusion of a BSSE correction would reduce this to ≈−2 kcal mol^{-1}. However, even using the uncorrected ΔH values for formation of this fifth adduct results in a positive ΔG and we conclude that directly coordinated $Ag(NH_3)_5^+$ does not exist. This is a surprising conclusion and potentially is in conflict with the experimental determination of a ΔH value reported for reaction (1) with $n = 4$. However, ΔG for formation of the solvated complex $Ag(NH_3)_4^+ \ldots NH_3$, **10-1S**, is negative but small (−1.3 kcal mol^{-1}) and, as the BSSE correction for this ion is likely to be very small, we conclude that this ion should exist and is probably the ion that was formed in the high pressure mass spectrometry study [17]. The calculated binding enthalpy for this ion of 8.4 kcal mol^{-1} is lower than the experimental value of 12.8 ± 0.2 kcal mol^{-1}.

The free energies for solvation by NH_3 of the smaller complexes, $Ag(NH_3)_n^+$, where $n = 1$–3, are all negative, indicating that ions **7-1S**, **8-1S**, and **9-1S** are stable toward dissociation. However, in each instance, the directly coordinated ions, **8**, **9** and **10**, have much better energies and are likely to be the dominant forms.

4.2. Experimental results for $Ag(NH_3)_n^+$ ions

Electrospraying a solution of $AgNO_3$, in the presence of 5% ammonia and using a potential difference of 0–0.5 V between the orifice and q0 produced a very simple spectrum comprising $Ag(NH_3)_2^+$ and <5% of $Ag(NH_3)^+$ and $Ag(NH_3)_3^+$. Increasing the potential difference led to fragmentation in the lens region of $Ag(NH_3)_2^+$ to $Ag(NH_3)^+$ and to Ag^+. This phenomenon is more apparent in an energy-resolved CID experiment (Fig. 5) wherein sequential cleavage of NH_3 from $Ag(NH_3)_2^+$ is evident. The low abundance of $Ag(NH_3)_3^+$ and the absence of $Ag(NH_3)_4^+$, even under conditions of nominally zero potential gradient, is attributed to the relatively low binding enthalpies of the third and fourth NH_3 to Ag^+, and to the large number of collisions (hence activation steps)

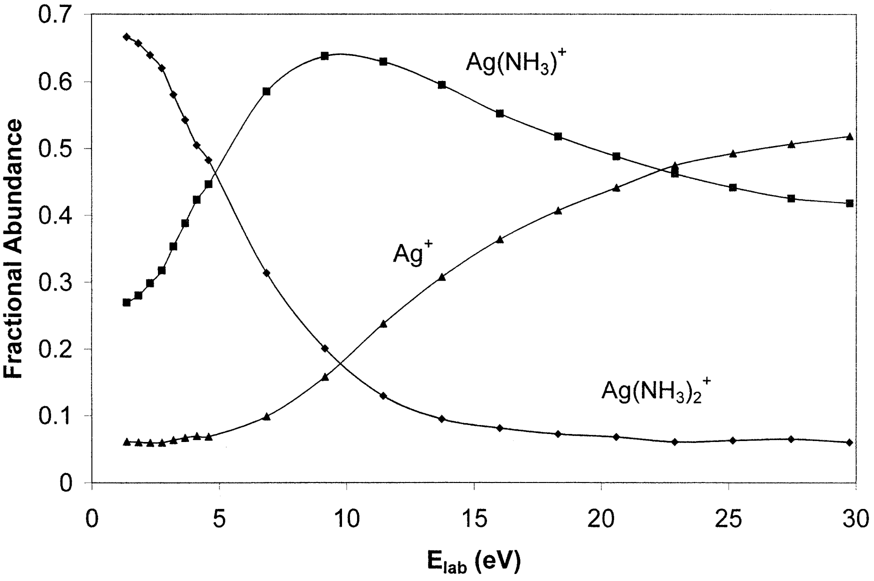


Fig. 5. Energy-resolved collision induced dissociation of $Ag(NH_3)_2^+$. Argon was used as the collision gas with a collision gas thickness of 1.1×10^{15} atoms cm^{-2} in $q2$. Solution used was 5 mM silver nitrate in a 5% ammonia/water (*V*/*V*).

the adduct ions underwent while being sampled from the source at atmospheric pressure to $q0$.

Observation of these ions encouraged us to "synthesise" $Ag(NH_3)_n^+$ ions in the SIFT apparatus. Three adducts were observed under our experimental conditions (Fig. 6). The rate coefficients (in cm^3 mole-

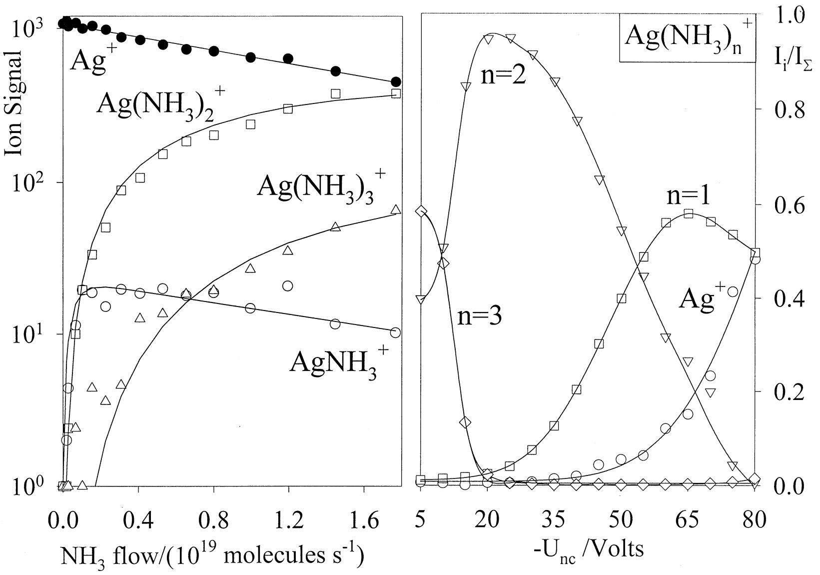


Fig. 6. (Left) Experimental data recorded for the reaction of Ag^+ with NH_3 in helium gas at 296 ± 2 K and 0.35 ± 0.01 Torr. The Ag^+ ions were produced in an ICP source. The solid lines represent a fit to the experimental data with the solution to the differential equations appropriate for the sequential addition reactions. Rate coefficients derived from the fit are given in the text. (Right) Results of multicollision CID experiments. The flow of NH_3 was 4.0×10^{20} molecules s^{-1}.

cule^{-1} s^{-1}) for the sequential addition reactions were found to be 2.6×10^{-12} for $n = 0$–1, 1.0×10^{-10} for $n = 1$–2, and 1.9×10^{-12} for $n = 2$–3. For the first reaction the collision rate coefficient calculated using transition state/classical trajectory theory is 2.1×10^{-9} cm^3 molecule^{-1} s^{-1} [35]. All are apparent bimolecular rate coefficients at 296 ± 2 K and at a helium buffer flow of 0.35 ± 0.01 Torr. We estimate that the relative uncertainty in these reaction rate coefficients does not exceed 10%; however, the absolute error may be as high as 30%. The higher rate coefficient for formation of the second adduct, as compared to that for the first, is attributed to the first addition being inefficient (only 0.13 efficient) due to the small number of degrees of freedom in the collision complex between Ag^+ and NH_3, resulting in a short-lived complex. The third addition is slower due to the much lower exothermicity of this reaction. The CID spectrum given in the right hand side of Fig. 6 shows the third adduct breaking up at lower collision energies, while the second and first adducts both require much higher nose-cone voltages for dissociation. This observation is in agreement with our molecular orbital calculations, where the binding energies of the first and second adducts are similar and are much larger than that of the third adduct. For the second, third, and fourth adducts Holland and Castleman's experimental ΔH and ΔG values [17] are in excellent agreement with our calculated values. The agreement with Deng and Kebarle's binding energy for formation of $Ag(NH_3)_2^+$ is less satisfactory. The calculations give a value of 76.2 kcal mol^{-1}, while the experimental value is 85.6 kcal mol^{-1} [18].

The lack of formation of adducts with n greater than three in the SIFT can be attributed to a combination of the low binding enthalpy of $Ag(NH_3)_4^+$ and the relatively short length of time that appreciable amounts of $Ag(NH_3)_3^+$ and NH_3 are together.

5. Conclusions

Molecular orbital calculations provide binding enthalpies that indicate formation of complexes $Mg(NH_3)_n^{+\cdot}$ with values of n up to six should be possible. However, the free energies for formation of ions $Mg(NH_3)_5^{+\cdot}$ and $Mg(NH_3)_6^{+\cdot}$ are very small. In keeping with these calculations, the first four adducts, ions 1–4, have been made in the SIFT and the fifth adduct has been detected in small amounts at high NH_3 flow rates. Formation of solvated ions in which the solvating NH_3 forms a hydrogen bond with a hydrogen atom of a ligated NH_3 molecule is always energetically less favourable relative to formation of the isomeric directly coordinated ions.

Molecular orbital calculations on ions $Ag(NH_3)_n^+$ show that the binding enthalpies of the two smallest complexes ($n = 1$ and 2) are large (approximately 40 kcal mol^{-1}), the binding enthalpies of the third and fourth adducts are much smaller (15.1 and 11.1 kcal mol^{-1}) and those of even higher adducts are almost zero. For adducts $Ag(NH_3)_5^+$ and $Ag(NH_3)_6^+$ the free energies of the reactions in which these ions are formed by addition of one NH_3 molecule are positive. We conclude therefore that only the first four adducts, ions **7–10**, should exist. The first three ions were detected in electrospray experiments, but with only mono- and diadducts being present in large amounts. The fifth adduct, for which the enthalpy of formation was measured from high pressure mass spectrometry, is most probably the fourth adduct with an additional NH_3 molecule providing solvation through hydrogen bonding (ion **10-1S**). Reaction of Ag^+ with NH_3 in the SIFT produced only the first three adducts, with no evidence of the fourth adduct even at high flow rates. CID experiments on these adducts showed $Ag(NH_3)_3^+$ to have a much lower dissociation energy than the two smaller complexes. There are thermochemical data for the addition of NH_3 to $Ag(NH_3)_4^+$, and based on our calculations, this appears to be for solvation of the tetrahedral complex rather than for the formation of the directly coordinated ion $Ag(NH_3)_5^+$.

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Note added in proofs

In a recent publication (A. Anderes, F. Munteau, D. Walter, C. Rue, P.B. Armentrout, J. Phys. Chem. A 104 (2000) 692) Armentrout and coworkers report that optimisation at MP2/6-31G(d) of mg$(NH_3)_4^{+\cdot}$ in which all four ammonia molecules are directly coordinated to the magnesium results in a distorted square planar structure (C_{2v} symmetry) as opposed to the tetrahedral structure that we report here. As a check on the validity of our results Dr C.F. Rodriquez of this Department has now used B3LYP/6-31++G(d,p) calculations to optimise structures for directly coordinated $Mg(NH_3)_4^{+\cdot}$ complexes and finds that *both* the tetrahedral and distorted square planar complexes are at minima with the *former* having the lower energy (by 1.3 kcal mol^{-1} when zero-point energy is included).

For directly coordinated $Mg(NH_3)_5^{+\cdot}$ using B3LYP/6-31++G(d,p) calculations Rodriquez was unable to find a critical point corresponding to the square pyramidal structure that Armentrout and coworkers report to be at the global minimum. The only directly coordinated structure that he found to be at a minimum using B3LYP/6-31++G(d,p) calculations has the trigonal bipyramidal structure reported here.

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