Explanation of the Anomalous Complexation of Silver(I) with Ammonia in Terms of the Poor Affinity of the Ion for Water

Michael Antolovich,*,† Leonard F. Lindoy,‡ and Jeffrey R. Reimers‡

School of Information Technology, Charles Sturt University, Bathurst, NSW 2795, and School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

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Silver(I) complexes with ammonia show the anomalous property that in aqueous solution the second association constant is larger than the first. This effect is known not to arise from gas-phase energetic effects or from any known mechanism through which similar anomalous behavior has been observed for other systems. Using density-functional theory (DFT) calculations for the inner-shell gas-phase complexes of Cu(I), Ag(I), and Au(I) with ammonia and/or aquo ligands, we conclude that the anomalous behavior of Ag(I) arises from its poor affinity for the solvent. Addition of the first ammonia results in the exclusion of not one but two water molecules from the inner solvation shell, selectively reducing the equilibrium constant for the first association. This is a strong specific solvation effect that cannot be described using dielectric continuum models of solvation.

Introduction

It is well established that ammonia has a strong preference to react with the Ag^+ in aqueous solution to produce the stable $[Ag(NH_3)_2]^+$ complex ion. This species also forms in the solid state.[1] In the past, the unusual propensity for silver toward two-coordination has been attributed to the linear sd hybridization[2−4] known for this group of the periodic table.[5] The stepwise formation constants for most simple metal complexes follow the general rule[2] that K_1 is the largest, with successive stepwise constants decreasing in a regular manner, reflecting progressive charge neutralization of the central metal ion, the increasing influence of steric hindrance, and/or statistical effects. As indicated in Table 1, the formation of $[Ag(NH_3)_2]^+$ is unusual in that K_2 is larger than K_1.[6,7] Occasionally, other complexes have been shown to exhibit similar anomalous stepwise stability behavior (see, for example, Irving et al.[8]), but this can usually be related to specific steric and/or electronic effects such as change in the metal's spin state. Silver(I) is a d^{10} metal ion and, hence, is unable to exhibit spin-state change, while ammonia is a small unidentate ligand, and so, interligand steric effects, at least for low coordination numbers, are expected to be minimal. Furthermore, previous gas-phase studies[9] have shown that this effect appears not to be intrinsically associated with the nature of the silver−ammonia bonding.

For small-to-medium-sized clusters of ammonia and/or water with Ag(I), calculations and gas-phase-cluster mass spectroscopy have shown that subtle solvent effects involving first and second coordination shells are extremely important.[10] Outer-sphere solvent effects are also known to be important for a number of processes including the *N*-alkylation of nickel and chromium amine complexes.[11] We examine the possibility that inner-sphere solvent effects are responsible for the anomalous equilibrium constant in the silver diammine case. Density-functional theory (DFT) calculations were performed to evaluate the free energies of the reactions in which the full inner coordination shell is explicitly included; in this model, the most important contributions from solvation are included in an approach amenable to high-level computations.[10] The observed product formation constants $\beta_2 = K_1K_2$ for the ammine complexes of Cu(I), Ag(I), and Au(I) are shown in Table 1; another irregularity is apparent for Ag(I), with its value of β_2 being much less than those for Cu(I) and Au(I). Hence, we investigated the inner-sphere ammine and/or mixed aquo complexes of Cu(I), Ag(I), and Au(I) in order to probe the causes of the observed anomalous properties of Ag(I).

TABLE 1: Observed Stepwise Formation Constants K_n's for the Production of $M^+(NH_3)$ and $M^+(NH_3)_2$ in Solution[a]

ion	log K_1	log K_2	log β_2[b]	ref
Cu(I)			11.381	41
Ag(I)	3.3	3.89	7.20	6
	3.367	3.884	7.251	7
Au(I)			26.5[c]	42

[a] For Cu(I), $K_3 = -1.42$ from ref 43, for Ag(I), $K_3 = -1.60$ from ref 44. [b] $\beta_2 = K_1K_2$. [c] Estimate only.

Methods

The DFT technique was used to determine molecular structures and vibration frequencies using *Gaussian 98*.[12] The SDD[13] basis set was used for Ag(I), Cu(I), and Au(I), while aug-cc-pVDZ[14] was used for the ligands. All calculations employed the B3LYP[15] density-functional and were repeated using PW91.[16] B3LYP was chosen because it has been shown to reproduce both experimental and high-quality ab initio data evaluated using the CCSD(T) method[9] for the ammination of Ag(I). A second density functional was used to provide an estimate of the reliability of the results; PW91 was chosen because this functional is in wide use throughout the physics community for the binding of organic molecules with metals and is known to be generally reliable.[17,18]

Gas-phase entropies, vibrational zero-point energies (ZPEs), and enthalpies at 298.15 K and 1 atm were computed from the

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* Corresponding author. E-mail: mantolovich@csu.edu.au.
† Charles Sturt University.
‡ University of Sydney.

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TABLE 2: Calculated M−L Distances for Gas-Phase Inner-Shell Complexes[a]

			Cu−N/O (Å)		Ag−N/O (Å)		Au−N/O (Å)	
series	species	symmetry	B3LYP	PW91	B3LYP	PW91	B3LYP	PW91
1	$M^+(NH_3)$	C_{3v}	1.93	1.90	2.21	2.17	2.10	2.07
2	$M^+(H_2O)$	C_{sv}	1.93	1.91	2.23	2.21	2.18	2.16
3	$M^+(NH_3)_2$	D_{3d}	1.92	1.91	2.16[b]	2.13[b]	2.09	2.07
4	$M^+(NH_3)(H_2O)$		1.91 N 1.91 O	1.89 N 1.90 O	2.16 N 2.18 O	2.13 N 2.16 O	2.07 N 2.12 O	2.05 N 2.10 O
5	$M^+(H_2O)_2$	C_{2v}	1.90	1.88	2.18	2.15	2.09	2.07
6	$M^+(NH_3)_3$	C_{3h}	2.07	2.04	2.32	2.29	2.30	2.28
7	$M^+(NH_3)_2(H_2O)$		−1w	−1w	−1w	−1w	−1w	−1w
8	$M^+(NH_3)(H_2O)_2$		−1w	−1w	−1w	−1w	−1w	−1w
9	$M^+(H_2O)_3$	C_{3h}	2.06	2.04	2.33	2.31	2.34	2.32

[a] "−1w" indicates spontaneous loss of a water molecule to the outer shell. [b] X-ray[33−35] values in the range 2.10−2.14 Å.

unscaled harmonic frequencies using standard statistical thermodynamics relations.[19] All single-point energy calculations were also performed using *Gaussian 98*[12] at these final optimized geometries. The use of the harmonic vibrational model to describe complexes such as these that possess significant numbers of low-frequency modes is not always appropriate as often these modes may be associated with hindered rotations whose barriers are less than the available thermal energy. We have considered this issue in detail for $[AgNH_3]^+$ and $[Ag(NH_3)_2]^+$ and find that all low-frequency modes do in fact remain harmonic in nature at the available thermal energy. Although this result is not necessarily general and every complex should be considered individually, it is anticipated that large errors are not introduced through the use of the harmonic approximation.

Free energies in solution are estimated from those in the gas phase by subtraction of the gas-phase translational entropy contribution and addition of solvation contributions estimated using the *COSMO*[20] self-consistent reaction-field method.

Historically, it has been usual to correct calculated binding errors for basis set superposition error (BSSE).[21] This is an undesirable feature associated with the use of restricted atomic basis sets that results in perceived overbinding of complexes. The basis set used in these calculations is sufficiently large to eliminate gross errors associated with BSSE, however, and it is now known that further expansion beyond this level results in increased binding caused by the allowed improved description of electron correlation being of greater importance than the associated reduction in the BSSE.[9,17,22−24] Hence, BSSE correction methods are not applied to the calculated binding energies; our calculations are estimated to display underbinding on the order of 2 kcal mol^{-1} compared to calculations performed at the complete basis set limit.[9,17]

Results

The gas-phase structures optimized using B3LYP and PW91 with the SDD/aug-cc-pVDZ basis set are shown in Table 2 for all compounds of the form M^+L_n where M = Cu, Ag, or Au; L is any mixture of H_2O or NH_3, and $n = 1-3$. Stable inner-shell coordinated structures were not obtained for all species, with some spontaneously losing a water molecule; this scenario is indicated as "−1w" in the table. The homoligand species for M = Ag and $n = 1-2$ have been considered in detail by us[9] and by others;[9,25−29] mixed-ligand species have been considered by Fox et al.,[10] and homoligand Cu species have also been studied.[4,30−32] On the basis of these results and other high-level calculations[17] for $Au^+(NH_3)$, the computational methods appear to overestimate the metal−ligand bond length by about 0.03 Å. As shown in Table 2, X-ray structural data[33−35] for species of the form $Ag^+(NH_3)_2$ confirm this.

It is well-known[9] that the point group symmetry of complexes of this type is very difficult to predict because the relative energies of possible isomers are typically only on the order of 0.1 kcal mol^{-1}. Changes to the basis set of the computational method can thus give rise to quite different predicted structures. However, this is expected to affect calculated binding energies only minimally. There will also be a configurational contribution to the molecular entropy that is not considered explicitly, but again, this term should only have a minor contribution to calculated free energies.

With the exception of the recent cluster solvation studies of Fox et al.,[10] most previous computational studies of the Ag(I)[9,25−29] and Cu(I)[4,30−32] ammine complexes have concentrated on the simple gas-phase reactions 1 and 2

$$M^+ + NH_3 \rightarrow M^+(NH_3) \tag{1}$$

$$M^+(NH_3) + NH_3 \rightarrow M^+(NH_3)_2 \tag{2}$$

Calculated values of the change in enthalpy, ΔH, change in entropy, ΔS, and change in the Gibb's free energy at 298 K, ΔG, for these reactions in the gas phase are given in Table 3 and compared to experimental data. The agreement between calculated and observed data is only semiquantitative, with B3LYP energies typically overbinding the complexes by up to 10 kcal mol^{-1}, while PW91 overbinds by up to 20 kcal mol^{-1}; these errors are sufficiently small that the major qualitative trends in the data are properly identified, however. One significant feature is that the silver ammines are much less strongly bound (by 10−20 kcal mol^{-1}) than the copper and gold ones, an effect that may be reflected by the predicted longer bond lengths for silver shown in Table 1. This effect can qualitatively explain the observed lower value of β_2 for Ag indicated in Table 1, and this is confirmed by the calculated and observed values for the sum of reactions 1 and 2 that are given in Table 3 as eq 3. Note that the absence of a linear

$$M^+ + 2NH_3 \rightarrow M^+(NH_3)_2 \tag{3}$$

progression in the properties of the Cu, Ag, and Au complexes most probably arises from the relativistic contraction of the gold orbitals rather than from anomalous properties of silver, however.

We are particularly concerned with the differences $\Delta\Delta H$, $\Delta\Delta S$, and $\Delta\Delta G$ between the thermodynamic properties of the second ammination, reaction 2, and the first ammination, reaction 1, and these are listed in Table 3 as eq 4. The values of $\Delta\Delta H$ are positive while all those for $\Delta\Delta S$ are negative, indicating that these two terms are predicted to reinforce each other in determining $\Delta\Delta G$. Experimental data for the difference

TABLE 3: Calculated and Observed Thermodynamic Data for Metal Ammination Reactions

reaction	M	ΔG°_{298} solution (kcal mol^{-1}) obsd	B3LYP	PW91	ΔG°_{298} gas (kcal mol^{-1}) obsd	B3LYP	PW91	ΔH°_{298} gas (kcal mol^{-1}) obsd	B3LYP	PW91	ΔS° gas (cal K^{-1} mol^{-1}) obsd	B3LYP	PW91
(1) $M^+ + NH_3 \rightarrow M^+(NH_3)$	Cu		−59.0	−66.1		−53.4	−60.2	−56.6 ± 3.6[f]	−60.4	−67.2		−23.3	−23.4
	Ag	−4.6[h]	−43.7	−49.0	−43.3 ± 2.3[e]	−38.9	−44.0	−48.7 ± 3.8,[e] −41.6 ± 3.0[c]	−45.5	−50.7	−18 ± 5[e]	−22.3[a]	−22.5[a]
	Au		−63.8	−72.8		−56.8	−65.4		−63.7	−72.4		−23.2	−23.4
(2) $M^+(NH_3) + NH_3 \rightarrow M^+(NH_3)_2$	Cu		−46.8	−51.7		−44.8	−49.4	−59.2 ± 2.4,[f] −48.8 ± >3.6[g]	−56.1	−60.8		−38.1	−38.2
	Ag	−5.3[h]	−34.8	−38.7	−27.1 ± 1.3[a]	−32.1	−36.8	−36.9 ± 0.8[a]	−43.5	−48.4	−32.7 ± 1.2[a]	−38.3[b]	−38.7[b]
	Au		−54.4	−58.1		−51.2	−55.4		−61.0	−67.1		−33.0	−39.4
(3) sum (1) + (2) $M^+ + 2NH_3 \rightarrow M^+(NH_3)_2$	Cu	−15.5[i]	−105.8	−117.8	−88.2[b]	−98.2	−109.6	−105.4,[b] −115.8 ± 6.0[f]	−116.5	−128.0	−57.8[a]	−61.3	−61.6
	Ag	−9.9[h]	−78.5	−87.7	−70.4 ± 1.0[d]	−71.0	−80.8	−85.6 ± 1.5[d]	−89.0	−99.1	−51 ± 6[d]	−60.6	−61.2
	Au	−36.1[j]	−118.2	−130.9		−107.9	−120.8		−124.7	−139.5		−56.2	−62.8
(4) difference[k] (2) − (1)	Cu		12.2	14.4		8.6	10.8	−2.6 ± 4.3,[f] 7.8 ± >3.6[g]	4.3	6.4		−14.8	−14.8
	Ag	−0.7[h]	8.9	10.3	16.2 ± 3.6[ae]	6.8	7.2	11.8 ± 4.6,[c] 4.7 ± 3.8[c,d]	2.0	2.3	−15 ± 6[a,e]	−16.0	−16.2
	Au		9.4	14.7		5.6	10.0		2.7	5.3		−9.8	−16.0

[a] From Holland and Castleman.[40] [b] From Deng and Kebarle.[38] [c] From El Aribi et al.[28] [d] From Deng and Kebarle.[36] [e] From reactions 2[40] and 3.[36] [f] From Walter and Armentrout.[37] [g] From reactions 1[37] and 3.[38] [h] From Garner et al.[7] [i] From Solis et al.[41] [j] From Skibsted et al.,[42] estimate only. [k] Referred to in the text as $\Delta\Delta H$, $\Delta\Delta S$, and $\Delta\Delta G$.

in ΔH is available for both the Ag and Cu complexes. For Ag, the most recent observed value of 4.7 ± 3.8 kcal mol^{-1} from the results of El Aribi et al.[28] and Deng and Kebarle[36] is very close to the calculated values of 2.0 and 2.3 kcal mol^{-1} from B3LYP and PW91, respectively. However, for Cu, the differences in ΔH are predicted to increase by 2−4 kcal mol^{-1}. Although experimental results[37,38] leading to $\Delta H = 7.8 \pm > 3.6$ kcal mol^{-1} support this, others[37] of −2.6 ± 4.3 kcal mol^{-1} may not. While density-functional calculations such as ours predict that enthalpy disfavors the second ammination with respect to the first,[31,32] ab initio calculations predict the opposite;[4,31,32] the effect has been attributed to sd hybridization of Cu and is favored as the level of electron correlation increases.[4,39] It is hence clearly important to resolve this issue and also obtain experimental free energies for these processes, both for gas-phase clusters and in aqueous solution. Nevertheless, as has been previously demonstrated,[9] from Table 3, the gas-phase calculated $\Delta\Delta G$ values are all in the range 9−15 kcal mol^{-1}, indicating that the successive calculated K values for each complex are predicted to decrease for all metals. This does not reflect the key experimental result that K_2 for the Ag complex in solution is larger than K_1, as shown in Table 1, with a negative value of $\Delta\Delta G$, as shown in Table 3. It is thus most likely that this phenomenon is caused by a solvent effect.[9,10]

The simplest approach that can be used to model solvent effects in this system is through use of self-consistent reaction field calculations. These treat the solvent as a continuum dielectric material that does not undergo specific chemical interactions with the reacting species. Solvation corrections to the gas-phase free energy changes for the reactions considered have been evaluated using *COSMO*,[20] and the results are given in Table 3. Dielectric solvation results in the $\Delta\Delta G$ values for reaction 2 less reaction 1 becoming more positive, increasing the energy by which the first ammination is favored compared to the second one. This change arises because dielectric solvation favors the smallest ions, as these have the greatest charge density. Dielectric solvation thus cannot explain the key observation that the second ammination of Ag^+ is most favored. In addition, it is clear from the experimental data in Table 3 that the total energy liberated by both ammination processes is dramatically reduced in solution compared to the gas phase, with the free energy changes for reaction 3 (i.e., reaction 1 plus reaction 2) being 60−75 kcal mol^{-1} less favored in solution. This solvent effect is also not reproduced by the dielectric solvation approach, because this method again predicts changes to occur in the alternate direction, with reactions in solution calculated to be more favored by ca. 15 kcal mol^{-1} caused largely by the loss of the translational entropy terms that favors gas-phase dissociations.

If the observed anomaly in the successive ammination binding constants arises from a solvent effect, then it is clear that this must involve specific solvation phenomena in which the solvent molecules form bonds to the reacting species. As a first approximation to understanding specific solvation, we investigate the properties of the solvated inner-sphere complexes described previously in Table 2. One of the most significant results is that, of the inner-shell compounds with three ligands, only the triammine and triaquo complexes are stable, with the mixed NH_3−H_2O ternary systems ejecting one of the water molecules into the second coordination shell to leave binary complexes. For silver, this effect has been studied in detail by Fox et al.,[10] while related effects are also known for Cu(I).[4,37] Reactions 1 and 2 may then be rewritten incorporating the effects of the inner-sphere solvent molecules, and the following gas-

TABLE 4: Calculated Thermodynamic Data for Additional Reactions of Inner-Sphere Complexes

reaction	M	ΔG°_{298} solution (kcal mol^{-1}) B3LYP	PW91	ΔG°_{298} gas (kcal mol^{-1}) B3LYP	PW91	ΔH°_{298} gas (kcal mol^{-1}) B3LYP	PW91	ΔS° gas (cal K^{-1} mol^{-1}) B3LYP	PW91
(5) $M^+(H_2O)_3 + NH_3 \rightarrow M^+(NH_3)(H_2O) + 2H_2O$	Cu	−15.7	−16.8	−16.9	−18.6	−5.4	−7.0	38.4	38.8
	Ag	−9.9	−11.3	−12.0	−14.0	−2.6	−4.5	31.4	31.9
	Au	−31.9	−32.1	−32.8	−33.5	−21.8	−24.2	36.9	31.0
(6) $M^+(NH_3)(H_2O) + NH_3 \rightarrow M^+(NH_3)_2 + H_2O$	Cu	−12.6	−14.2	−14.6	−16.8	−16.2	−18.0	−5.1	−4.1
	Ag	−12.1	−13.9	−13.1	−15.4	−15.1	−17.1	−6.7	−5.7
	Au	−20.6	−20.7	−22.5	−22.9	−21.7	−24.0	2.5	−3.6
(7) sum (5) + (6) $M^+(H_2O)_3 + 2NH_3 \rightarrow M^+(NH_3)_2 + 3H_2O$	Cu	−38.6	−41.3	−31.5	−35.4	−21.6	−25.1	33.25	34.75
	Ag	−32.2	−35.6	−25.1	−29.5	−17.8	−21.7	24.71	26.17
	Au	−62.8	−63.1	−55.3	−56.4	−43.6	−48.2	39.38	27.37
(8) difference[c] (6) − (5)	Cu	3.0	2.5	2.2	1.8	−10.7	−11.0	−43.5	−42.9
	Ag	−2.2	−2.6	−1.1	−1.4	−12.5	−12.6	−38.1	−37.6
	Au	11.3	11.3	10.4	10.5	0.1	0.2	−34.5	−34.6
(9) $M^+(NH_3) + H_2O \rightarrow +(NH_3)(H_2O)$	Cu	−24.3	−27.2	−30.1	−32.6	−40.0	−42.8	−32.9	−34.1
	Ag	−19.2	−22.5	−19.0	−21.4	−28.4	−31.2	−31.6	−33.0
	Au	−29.1	−33.3	−28.7	−32.4	−39.3	−43.1	−35.4	−35.8
(10) $M^+(H_2O) + NH_3 \rightarrow M^+(NH_3)(H_2O)$	Cu	−34.9	−40.4	−48.3	−54.3	−59.1	−64.9	−36.3	−35.5
	Ag	−28.0	−33.9	−33.9	−39.4	−44.3	−49.6	−34.8	−34.4
	Au	−48.0	−55.2	−55.0	−61.9	−66.0	−72.9	−36.8	−37.0
(11) $M^+(H_2O)_3 \rightarrow M^+ + 3H_2O$	Cu	46.3	54.8	66.7	74.2	94.9[a]	102.9[a]	94.6	96.3
	Ag	41.8	48.9	45.8	51.3	71.3[b]	77.4[b]	85.3	87.4
	Au	41.8	59.8	52.6	64.4	81.1	91.2	95.6	90.1
(12) $M^+(H_2O)_3 \rightarrow M^+ (H_2O) + 2H_2O$	Cu	19.3	23.6	31.4	35.7	53.7	57.8	74.7	74.3
	Ag	18.1	22.6	21.9	25.3	41.6	45.1	66.2	66.3
	Au	15.1	23.1	22.2	28.5	44.2	48.7	73.7	67.9

[a] Observed[37] 89 kcal mol^{-1}, but this may be for a more stable outer-sphere complex. [b] Observed[40] 70.8 kcal mol^{-1} after a correction[10] of 1.9 kcal mol^{-1} for outer-sphere binding. [c] Referred to in the text as ΔΔ*H*, ΔΔ*S*, and ΔΔ*G*.

phase reactions are thus considered a better model for the formation of the diammine complexes in solution.

$$M^+(H_2O)_3 + NH_3 \rightarrow M^+(NH_3)(H_2O) + 2H_2O \qquad (5)$$

$$M^+(NH_3)(H_2O) + NH_3 \rightarrow M^+(NH_3)_2 + H_2O \qquad (6)$$

The calculated changes in the enthalpy, entropy, and free energy of these gas-phase inner-sphere aquated systems are given in Table 4, along with free energies for these processes in solution estimated using *COSMO*,[20] as before. The calculated free energy changes for reactions 5 and 6, both in the gas phase and in solution, show marked decreases compared to those for the bare-ion reactions 1 and 2. Reaction 6 involves ligand replacement rather than ligand addition as in reaction 2, and hence, the magnitude of the free energy change driving the process is reduced by ca. 20−30 kcal mol^{-1}. However, reaction 5 involves the replacement of two ligands with just one, and so, the effect of inner-sphere solvation on the free energy change is even more pronounced. These effects are best appreciated by considering the calculated values for the sum of reactions 5 and 6, shown in Table 4 as reaction 7. The calculated changes

$$M^+(H_2O)_3 + 2NH_3 \rightarrow M^+(NH_3)_2 + 3H_2O \qquad (7)$$

in the free energy in going from the gas phase to the inner-sphere complexes range from 40 to 60 kcal mol^{-1}, a significant fraction of experimentally observed changes in going from the gas phase to solution of 60−70 kcal mol^{-1}. This indicates that reactions 5 and 6 are much better descriptions of the process in solution than reactions 1 and 2; furthermore, the dielectric solvation effects that pushed reactions 1 and 2 in the wrong direction now generate changes of the correct sign, indicating that a physically realistic model of the chemistry is now obtained. Furthermore, the experimental observations that Δ*G* for reaction 7 is less exothermic for Cu^+ and Au^+ than for Ag^+ by 5.6 and 26.2 kcal mol^{-1}, respectively, are quantitatively reproduced by the calculated values of (for B3LYP) 6.4 and 30.6 kcal mol^{-1}, respectively.

The difference values between reactions 6 and 5, ΔΔ*H*, ΔΔ*S*, and ΔΔ*G*, are shown as eq 8 in Table 4. The calculated values (in solution, obtained using B3LYP) of 3.0 kcal mol^{-1} for Cu, −2.2 kcal mol^{-1} for Ag, and 11.3 kcal mol^{-1} for ΔΔ*G* indicate that for Ag^+ the second ammination reaction does have a more negative Δ*G* value than that for the first ammination. Hence, these calculations predict that for silver the calculated K_2 is now larger than the calculated K_1. This inner-shell specific solvation aquated-ion model thus provides a chemical interpretation for the observed anomalous ammination equilibria of Ag^+. It is possible that these calculated numbers are only in fortuitous agreement with the experimental data, because the absolute errors depicted in Table 3 for Δ*G* and Δ*H* evaluated for gas-phase complexes range up to 10 kcal mol^{-1} for B3LYP and 20 kcal mol^{-1} for PW91, errors that are large compared to the calculated values of ΔΔ*G*, which range from −3 to 11 kcal mol^{-1}. However, the maximum difference between the B3LYP and PW91 results for ΔΔ*G* in Table 4 is just 0.5 kcal mol^{-1}, indicating that the errors in the calculations cancel and, hence, the calculated free energy differences are expected to be much more reliable than the free energies themselves.

Further insight into the origins of this effect can be obtained by considering the following reactions:

$$M^+(NH_3) + H_2O \rightarrow M^+(NH_3)(H_2O) \qquad (9)$$

$$M^+(H_2O) + NH_3 \rightarrow M^+(NH_3)(H_2O) \qquad (10)$$

These show the formation of the mixed binary complex from two different pathways. The calculated Δ*G* values for these processes are given in Table 4 and indicate that the $Ag^+(NH_3)(H_2O)$ complex has a lower stability compared to the equivalent Cu^+ and Au^+ complexes. It is proposed that the unusually low stability of $Ag^+(NH_3)(H_2O)$ enhances the binding of the second NH_3, resulting in the observed higher K_2 value for $Ag^+(NH_3)_2$. As is well-known,[10,17,36−38,40] these results also indicate that the binding of Cu^+, Ag^+, and Au^+ to water is much weaker than it is to ammonia. Also significant are the following reactions:

$$M^+(H_2O)_3 \rightarrow M^+ + 3H_2O \qquad (11)$$

$$M^+(H_2O)_3 \rightarrow M^+(H_2O) + 2H_2O \qquad (12)$$

Data for these are also given in Table 4; reaction 5 can be written as a combination of reactions 1, 9, and 11.

$$M^+(H_2O)_3 \rightarrow M^+ + 3H_2O \qquad (11)$$

$$M^+ + NH_3 \rightarrow M^+(NH_3) \qquad (1)$$

$$M^+(NH_3) + H_2O \rightarrow M^+(NH_3)(H_2O) \qquad (9)$$

$$M^+(H_2O)_3 + NH_3 \rightarrow M^+(NH_3)(H_2O) + 2H_2O \qquad (5)$$

For it, the relative instabilities of the M^+H_2O species in reactions 9 and 11 would thus tend to balance out because they appear equally distributed among reactants and products. However, by analogy reaction 6 can be expressed in terms of reaction 2.

$$M^+(NH_3)(H_2O) \rightarrow M^+(NH_3) + H_2O \qquad (-9)$$

$$M^+(NH_3) + NH_3 \rightarrow M^+(NH_3)_2 \qquad (2)$$

$$M^+(NH_3)(H_2O) + NH_3 \rightarrow M^+(NH_3)_2 + H_2O \qquad (6)$$

For it, particularly unstable aquated species for M^+ appear only as reactants. Hence, the second ammination of M^+ appears to be anomalously enhanced because of the generic poor stability of the associated inner-coordination-sphere solvated complexes M^+. The effect is calculated to be large for $M^+ = Cu^+$ and Ag^+ but small for Au^+. Although the calculations predict that the second addition is more exothermic for Ag^+ only, the small energy differences involved raise the possibility that a similar anomaly could also be observed for Cu^+.

Conclusions

The unusual behavior of the Ag(I) ammine complexes for which the second stability constant for ammine complexation, K_2, is anomalously larger than the first, K_1, in aqueous solution is attributed to the poor affinity of Ag(I) for the solvent. This is a specific solvation effect caused by ligation of the solvent to the metal that cannot be described using continuum solvation models. It could possibly also occur for Cu(I) but is not anticipated for Au(I), and further experimental work is required to verify these predictions. Improved computational investigations employing full liquid simulations and free energy calculations are planned. These will allow all ligation processes between the metal ions and the surrounding solvent to be treated equally and should determine whether distinct inner-sphere and outer-sphere hydrated complexes are differentiable in solution, as we have demonstrated them to be for small clusters. Regardless of this feature, such simulations are expected to reveal the same trends in binding and solvation.

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References and Notes

(1) Yamaguchi, T.; Lindqvist, O. *Acta Chem. Scand., Ser. A* **1983**, *37*, 685.

(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988.

(3) Orgel, L. E. *J. Chem. Soc.* **1958**, *90*, 4186.

(4) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1991**, *94*, 2068.

(5) Miyawaki, J.; Sugawara, K.-i. *J. Chem. Phys.* **2003**, *119*, 6539.

(6) Nasanen, R. *Acta Chem. Scand.* **1947**, *1*, 763.

(7) Garner, R.; Yperman, J.; Mullens, J.; Van Poucke, L. C. *J. Coord. Chem.* **1993**, *30*, 151.

(8) Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5222.

(9) Widmer-Cooper, A. N.; Lindoy, L. F.; Reimers, J. R. *J. Phys. Chem. A* **2001**, *105*, 6567.

(10) Fox, B. S.; Beyer, M. K.; Bondybey, V. E. *J. Am. Chem. Soc.* **2002**, *124*, 13613.

(11) Clark, T.; Hennemann, M.; van Eldik, R.; Meyerstein, D. *Inorg. Chem.* **2002**, *41*, 2927.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(14) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(17) Lambropoulos, N. A.; Reimers, J. R.; Hush, N. S. *J. Chem. Phys.* **2002**, *116*, 10277.

(18) Bilic, A.; Reimers, J. R.; Hush, N. S.; Hafner, J. *J. Chem. Phys.* **2002**, *116*, 8981.

(19) Del Bene, J. E.; Mettee, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. *J. Phys. Chem.* **1983**, *87*, 3279.

(20) Eckert, E.; Klamt, A. *AIChE J.* **2002**, *48*, 369.

(21) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(22) Dargel, T. K.; Hetwig, R. H.; Koch, W.; Horn, H. *J. Chem. Phys.* **1998**, *108*, 3876.

(23) Feller, D.; Glendening, E. D.; de Jong, W. A. *J. Chem. Phys.* **1999**, *110*, 1475.

(24) Feller, D. A.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154.

(25) Ma, N. L. *Chem. Phys. Lett.* **1998**, *297*, 230.

(26) Chattaraj, P. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 1067.

(27) Shoeib, T.; Milburn, R. K.; Koyanagi, G. K.; Lavrov, V. V.; Bohme, D. K.; Siu, K. W. M.; Hopkinson, A. C. *Int. J. Mass Spectrom.* **2000**, *201*, 87.

(28) El Aribi, H.; Rodriquez, C. F.; Shoeib, T.; Ling, Y.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. A* **2002**, *106*, 8798.

(29) Boutreau, L.; Leon, E.; Luna, A.; Toulhoat, P.; Tortajada, J. *Chem. Phys. Lett.* **2001**, *338*, 74.

(30) Luna, A.; Amekraz, B.; Tortajada, J. *Chem. Phys. Lett.* **1997**, *266*, 31.

(31) Hoyau, S.; Ohanessian, G. *Chem. Phys. Lett.* **1997**, *280*, 266.

(32) El-Nahas, A. M.; Tajima, N.; Hirao, K. *THEOCHEM* **1999**, *469*, 201.

(33) Yamaguchi, T.; Linqvist, O. *Acta Chem. Scand., Ser. A* **1983**, 685.

(34) Pajunen, A.; Pajunen, S. *Acta Crystallogr., Sect. C* **1994**, *50*, 1884.

(35) Zheng, S.-L.; Tong, M.-L.; Chen, X.-M.; Ng, S. W. *J. Chem. Soc., Dalton Trans.* **2002**, 360.

(36) Deng, H.; Kebarle, P. *J. Phys. Chem. A* **1998**, *102*, 571.

(37) Walter, D.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 3176.

(38) Deng, H.; Kebarle, P. *J. Am. Chem. Soc.* **1998**, *120*, 2925.

(39) Caraiman, D.; Shoeib, T.; Siu, K. W. M.; Hopkinson, A. C.; Bohme, D. K. *Int. J. Mass Spectrom.* **2003**, *228*, 629.

(40) Holland, P. M.; Castleman, A. W., Jr. *J. Chem. Phys.* **1982**, *76*, 4195.

(41) Solis, J.; Hefter, G.; May, P. *Aust. J. Chem.* **1995**, *8*, 1283.

(42) Skibsted, L. H.; Bjerrum, J. *Acta Chem. Scand., Ser. A* **1974**, *28*, 740.

(43) Bjerrum, J. *Acta Chem. Scand., Ser. A* **1986**, *40*, 233.

(44) Bjerrum, J. *Acta Chem. Scand., Ser. A* **1986**, *40*, 392.