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The Effect of Alkylation of N- and O-Donor Atoms on Their Strength of Coordination to Silver(I)

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The observation that alkylation of amine ligands can lead to enhanced coordination to silver(I) is investigated through the determination of structures and incremental binding enthalpies for $Ag^+(L)_n$ ionic clusters (with $L = NH_3$, NH_2Me, $NHMe_2$, NMe_3, H_2O, MeOH, and Me_2O for $n = 1-2$), using density-functional and CCSD(T) electronic structure methods. For the nonalkylated complexes $Ag^+(H_2O)$, $Ag^+(NH_3)$, $Ag^+(H_2O)_2$, and $Ag^+(NH_3)_2$, the calculated binding enthalpies agreed well with experimental values for all but $Ag^+(NH_3)_2$, while good agreement between the binding entropies was achieved for all but $Ag^+(H_2O)$. As a function of the degree of alkylation, the calculated binding enthalpies initially increase but then decrease. The results are interpreted in terms of the bonding models of Meyerstein and of Deng et al. as arising from increased ligand σ-donating ability and reduced ion-ligand electrostatic interactions. It is clear that gas-phase effects are insufficient to explain the sometimes observed increased binding energies of tertiary macrocyclic amines compared to secondary ones.

I. Introduction

Many industrial and other applications exist for ligands which selectively bind particular ions in solution.[1] For certain silver(I)-amine complexes, conversion of nitrogen atoms from secondary amines to tertiary amines has been shown to lead to either little change or even an increase in the stability of the complex in solution.[2−4] This is unusual as tertiary amines are generally weaker ligands than secondary ones, and this property can potentially be exploited to design ligands with increased selectivity for silver(I) over a number of other industrially important metal ions.[5] To do so rationally, we would like to know how *N*-alkylation of amine ligands modifies the properties of their metal complexes. However, a variety of often opposing effects are implicated and many of these have been discussed by Meyerstein.[6] Moreover, other effects have also been discussed in this context[7,8] and it is clear that a comprehensive model for the effects of alkylation of oxygen and nitrogen donors on the ability of the ligand to bind to a metal ion is yet to be established.

Meyerstein's work[6] has successfully explained the majority of the observed effects of converting secondary amines to tertiary ones on metal binding constants in solution: typically, a reduction in the binding constant. In total, five chemical influences are considered of which four act to reduce the binding constant while one, improving ligand σ-donating ability on *N*-alkylation, increases it. Solvation effects which act to reduce the binding constant are concluded to be, in general, of the greatest importance. Our interest here is with Ag(I) complexes, complexes which often provide an exception to the general picture.[2−5] Within the framework of Meyerstein's theory, it is the improving ligand σ-donating ability on *N*-alkylation which can give rise to such exceptions, and indeed Meyerstein[6] has suggested that for large monovalent cations such as silver(I) this could be the major contributing factor. A prerequisite for this to be correct for complexes in solution is that it must also apply for these complexes in the *gas phase*.

Results from semiempirical molecular orbital calculations[6,9,10] indicate that, in general, ligand σ-donation ability is the most important effect operative for gas-phase complexes. Experimental evidence supporting this comes from studies of the binding enthalpies for the complexation of nickel(I) with a variety of ligands by Kappes and Staley[11] and for that of copper(I) by Deng and Kebarle.[8] These show that the enthalpy *does* increase as the donor atom is alkylated, and, for at least Ni(I), that this process is independent of the type of donor group or type of alkylation. However, analogous experimental data for the complexation of silver(I) with amine ligands are not available, such data only being reported for the addition of ammonia.[8,12] In this work, we calculate the effect of alkylation on the strength of gas-phase silver(I)-ligand bonds using high-level quantum-mechanical methods.

Highly correlated ab initio methods such as Coupled-cluster singles and doubles theory with perturbative corrections for triples excitations (CCSD(T)) have been shown to give relatively good values for the reaction enthalpies, in comparison to experiment, for the complexation of silver(I) by H_2O,[13] and by NH_3.[14,15] However, such calculations are not feasible for the larger alkylated systems due to the rapidly increasing computational cost. Density-functional theory (DFT) methods present a possible alternative. Nonlocal functionals such as BP86 and B3LYP have been found to be superior to Hartree−Fock (HF) and Møller−Plesset second-order perturbation theory (MP2) methods for calculating thermodynamic properties of a variety of metal−ligand complexes,[16,17] and have found increasing use in coordination chemistry.[18] They are also feasible to apply to metal complexes of smaller macrocyclic ligands,[19−21] including studies by us of macrocyclic ligand complexes of silver(I).[4]

In the present study we use DFT methods to calculate the stepwise enthalpies for the addition of one and two of the following amines to silver(I): NH_3, NH_2Me, $NHMe_2$, and NMe_3. We have also calculated the stepwise enthalpies for the addition

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TABLE 1: Basis Sets Used in the Calculations

name	Ag[a]	N, O, C	H
SV(P)	SV(P)[b] [5s3p2d]	SV(P)[b] [3s2p1d]	SV(P)[b] [2s]
VDZ	SV(P)[b] [5s3p2d]	cc-pVDZ[c] [3s2p1d]	cc-pVDZ[c] [2s1p]
aVDZ	SV(P)[b] [5s3p2d]	aug-cc-pVDZ[d] [4s2p2d]	aug-cc-pVDZ[d] [3s2p]
aVTZ	ecp-28-mwb[e] [6s5p3d]	aug-cc-pVTZ[d] [5s4p3d2f]	aug-cc-pVTZ[d] [4s3p2d]
aVTZ(f)	ecp-28-mwb(f)[f] [6s5p3d1f]	aug-cc-pVTZ[d] [5s4p3d2f]	aug-cc-pVTZ[d] [4s3p2d]
aVDZ(f)	ecp-28-mwb(f)[f] [6s5p3d1f]	aug-cc-pVDZ[d] [4s2p2d]	aug-cc-pVDZ[d] [3s2p]

[a] For use with the 28 electron RECP of Andrae et al.[25] [b] Reference 22. [c] Reference 23. [d] Reference *24*. [e] Reference 25. [f] Reference 25 with an added f function of exponent 1.7 optimized for use with silver(I) complexes.[15]

of one and two of the following oxygen-donor ligands to silver(I): H_2O, MeOH, and Me_2O. The effect of *O*-alkylation was studied to provide a parallel comparison of the manner by which the binding enthalpy responds to alkylation of this donor-atom. In addition, some highly correlated ab initio CCSD(T) geometry optimizations and normal-mode analyses are performed on the ammonia complexes; geometry optimizations for the oxygen complexes have been performed by Feller et al.,[13] and we extend this work to the calculation of vibration frequencies.

II. Computational Methods

A. Hamiltonian and Basis Set. Three independent computational techniques are employed, a DFT technique to determine molecular structures and vibration frequencies, a (more accurate but more costly) DFT technique to evaluate single-point energies at these optimized structures, and an ab initio CCSD(T) technique for application to the smaller molecules as a standard. All three techniques require the choice of a basis set.

The basis sets used were obtained by combining various basis sets for silver with ones for the ligands, and the names used for the overall basis set and their components are listed in Table 1. For the ligands, the basis sets employed were SV(P),[22] cc-pVDZ,[23] aug-cc-pVDZ, and aug-cc-pVTZ.[24] For silver, no all-electron basis sets were used due to the substantial relativistic corrections required for this heavy element. Instead, the 28-electron relativistic effective core potential (RECP) of Andrae et al.[25] was used in conjunction with the SV(P) [22] and ecp-28-mwb[25] basis sets; note that ecp-28-mwb was actually optimized for use with this RECP. In addition, the effect of adding an f function (of exponent of 1.7, optimized for use with silver(I) complexes)[15] to the ecp-28-mwb basis set was considered, and we name the expanded basis set ecp-28-mwb(f). The number of contracted basis functions in each complete molecular basis set are also shown in Table 1; in increasing order of size, these are named: SV(P), VDZ, aVDZ, aVDZ(f), aVTZ, and aVTZ(f).

The DFT geometries and frequencies were calculated using the BP86[26,27] functional with the small SV(P) basis set while the DFT single-point energy calculations were performed using the B3LYP[28,29] hybrid functional with the large aVTZ(f) basis. All CCSD(T) calculations were performed using the aVDZ(f) basis set. In the Appendix, arguments supporting these choices are presented, along with estimates of errors in calculated properties.

B. Software. Geometry optimizations were initially carried out using Turbomole.[30] For calculations with the nonhybrid functional BP86, the additional approximation was used that the Coulomb integrals are approximated by a sum of atom centered s, p, d, etc., functions—the auxiliary (or fitting) basis.[31] This allows for very efficient treatment of the Coulomb interactions and hence decreases the time taken for a given calculation. In this case, the SV(P) auxiliary basis set[32] was used for all atoms.

DFT vibrational frequency calculations were performed using Gaussian98[33] after final optimization using the "tight" gradient convergence criterion. The BP86 functional has previously been demonstrated to yield good results for zero-point energies, low-frequency vibrations and vibrational entropies using scaling factors very close to unity.[34] Entropies, vibrational zero-point energies (ZPEs), and enthalpies at 298.15 K and 1 atm were computed from the unscaled harmonic frequencies using standard statistical thermodynamics relations.[35] All single-point energy calculations were also performed using Gaussian98 with these final optimized geometries.

The CCSD(T) geometry optimizations were carried out using AcesII;[36] the frequency calculations were performed using MOLPRO-97[37] driven by our own software for double-numerical differentiation of the energy. Entropies and enthalpies at 298.15 K and 1 atm were again computed from the unscaled harmonic frequencies using standard statistical thermodynamics relations.[35]

The thermodynamics calculations involving the treament of vibrational modes as free rotors were performed using the UNIMOL software.[38]

C. Basis-Set Superposition Error. The basis-set superposition error (BSSE) was determined for a number of DFT calculations on small complexes by the counterpoise (CP) procedure of Boys and Bernardi.[39] BSSE is an undesirable consequence of using finite basis sets that leads to an overestimation of the binding energy. For CCSD(T) calculations with augmented correlation consistent basis sets it has previously been observed that the uncorrelated binding energies are closer to the ligand complete basis set (CBS) limit than CP-corrected values.[13] Therefore, we do not apply BSSE corrections to CCSD(T) calculations. Also, in the Appendix it is shown through comparison of calculated energies and BSSEs that B3LYP/aVTZ(f) calculations are close to the ligand CBS limit. Hence, *none* of the results presented in the subsequent results tables are corrected for BSSE. Expansion of the basis set of the silver is also likely to have a significant effect on calculated binding energies for both CCSD(T) and B3LYP calculations,[40] with effects observed for the binding of CO to Au^+ of the order of 5 kcal mol^{-1}. However, better results are again obtained for small basis sets without the use of BSSE correction.

III. Properties of the Parent Aqua and Amine Complexes

For the complexes of silver(I) with one or two H_2O or NH_3 molecules, CCSD(T)/aVDZ(f) and BP86/SV(P) optimized coordinates and normal vibrational modes are provided in full in the Supporting Information. Also, the Duschinsky matrices which relate the normal coordinates obtained from the two approaches are provided, as is an analysis of the (small) differences between the calculated geometries in terms of normal-mode contributions. Key structural properties and the calculated zero-point energy changes ΔE_{ZPT}, dissociation energies D_e, and thermodynamic properties $-\Delta H$ (binding enthalpy),

TABLE 2: Calculated Geometries and Binding Energies D_e for $Ag^+(L)_n$, Where L = NH_3 or H_2O, and n = 1 or 2, as Well as Harmonic−Vibration Changes in Zero-Point Energy ΔE_{ZPT} and Corrected Binding Energies, Enthalpies, Entropies, and Free Energies for Stepwise Ligand Addition[a]

				geometry							
molecule	method	basis set	symmetry	R_{agN}	R_{NH}	∠HNH	D_e	ΔE_{ZPE}	$-\Delta H^{298}$	$-\Delta S$	$-\Delta G^{298}$
$Ag^+(NH_3)$											
	BP86	SV(P)	C_{3v}	2.176	1.036	107.2	58.6	2.6	57.1	24.7	49.8
	B3LYP[b]	aVTZ					46.8		45.3		38.0
	B3LYP[b]	aVTZ(f)					47.2		45.7		38.3
	CCSD(T)	aVDZ(f)	C_{3v}	2.199	1.025	106.2	46.0	2.5	44.6	24.6	37.3
		expt							48.7 ± 3.8[c]		

				geometry							
molecule	method	basis set	symmetry	R_{AgO}	R_{OH}	∠HOH	D_e	ΔE_{ZPE}	$-\Delta H^{298}$	$-\Delta S$	$-\Delta G^{298}$
$Ag^+(H_2O)$											
	BP86	SV(P)	C_s	2.191	0.986	108.0	41.2	1.6	40.4	20.5	34.3
	B3LYP[b]	AVTZ					30.3		29.5		23.4
	B3LYP[b]	aVTZ(f)					30.6		29.8		23.7
	CCSD(T)[d]	aVDZ(f)	C_{2v}	2.210	0.968	106.2	30.4	1.3	29.7	20.3	23.7
	CCSD(T)[d]	est CBS					32.4		31.9		25.7
		exptl							33.3 ± 2.2[e]	28.4 ± 3.4[e]	24.8 ± 3.2[e,h]

				geometry							
molecule	method	basis set	symmetry	R_{AgN}	R_{NH}	∠HNH	D_e	ΔE_{ZPE}	$-\Delta H^{298}$	$-\Delta S$	$-\Delta G^{298}$
$Ag^+(NH_3)_2$											
	BP86	SV(P)	D_{3h}	2.133	1.036	106.8	56.3	3.2	53.7	30.9[i]	44.5
	B3LYP[b]	aVTZ					45.3		42.7		33.5
	B3LYP[b]	aVTZ(f)					45.3		42.7		33.5
	CCSD(T)	aVDZ(f)	D_{3h}	2.151	1.024	106.2	47.2	3.1	44.7	31.3[j]	35.4
		exptl							36.9 ± 0.8[e]	32.7 ± 1.2[e]	27.2 ± 1.3[e,h]

				geometry								
molecule	method	basis set	symmetry	R_{AgO}	R_{OH}	∠HOH	∠OAgO	D_e	ΔE_{ZPE}	$-\Delta H^{298}$	$-\Delta S$	$-\Delta G^{298}$
$Ag^+(H_2O)_2$												
	BP86	SV(P)	C_2	2.148	0.985	108.0	177.9	40.8	2.2	39.0	30.5[k]	29.9
	B3LYP[b]	aVTZ						29.4		27.5		18.5
	B3LYP[b]	aVTZ(f)						29.4		27.6		18.5
	CCSD(T)[d]	aVDZ(f)	C_2	2.177	0.968	106.6	176.5	30.1	1.9	28.3	26.3[l]	20.5
	CCSD(T)[d]	est CBS						29.6		27.8		20.0
		exptl								25.4 ± 0.3[e]	22.3 ± 0.5[e]	18.8 ± 0.5[e,h]
										24.6 ± 3[g]		18.0 ± 3[g,h]

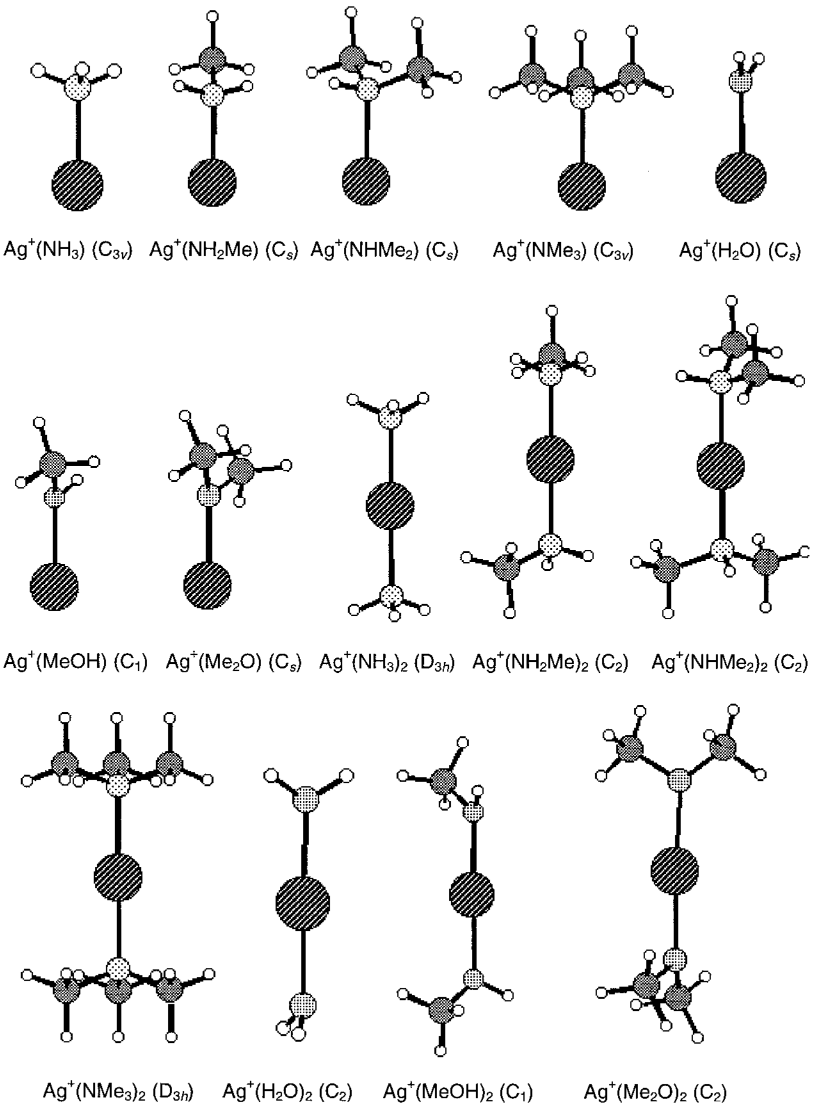
[a] Angles are in degrees and bond lengths are in angstroms. The vibrational zero-point energies and incremental binding energies, enthalpies, and free energies are given in kcal mol^{-1}. Binding entropies were calculated from unscaled frequencies using the harmonic approximation and are in cal K^{-1} mol^{-1}. The zero-point energies are unscaled. No corrections have been made for basis set superposition error. [b] At the optimized BP86/SV(P) geometry; the BP86/SV(P) vibrational contributions to ΔH and entropies are used. [c] Calculated from the value for the double addition of ammonia, ref 8, and the value for the second addition of ammonia, ref 12. [d] From Feller et al., ref 13, using CCSD(T)/aVDZ(f) vibrational corrections rather than MP2 ones. [e] High-pressure mass spectrometry values from Holland and Castleman, ref 12. [f] Recalculated from enthalpy and entropy data. [g] From Deng and Kebarle, ref 8. [h] From the observed enthalpies and entropies. [i] 34.0 after free-rotor correction. [j] 33.4 after free-rotor correction. [k] 30.1 and 30.4 after free-rotor correction from C_2 and D_{2d} structures, respectively. [l] 22.4 and 20.7 after free-rotor correction from C_2 and D_{2d} structures, respectively.

$-\Delta S$ (binding entropy), and $-\Delta G$ (binding free energy) are given in Table 2 while the structures themselves are shown in Figure 1. Also shown are calculated B3LYP/aVTZ and B3LYP/aVTZ(f) dissociation energies and thermodynamic properties $-\Delta H$ and $-\Delta S$ obtained using BP86/SV(P) corrections, as well as CCSD(T) results by Feller et al.[13] for the aqua complexes extrapolated to the ligand complete-basis-set (CBS) limit combined with our CCSD(T)/aVDZ(f) vibrational corrections.

Likely errors in these calculated properties are discussed in detail in the Appendix. In brief, the B3LYP/aVTZ(f) energies are believed to be close (within ca. 0.5 kcal mol^{-1}) of the ligand CBS limit, and these differ from CCSD(T) results in the ligand CBS limit by up to 2 kcal mol^{-1}. Larger deviations for the expansion of the basis set of the metal toward the CBS limit are possible, however.[40] For density-functional methods, expanding the basis set toward the CBS limit does not always produce improved results, and one may argue that only basis sets of the size used in the original parametrization of the density functional should be used. However, for calculations like these in which we are concerned with a weakly bound complex for which basis-set superposition effects must be considered, use of large basis sets is demanded.

Both CCSD(T)/aVDZ(f) and B3LYP/aVTZ(f) binding energies ($-\Delta H$) *underestimate* the observed ones by 3−4 kcal mol^{-1} for the monoligand complexes $Ag^+(H_2O)$ and $Ag^+(NH_3)$. While the DFT calculations are near the CBS limit, basis-set expansion (for the aqua complex[13] at least) is expected to reduce the discrepancy to about half. Also, the experimental error bounds are 2.2 and 3.8 kcal mol^{-1} for the aqua and amine complexes respectively, so that the agreement with experiment for both mono-ligated species is actually quite good.

In contrast, the calculations *overestimate* the binding enthalpies for the additions of the second ligands compared to the observed values by about 3 kcal mol^{-1} for $Ag^+(H_2O)_2$ and by



$Ag^+(NH_3)$ (C_{3v}) $Ag^+(NH_2Me)$ (C_s) $Ag^+(NHMe_2)$ (C_s) $Ag^+(NMe_3)$ (C_{3v}) $Ag^+(H_2O)$ (C_s)

$Ag^+(MeOH)$ (C_1) $Ag^+(Me_2O)$ (C_s) $Ag^+(NH_3)_2$ (D_{3h}) $Ag^+(NH_2Me)_2$ (C_2) $Ag^+(NHMe_2)_2$ (C_2)

$Ag^+(NMe_3)_2$ (D_{3h}) $Ag^+(H_2O)_2$ (C_2) $Ag^+(MeOH)_2$ (C_1) $Ag^+(Me_2O)_2$ (C_2)

Figure 1. Optimized structures for complexes of silver(I).

6−8 kcal mol^{-1} for $Ag^+(NH_3)_2$. For both complexes, experimental measurements were made in 1982 by Holland and Castleman[12] who quoted error bars of ± 0.3 and 0.8 kcal mol^{-1}, respectively. For $Ag^+(H_2O)_2$ the subsequent 1998 work by Deng and Kebarle[8] suggested a similar value for ΔH but provided a more conservative error estimate of ±3 kcal mol^{-1}, however, and within this range the calculated and experimental data are in agreement. While this 3 kcal mol^{-1} error could arise from shortcomings of the calculations, it is in fact the *largest* deviation found by Feller et al.[13] between enthalpies calculated at this level of theory and experimental ones for a range of clusters of water with the cations Cu(I), Ag(I), and Au(I). More dramatically, our calculated values for $Ag^+(NH_3)_2$ differ from experiment by over twice this margin and a revised experimental determination of ΔH is clearly warranted.

Binding enthalpies obtained using the computationally efficient BP86/SV(P) method overestimate those from B3LYP/aVTZ(f) by 11.4, 10.6, 11.0, and 12.4 kcal mol^{-1} for $Ag^+(NH_3)$, $Ag^+(H_2O)$, $Ag^+(NH_3)_2$, and $Ag^+(H_2O)_2$, respectively. This magnitude is too large to permit the use of this method in quantitative predictions of absolute binding enthalpies, but the errors are systematic and the correct qualitative ordering is achieved. Hence BP86/SV(P) without subsequent single-point energy calculations at a higher level is of use in comparative studies such as ours[4] on macrocyclic ligand binding.

Entropy changes ΔS evaluated using the harmonic approximation to the vibrational motion by CCSD(T)/aVDZ(f) and BP86/SV(P) are shown in Table 2, along with the observed values for $Ag^+(H_2O)$, $Ag^+(NH_3)$, and $Ag^+(NH_3)_2$. The two sets of computed values agree very well with each other, the only significant difference being for $Ag^+(H_2O)_2$ for which the potential-energy surface is very flat and hence the structure, vibration frequencies, and entropy and more difficult to evaluate. For $Ag^+(NH_3)_2$, the agreement between both computed results and experiment is within the experimental uncertainty. However, there is significant deviation between experiment and the CCSD(T)/aVDZ(f) results for $Ag^+(H_2O)_2$ (4 cal mol^{-1} K^{-1}) and large deviation for $Ag^+(H_2O)$ (8 cal mol^{-1} K^{-1}).

A possible source of error in the computed values is the use of the harmonic approximation to describe the vibrational motion of floppy complexes with various low-frequency motions. We have evaluated the CCSD(T)/aVDZ(f) energy as a function of curvilinear vibrational motion for each calculated low-frequency mode for each complex and find that most motions are indeed harmonic to energies much in excess of thermal energy at 298 K. The only exceptions occur for the diligand complexes and

TABLE 3: Optimal Silver-Donor Bond Lengths and Changes in Zero-Point Energies for Complexes of Silver(I), and Incremental Changes in Zero-Point Energies, Binding Energies, Enthalpies, Entropies, and Free Energies for the Stepwise Formation of These Complexes[a]

molecule	R_{AgN} or R_{AgO}	NLFV[b]	ΔE_{ZPE}	ΔE_{incr}	$-\Delta H^{298}$	$-\Delta S$	$-\Delta G^{298}$
$Ag^+(NH_3)$	2.176	1	2.6	47.2	45.7	24.7	38.3
$Ag^+(NH_2Me)$	2.181	3	2.2	50.5	49.1	25.7	41.4
$Ag^+(NHMe_2)$	2.194	6	2.0	51.4	50.0	26.5	42.1
$Ag^+(NMe_3)$	2.215	9	1.7	50.7	49.4	27.1	41.3
$Ag^+(NH_3)_2$	2.133	5	3.2	45.3	42.7	30.9	33.5
$Ag^+(NH_2Me)_2$	2.143	10	2.7	46.3	43.7	35.6	33.1
$Ag^+(NHMe_2)_2$	2.156	15	2.6	45.2	42.7	38.2	31.3
$Ag^+(NMe_3)_2$	2.173	21	2.1	42.9	40.5	36.8	29.5
$Ag^+(H_2O)$	2.191	3	1.6	30.6	29.8	20.5	23.7
$Ag^+(MeOH)$	2.186	4	1.2	34.5	33.7	23.3	26.7
$Ag^+(Me_2O)$	2.190	6	1.2	35.4	34.5	22.5	27.8
$Ag^+(H_2O)_2$	2.148	9	2.3	29.4	27.6	30.5	18.5
$Ag^+(MeOH)_2$	2.142, 2.144	11	1.6	32.3	30.4	29.6	21.6
$Ag^+(Me_2O)_2$	2.150	15	1.4	32.4	30.5	31.2	21.2

[a] Bond lengths are in angstroms. The vibrational zero-point energies and incremental binding energies, enthalpies and free energies are given in kcal mol^{-1}. Binding entropies were calculated from unscaled frequencies using the harmonic approximation and are in cal K^{-1} mol^{-1}. The changes in zero-point energies are unscaled. No corrections have been made for basis set superposition error. [b] NLVF is the number of low-frequency vibrations (<600 cm^{-1}) per complex.

are the ligand wag modes for $Ag^+(H_2O)_2$ and the twisting motion about the ligand−metal−ligand axis for both. We evaluated the barriers for free axial rotation of the ligands to be much less than thermal energy and hence the twisting motions may be adequately represented as free internal rotors. This is the only anharmonic correction found to be necessary for $Ag^+(NH_3)_2$; its effect is to increase slightly $-\Delta S$ with CCSD(T)/aVDZ(f) predicting $-\Delta S = 31.3$ cal mol^{-1} K^{-1}, in excellent agreement with the value observed by Holland and Castleman[11] of 32.7 ± 1.2 cal mol^{-1} K^{-1}.

The ligand wag motions are clearly important for $Ag^+(H_2O)_2$ as the potential energy surface has a sombrero shape with minima of C_2 symmetry (distorted 21°) about a saddle point of D_{2d} symmetry. We evaluated the potential energy along these wag coordinates and found that it increases rapidly to over thermal energy at distortions of ca. 30° from D_{2d}. The potential-energy profile supported by UNIMOL which most closely resembles the calculated one is that of two hindered 1-dimensional rotors that are free to move within 30° from the high-symmetry D_{2d} configuration. We made two estimates for anharmonic corrections to the entropy of $Ag^+(H_2O)_2$ for wag and twist motion, one based on the C_2 equilibrium geometry and another based on the low-energy D_{2d} saddle point. Using CCSD(T)/aVDZ(f), this produced $-\Delta S = 22.4$ and 20.7 cal mol^{-1} K^{-1}, respectively, in satisfactory agreement with the experimental value of 22.3 ± 0.5 cal mol^{-1} K^{-1}.

For $Ag^+(H_2O)$, the CCSD(T)/aVDZ(f) harmonic-calculated entropies appear not to require anharmonicity correction and differ from the observed value by 8 cal mol^{-1} K^{-1}. As this discrepancy is much larger than that found for any other system, the experimental result requires reinvestigation.

IV. Effects of Alkylation

A large number of conformers for the alkylated complexes were found by BP86/SV(P); the lowest-energy ones are described in Figure 1 and Table 3. Typically, the conformers differ in the arrangement of the methyl hydrogens with respect to the metal−ligand bond. The lowest-energy conformers have the same internal ligand configurations as those found for the free ligands and their conjugate acids;[41] when attached to the metal, these configurations minimize the metal−hydrogen interactions which probably leads to an increase in their relative stability.

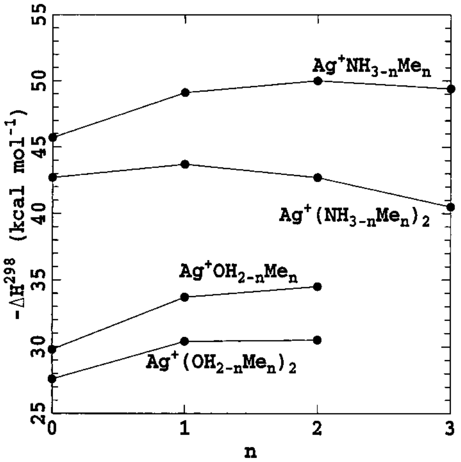


Figure 2. Binding enthalpies ($-\Delta H$) for the addition of a ligand to form various silver(I) complexes, as a function of the degree of methylation *n*.

A subtle structural feature of the aqua complexes is the orientation of the planes of the water molecules with respect to the metal-donor bonds. As shown in Table 2, BP86/SV(P) predicts that $Ag^+(H_2O)$ is nonplanar, in contrast to CCSD(T) and most other methods.[13] BP86/SV(P) also predicts similar "kinked" structures for the alkylated complexes. This ambiguity in the structure is not expected to induce significant errors in calculated binding enthalpies, however, because the calculated energy differences relative to the planar structures of $Ag^+(H_2O)$, $Ag^+(MeOH)$, and $Ag^+(Me_2O)$ are just 0.03, 0.3, and 0.4 kcal mol^{-1}, respectively. These small energy differences between the kinked and planar forms indicate that there is little preference for sp^2 over sp^3 hybridization for Ag(I)-coordinated oxygen atoms.

The calculated silver-donor bond lengths for the complexes and thermodynamic data for the ligand binding are shown in Table 3. Entropies and free energies are also included, evaluated using the harmonic approximation for the vibrational energy. Although the large number of low frequency modes for the complexes are unlikely to all be treated adequately, only small errors in the thermal energy are expected and these should partially cancel out. As a consequence, the relative errors in the calculated enthalpies should be quite small.

Some trends in the calculated silver-donor bond lengths occur, see Table 3. The Ag−N bond length increases by 0.005, 0.007, and 0.021 Å for the substitution of $Ag^+(NH_3)$ by the first, second, and third methyl groups, respectively, and by 0.010, 0.012, and 0.017 Å for each pair of substitutions of $Ag^+(NH_3)_2$. We have also reported a similar increase in the Ag−N bond length upon *N*-alkylation of some macrocycle complexes of silver(I) in both the gas-phase calculated and X-ray crystal structures.[4] However, the calculated Ag−O bond lengths do not behave analogously, the first methylation producing a small bond-length contraction while the second methylation produces the reverse effect. For all complexes the silver-donor bond lengths are about 0.04 Å shorter in the diligand complexes compared to the corresponding monoligand ones.

The effect that donor-methylation has on the binding enthalpy is shown in Table 3 and in Figure 2. The binding enthalpies *increase* with (at least) the first methylation of the donor atom. Continued methylation results in decreased calculated stability of the amine complexes. Clearly, these calculations do not anticipate the unexpected enhanced stability found for some tertiary-amine containing macrocyclic silver(I) complexes in solution..[2−4]

V. Interpretation and Conclusions

To investigate the effects of alkylation on the ability of oxygen and nitrogen donors (specifically H_2O and NH_3) to bind to Ag(I), we have developed a DFT computational technique and showed that it makes realistic predictions concerning the binding of the parent molecules through comparison with both detailed experimental and ab initio computational data. Both computational methods are found to predict results in good agreement with each other, though some significant differences with experiment are found. While the most important data, including the relative energetics for the addition of the first and second ligands of a series, is qualitatively reproduced, our results suggest that the experimental enthalpy for the second addition of ammonia, as well as the experimental entropy for the first water addition, be reexamined.

In a recent review, Meyerstein[6] described the effects of *N*-alkylation of amine ligands on the properties of their metal ion complexes in terms of five contributions. Of these, the first and second are only applicable in solution and will both lead to unfavorable consequences of *N*-alkylation, decreasing the binding energy to the metal; we do not consider these here. The third effect is that alkylation is expected to increase the metal to donor bond lengths due to steric interactions between the metal and the methyl groups, thus reducing the binding energy. The fourth effect is that the alkyl substituents are electron donating groups, making the binding nitrogen a better σ-electron donor and hence increasing the binding energy. Last, the fifth effect is that *N*-alkylation may induce internal ligand skeleton strain and bond angle distortions due to steric hindrance, and will hence be unfavorable. This is only applicable to large ligands containing a skeleton and is not appropriate here (in all cases our calculated internal ligand conformers are invariant to complexation and very similar to those for the free ligands[41]).

Supplementary to the Meyerstein analysis,[6] it has been suggested by Deng and Kebarle[8] that the bonding between Ag^+ and oxygen, sulfur, and nitrogen-donating ligands is mainly electrostatic in origin, being less related to the hardness of the base. The primary electrostatic interaction is between the charged metal atom and the permanent moments of the ligands, but this is modulated by the degree of charge transfer from the ligands to the metal and so is coupled to other effects. Other electrostatic interactions (not explicitly considered by Deng and Kebarle) involve the polarizability of the ion and its ligands. Additional effects which are yet to be considered include the dispersive interactions between the ligand and metal. As both the polarizability and dispersive strength of a ligand increase with its number of electrons, these binding effects are actually expected to become significantly more important with methylation and should be included in a comprehensive treatise.

A variety of methyl substituent effects in the gas phase have been observed for different central ions.[11,42,43] For H^+, $FeBr^+$ and Ni^+, the binding enthalpies increase with the degree of *N*-methylation, although the effect is weakest for Ni^+ for which the binding enthalpies with $NHMe_2$ and NMe_3 are similar. Alternatively, for Li^+ and $CpNi^+$, the order is reversed with the binding enthalpy for the addition of $NHMe_2$ being larger than that for NMe_3. This latter behavior is similar to that predicted here for Ag^+. Clearly, at least two opposing forces are implicated, one which *strengthens* the bonding on methylation, and one which *weakens* it.

The weakening of the bonding associated with Li^+ on ligand methylation has been attributed by Woodin et al.,[7] on the basis of simple electrostatic calculations, to a large *electrostatic* repulsion between Li^+ and the methyl groups of NMe_3. This argument is parallel to (but significantly different from) Meyerstein's third effect, that *steric* repulsions between the ion and the methyl groups are important. Our calculated geometries mitigate against either factor being dominant as the calculated Ag to C minimum separations *decrease* with increasing degree of methylation while the corresponding Ag to N bond lengths lengthen (see Supporting Information) to indicate weaker Ag−N bonds. The lengthening of the Ag−N bonds may rather be caused by factors such as a significant decrease in the ion−dipole interaction energy with methylation. Our B3LYP/aVTZ(f) calculated dipole moments for the ligands are 1.49, 1.30, 0.93, and 0.44 D for NH_3 to NMe_3, respectively, and so a large reduction of the primary electrostatic interaction energy is anticipated on methylation. A key contribution to this reduced energy is that due to the large reduction of the partial nitrogen charge implied by the dipole moment changes.

On the basis of the above results, it appears most likely that the major effect operating to reduce the binding energy of alkylated N- and O- donor complexes of Ag(I) of the present type in the gas phase is the change in the electrostatic energy associated with the reduced ligand dipole moment; it is this change that serves to drive the calculated increase in the metal to ligand bond lengths.

The only contribution which increases the binding energy on methylation included in the analysis of Meyerstein[6] is the increasing σ-donating ability of the ligands. While this will lead to an increase in the covalent nature of the bonding, such electron donation will also increase the effective size of the ion and thereby increase the metal-donor bond length and hence decrease the electrostatic component of the bonding. Such electron donation is expected to have a large effect for a d^{10} ion such as Ag(I) compared to an ion with an incomplete d-shell such as Ni(I), as the additional electron density would need to occupy the (spatially) outermost atomic *s* orbital and thereby increase the effective size of the ion to a greater extent. In this respect, coodination to Li(I) is analogous to that for Ag(I), while coordination to H^+, in contrast, is an extreme example of control by covalent bonding effects.[43] Hence, by considering the interplay of covalent-bonding and electrostatic effects, it is possible to classify $M(I)-NH_3$, $M(I)-(NH_3)_2$, $M(I)-H_2O$, and $M(I)-(H_2O)_2$ complexes into ones in which a monotonic increase of binding energy with the degree of methylation is expected and ones in which at some stage the binding energy will start to decline. Other attractive forces which increase with alkylation, such as those associated with ligand polarizability and dispersive interactions, are less likely to correlate so well with changes in the identity of the ion, however.

While a plausible scenario for the effects of alkylation of oxygen and nitrogen donors is proposed, much work is required in order to establish more definitive results. Experimentally, further data concerning binding to different ions by appropriate ligands is required. Computationally, progress may also involve the use of sophisticated analyses of binding such as those of Roby−Davidson[44] and Morokuma,[45] but again it is clear that for a comprehensive analysis, the simultaneous description of the binding properties of a wide range of ions is required.

Appendix: Estimated Errors in the DFT Computational Techniques

The primary elements in the computational strategy are the choice of the DFT functionals and the choice of basis set. It is necessary to establish that the method used to determine molecular geometries is sufficiently accurate, as is the method used to determine single-point energies. We do this by considering results, shown in Table 2, for the properties of Ag(I) complexes with one or two H_2O or NH_3 molecules. The DFT predictions are compared to both observed data and to results predicted using CCSD(T).

A. Geometries. The method used to determine molecular geometries and vibration frequencies is BP86/SV(P), a fast nonhybrid density functional with a small basis set. Table 2 shows that geometries predicted by it are quite comparable with ones evaluated using CCSD(T)/aVDZ(f), an expensive but accurate ab initio method used with a large basis set. The silver-donor bond lengths are within 0.02−0.03 Å of each other, and further expansion of the basis set used in the CCSD(T) calculations is likely to reduce these differences even more. The N−H and O−H bonds are overestimated by 0.01−0.02 Å using BP86/SV(P), an effect which is due to the lack of polarization functions on hydrogen in the SV(P) basis set. This error is common to all calculations and hence is expected to have an insignificant effect on the calculated binding energies. For the bond angles, agreement is very good, to within 1° − 2°. We investigated the convergence of the calculated geometries with respect to expansion of the SV(P) basis set and found only small changes of order 0.02 Å in bond lengths and 0.5° in bond angles when the large aVTZ basis is used. Also, the further addition of an f function to the basis set of silver had negligible effect.

Of all the geometrical properties, the most significant difference between the two sets of calculated structures is that the ground-state structure for $Ag^+(H_2O)$ is predicted to be nonplanar (C_s) using DFT and planar (C_{2v}) using HF, MP2, and CCSD(T).[13] The DFT structure is similar to that which has actually been found for $Au^+(H_2O)$,[13] with the water molecule bent slightly out of the plane; this is illustrated in Figure 1. Of major importance herein is the magnitude of the error in the calculated binding energies that is likely to result from use of an incorrect structure. For this complex, the calculated energy difference between the C_s and C_{2v} configurations at the BP86/SV(P) level is extremely small, just 0.03 kcal mol^{-1}, and hence small uncertainties in the conformations of the clusters are not expected to affect the calculated binding energies. Energy differences of this order do flag difficulties with the use of harmonic approximations in the evaluation of thermodynamic properties, however.

B. Vibration Frequencies. Unfortunately, no observed vibration frequencies are available for comparison with the calculated quantities. However, the calculated BP86/SV(P) and CCSD(T)/aVDZ(f) frequencies are in good agreement with each other. Specifically, for the total of 28 intermolecular modes of the complexes, the largest difference in calculated frequency is 108 cm^{-1} while the root-mean-square difference is just 49 cm^{-1}. Our primary use of the calculated frequencies is for the estimation of the ZPEs, corrections to the binding internal energy to evaluate ΔH, and to estimate ΔS. The ZPE corrections evaluated using the two methods are in good agreement, differing by at most 0.3 kcal mol^{-1}. The binding entropies calculated using the two methods agree to within 0.5 cal K^{-1} mol^{-1}.

C. Single-Point Energies. Our single-point energy calculations require the greatest absolute accuracy of the computational method, and results near the CBS limit are essential. For the DFT calculations basis set convergence was estimated considering the BSSE for the first two additions of ammonia to silver(I). The addition of diffuse functions to the ligands was found to be crucial, with the BSSEs for the SV(P), VDZ and aVDZ basis sets being 9.6, 7.4, and 0.95 kcal mol^{-1} respectively. Adding diffuse functions to silver decreased the BSSE further, to 0.44 kcal mol^{-1} for the aVTZ basis set, but the addition of an f polarization function did not alter the BSSE. On the basis of sample calculations of the BSSE for the first and second additions of ammonia (0.13 and 0.31 kcal mol^{-1}, respectively) and for the first addition of trimethylamine (0.29 kcal mol^{-1}) (discussed in section IV), the BSSE at the B3LYP/aVTZ(f) level is estimated to be less than 0.5 kcal mol^{-1} for a single addition of ligand, and the relative BSSE between the addition of different ligands is estimated to be less than 0.2 kcal mol^{-1}.

Convergence of the DFT calculations with respect to basis set expansion was also monitored through examination of the calculated binding energies. Similar effects were seen as found previously through examination of the BSSE. However, inclusion of the f function on silver changed the binding energies by 0.3−0.4 kcal mol^{-1}, and hence this function was included in subsequent calculations. The difference in the calculated DFT binding energies between the aVTZ(f) and aVDZ(f) basis sets for $Ag^+(NH_3)_2$ is just 0.6 kcal mol^{-1} indicating that the larger calculations are indeed very close to the ligand CBS limit. The inclusion of an f function on silver has been shown to have much larger effects for CCSD(T) calculations, however, and in this context expansion to the infinite basis set limit has also been considered by Feller et al.[13] and, for Au^+CO, by Dargel et al..[40]

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Supporting Information Available: Provided in ASCII text format are the DFT/SV(P) calculated geometries and vibration frequencies for all of the complexes considered, with in addition analogous results for the ligands H_2O and NH_3; CCSD(T)/aVDZ(f) normal modes also provided for the nonmethylated species, as are the Duschinsky matrices which relate the DFT and CCSD(T) normal modes. This material is available free of charge via the Internet at http://pubs.acs.org.

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