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Communication

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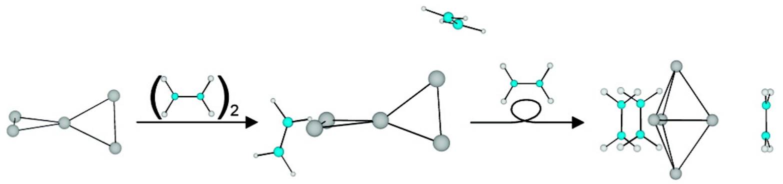

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Probing the Structure of Gas-Phase Metallic Clusters via Ligation Energetics: Sequential Addition of C_2H_4 to Ag_m^+ ($m = 3-7$)

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Small metal particles have long played an important role in many catalytic processes. Historically, these catalysts have been developed empirically, but in recent years a determined effort has been made to understand the details of these processes on a "molecular" or "nano" scale. One particularly hopeful method is the study of size-selected clusters both in the gas-phase[1] and deposited on various solid substrate materials.[2,3] Of special interest are the so-called coinage metals, copper, silver, and gold. Evidence indicates that deposited gold clusters have displayed size-specific activity[4a] and silver particles selectively epoxidize ethene and propene.[4b,c] There is currently intense interest in trying to understand their size dependence[5] and to develop robust theoretical models that are independent of both the metal (Cu, Ag, Au) and the substrate. Detailed results on gas-phase clusters can provide important information, both as data for testing theoretical models and to establish structural, energetic, and reactive properties for size-selected clusters independent of the substrate.

Here, our focus will be on small cationic silver clusters, Ag_m^+ ($m = 3-7$). Our goal is to use measured ligand-binding energies and entropies to unambiguously obtain structural information. Weis et al.[6] have used ion mobility methods[7,8] to obtain size-selected cross sections consistent with theoretical structural predictions. However, in several cases, candidate structures had similar cross sections and a unique determination could not be made. Further, addition of one or more ligands may cause substantial rearrangement of the metal cluster. This effect has obvious implications in studies of size-selected cluster catalysis. Through the proper choice of ligand, these experiments, together with theoretical calculation, can determine both the nascent and modified structures.

Others have used ligand attachment to infer metal cluster structure. Usually, "saturation" experiments are performed and a set of empirical rules used to interpret the data.[9] Here, we take a different approach. Recent theoretical work indicates that the LUMO on Ag and Au clusters is primarily located on "corner" atoms in the cluster.[10] The LUMO location strongly affects the charge distribution in Ag_m^+. For electron-donating ligands, such as C_2H_4, the binding energy at a particular cluster site should correlate with the charge distribution. Our hypothesis is that measured bond energies will correlate with charge distributions and allow us to identify equivalent, or near equivalent, "corners" in the clusters.

Thermodynamic information for the binding of C_2H_4 to Ag_m^+ was obtained using temperature-dependent equilibrium methods.[11−13] Measured equilibrium constants yield values of $\Delta G_T°$. The $\Delta G_T°$ values are plotted versus temperature to obtain $\Delta S_T°$ and $\Delta H_T°$ for each ligand addition.

A plot of $\Delta G_T°$ versus T for the first four C_2H_4 ligand additions to Ag_3^+ is shown in Figure 1. The first three additions form a family, having similar values of $\Delta H_T°$ and $\Delta S_T°$. The fourth ligand is much less strongly bound with a more positive value for $\Delta S_T°$. These data suggest three similar binding sites for the first three ethene ligands, with the fourth C_2H_4 occupying a second solvation shell.

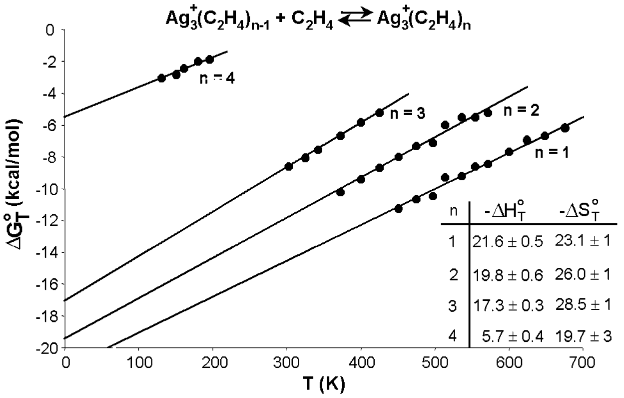

Figure 1. Plot of $\Delta G_T°$ versus temperature data for the Ag_3^+/C_2H_4 system. $\Delta H_T°$ (kcal/mol) and $\Delta S_T°$ (cal mol^{-1} K^{-1}) in insert.

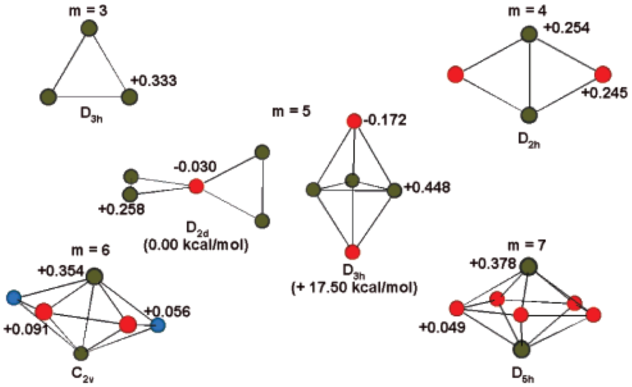

Figure 2. Calculated Ag_m^+ ($m = 3-7$) structures obtained from density functional theory (DFT)[14] using the Gaussian 03 package.[15] All minimum energy structures are consistent with those reported by Weis et al.[6] Ag atoms with equal charge distributions are colored identically for a given cluster. Charges are taken from NBO population analysis.[16] Energies reported for the Ag_5^+ cluster are relative to the D_{2d} conformer (DFT). Details are given in Supporting Information.

The data are consistent with the triangular lowest-energy theoretical structure shown in Figure 2.

The $\Delta G_T°$ versus T data for Ag_4^+ show a family of four, roughly equivalent C_2H_4 additions. A fifth ligand addition could be observed only at extremely low temperatures, indicating weak binding and a second solvation shell. Thus, a structure with four similar binding sites is predicted. This result is also consistent with the lowest-energy theoretical structure (Figure 2).

There is little ambiguity with the Ag_3^+ and Ag_4^+ systems. This changes with Ag_5^+. The $\Delta G_T°$ versus T data are shown in Figure 3. Six ligands additions are observed. The first two yield similar thermodynamic quantities. The third addition gives values of $-\Delta H_T°$ and $-\Delta S_T°$ that are substantially larger than the previous two additions. The fourth and fifth additions form a family of less strongly bound ligands, and the sixth ligand appears to add in the

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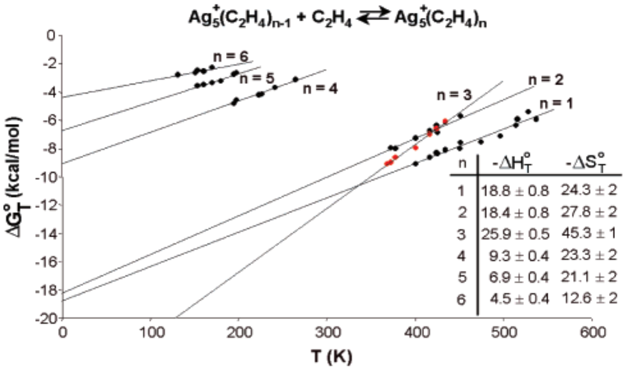

Figure 3. Plot of $\Delta G_T°$ versus temperature data for the Ag_5^+/C_2H_4 system. The $n = 3$ data points are shown in red for clarity. $\Delta H_T°$ (kcal/mol) and $\Delta S_T°$ (cal mol^{-1} K^{-1}) in insert.

second solvation shell. Thus, experiment indicates two equivalent "strong" sites, a third even stronger site not originally available, two weaker sites, and then the second solvation shell.

Two Ag_5^+ cluster geometries are shown in Figure 2. The lowest-energy structure has four equivalent corners carrying the positive charge and a central atom with essentially no charge. The first two additions are consistent with this structure. However, the next three additions are not. The second Ag_5^+ structure, 17.5 kcal/mol higher in energy, is consistent with three strong additions followed by two weak additions. The data suggest a structural change upon addition of the third ligand from the D_{2d} lowest-energy structure to the D_{3h} higher-energy structure. On the basis of the measured binding energies, this process becomes exoergic on addition of the third C_2H_4 ligand. Note that the D_{3h} structure cannot be the initial gas-phase structure since we would have seen a family of three similar additions for the first three ligands.

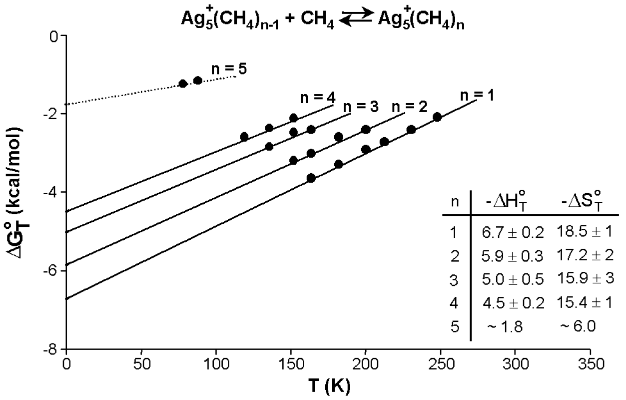

Figure 4. Plot of $\Delta G_T°$ versus temperature data for the Ag_5^+/CH_4 system. $\Delta H_T°$ (kcal/mol) and $\Delta S_T°$ (cal mol^{-1} K^{-1}) in insert.

To test this interpretation, Ag_5^+ was ligated with CH_4, a more weakly binding ligand than C_2H_4 (Figure 4). In this case, the first four ligands have similar binding energies and entropies, while the fifth occupies the second solvation shell. These results are entirely consistent with the lowest-energy D_{2d} Ag_5^+ structure, which has four equivalent binding sites, and with the fact that CH_4 ligation energies are too weak to induce structural isomerization of Ag_5^+.

For Ag_6^+ and Ag_7^+, the number of observed C_2H_4 additions equals the number of atoms in the two clusters, respectively. In both systems, the first two C_2H_4 ligands are strongly bound. For Ag_7^+, the final five additions yield similar $\Delta H_T°$ and $\Delta S_T°$ values. For Ag_6^+, the final four ligands bind to the cluster in a pairwise manner. Hence, the experiment predicts that there are three sets of two equivalent binding sites for Ag_6^+ and a set of two and a set of five equivalent sites for Ag_7^+. For both Ag_6^+ and Ag_7^+ (Figure 2), DFT indicates that the two atoms that lie above and below the planar region of the clusters have relatively high partial-positive charge. The planar region of Ag_7^+ is a pentagon, consistent with five equivalent additions of C_2H_4. In Ag_6^+, the four planar Ag atoms of the cluster are not equivalent. The electron density is asymmetrically distributed, giving rise to two distinguishable pairs of Ag atoms. The experiment is again in excellent agreement with the DFT calculations, indicating that the planar region of Ag_6^+ is not comprised of four equivalent atoms.

In summary, we have shown that the global structures of gas-phase silver cation clusters can be obtained from temperature-dependent equilibrium data. These structures are consistent with theory. The method is also sensitive to ligand-induced changes in bare cluster conformations, and results can be fine-tuned by changing ligands and, hence, ligand-binding energies. Details of the structures of the ligated clusters and the values of $\Delta H_T°$ and $\Delta S_T°$ for each ligation step will be published elsewhere.[17]

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Supporting Information Available: Details of the experimental and theoretical methods and the full citation for ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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