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Article

Bonding Interactions of Metal Clusters [M_n (M= Cu, Ag, Au; n=1-4)] with Ammonia. Are the Metal Clusters Adequate as a Model of Surfaces?

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Cálculos de densidade funcional (B3LYP/LANL2DZ) para clusters metálicos de amônia foram efetuados para obter comprimentos de ligação, modos de estiramento vibracional M-N, energias de ligação, cargas atômicas de Mulliken e potenciais adiabáticos de ionização. Os resultados indicam que átomos de cobre formam ligações mais intensas com amônia do que com prata ou ouro. A interação da ligação Ag_n com amônia é a mais fraca de todos os sistemas. A ligação das moléculas de amônia à clusters metálicos é comparável à de sistemas piridina-M_n Ambas moléculas apresentam uma interação dativa do par de elétrons isolado no átomo de nitrogênio. Cargas atômicas de Mulliken mostram uma pequena transferência de carga da molécula NH_3 para o átomo metálico ou cluster, sugerindo a formação da ligação dativa. Depois da transferência de carga da molécula de amônia, os clusters metálicos sofrem uma redistribuição das cargas e isto pode ser importante na estabilização do sistema. Na superfície, a redistribuição de carga deve ser menos significativa. Nesse sentido, o uso de clusters metálicos como modelo de superfície pode ser um modelo inadequado.

Density Functional (B3LYP/LANL2DZ) calculations for ammonia metal clusters were done in order to obtain bond lengths, M-N stretching vibrational modes, binding energies, Mulliken atomic charges and adiabatic ionization potentials. The results indicate that copper atom forms stronger bonds with ammonia than silver or gold. The bond interaction between Ag_n and ammonia is the weakest of all the systems. The bond of the ammonia molecule to the metal clusters can be compared with the pyridine-M_n systems. Both molecules present a donation interaction from the lone-pair of electrons on the nitrogen atom. Mulliken atomic charges show a small charge transfer from the NH_3 molecule to the metal atom or cluster, suggestive of a dative bond formation. After the charge transfer from the ammonia molecule, the metal clusters undergo a redistribution of the charge and this could be important for the stabilization of the system. In a surface, the redistribution of the charge should be less significant. In this sense, the use of metal clusters as a model of the surface may be an inadequate model.

Keywords: metal clusters, bond lengths, M-N stretching vibrational modes, binding energies, Mulliken atomic charges and adiabatic ionization potentials

Introduction

Complexes of bare metal clusters with simple molecules are important model systems for fundamental studies of metal-ligand bonding in cluster and surface chemistry.[1-17] Of particular interest is the relationship between cluster and bulk surface chemistry. In this area, Mitchell *et al.*[15] studied the reactions of copper and silver dimers with ammonia in the gas phase, while Chan and Fournier[17] reported a theoretical study of the binding of ammonia to small copper and silver clusters. A simple picture of the bonding mechanism was reported, and comparisons were made between ammonia adsorbed on the metal atoms and on bulk surfaces.

The theoretical study of the bonding in metal-ligand systems is challenging and has great importance in many fields.[18,19] There is a strong correlation between cluster ligand chemistry, stereochemistry, structure, and surface-ligand simulations. Given this correlation, it is possible to learn much about metal-centered reactivity from studies of small, unligated metal clusters and their reactions with atoms and small molecules.[20] In order to explore the reliability of the computational methods for this kind of systems, Lambropoulos and Reimers[14] reported an extensive study of the binding between a single neutral gold atom and ammonia, applying a range of density

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functional and *ab-initio* computational methods. They reported that the $AuNH_3$ complex can be used as a model of a gold (111) surface, but qualitative and quantitative differences are visible, the primary dissimilarity being the prediction of charge transfer within the complex and its relation with the binding strength. These results may have profound implications for molecular electronics in which small metal clusters are used to represent macroscopic electrodes.

On the other hand, pyridine, a model chromophore molecule, has been studied by numerous experimental and theoretical methods since surface enhanced Raman spectroscopy was observed on pyridine adsorbed on a rough silver electrode.[13,21] The theoretical investigation of the binding interactions between pyridine and small metal clusters such as copper, silver and gold in different sizes (1 to 4 atoms) indicates that the order in the binding energies between the pyridine and the metals is Cu-Au>Ag, *i.e.,* the interaction between the pyridine and silver is the weakest among the three metals. Also, the donation of the lone pair electrons on the nitrogen atom of the pyridine molecule was found as the major contribution to the binding interaction. A weak back-donation interaction from the metal atoms was also reported, with the conclusion that the structural change on pyridine is probably sensitive to this back-donation interaction. The comparison of the binding energies with the experimental desorption energies of the absorbed pyridine on copper and silver surfaces indicates that the chemisorbed bonds for pyridine on these metal surfaces are localized. Therefore, the small metallic cluster model is probably a good approximation to describe the chemisorption influence on the structure of the adsorbed pyridine.

According to Lambropoulos and Reimers,[14] small gold clusters may prove to provide an inadequate model to represent macroscopic electrodes. Wu *et al.,*[13] based on the comparison with some experimental results, established that a small metallic cluster model is probably a good approximation to describe the chemisorption interaction and its influence on the structure of the absorbed pyridine. In this context, and in order to explain the bonding and reaction of ammonia with metal atom and clusters, density functional studies on MNH_3, M_2NH_3, M_3NH_3, and M_4NH_3 (with M=Cu, Ag and Au) were performed. Bond distances, equilibrium geometries, binding energies, Mulliken atomic charges and adiabatic ionization energies are presented. The goal of this work is to compare these results with those previously reported for pyridine, in order to understand the different bonding situations. The bonding has been analysed in terms of molecular orbitals. As discussed below, metal clusters with simple molecules are important model systems for fundamental studies of metal-ligand bonding in clusters and surface chemistry, but caution is required when metal clusters are used to represent macroscopic systems.

Methodology

All calculations were performed using Gaussian-98[22] and the hybrid B3LYP functional.[23] These calculations were carried out with the LANL2DZ[24-26] atomic orbital basis functions. Full geometry optimization without symmetry constraints has been performed, starting from several initial geometries to locate different minima on the potential energy surface. One can not exclude the possibility that true global minima were missed in the optimization procedure, but the number of different initial geometries that were considered is sufficiently high to lend confidence that the global minimum has been identified. Optimized geometries were verified by frequency calculations.

The hybrid B3LYP method yielded accurate dipole moments and infrared intensities in general, and accurate dipole polarizabilities in metal clusters.[27] Lambropoulous *et al.*[14] performed accurate calculations of the energy of $AuNH_3$, and they reported that the calculations with small basis such as LANL2DZ provide excellent quality for the computational resources required, but B3LYP underestimates the interaction energy by 5 kcal mol^{-1}, approximately. This value is within on the known density functional calculations error.

The systems under study are small, and more precise (and expensive) calculations can be done. However, comparative studies with several models and basis were performed by other authors,[14,17] validating the methodology that is used in this paper. B3LYP is a highly controversial hybrid functional. However, there is a long list of references[28] were the B3LYP functional has been reported to produce good results when compared with experiments and other more sophisticated calculations. Based on those previous results, it is possible to say that the computations are enough to obtain reliable information on the studied systems.

There is no universally accepted method of calculating atomic charges, and no experimental technique is available to measure them directly. In a previous work, de Oliveira *et al.*[29] reported an investigation testing the quality of Mulliken and Bader charges. They found a good agreement between both methods for a qualitative description of the atomic charges. For this reason, in this paper the Mulliken atomic charges are used to discuss the qualitative behavior of the charge transfer process.

Results and Discussion

Geometries and vibrational frequencies

Figures 1 to 3 show the optimized geometries for the most stable structures that were considered. Also for comparison, the previously reported[13] optimized structures of pyridine-M_n (with M=Cu, Ag and Au; n=1-4) are shown. All the structures are minimum on the potential energy surfaces.

It is well known that, for electron-donor ligands such as NH_3, the atop site is preferred on metal clusters.[17] A few test calculations for adsorption sites other than atop were performed, but these species relaxed towards the atop geometry upon optimization. As can be seen in Figures 1 to 3, the compounds are linear or planar structures and the M-M bond distances become larger when one goes from the complex with two metal atoms to the cluster with four metal atoms. For all the systems, the end-on coordination geometry is the most stable. The Cu-N bond distances are similar for the atom and the clusters, while for Ag and Au the behaviour is different because the M-N bond distance becomes shorter for bigger clusters. In general, for silver and gold atoms and clusters, the M-N distance decreases when one goes from the complex with one metal atom to the cluster with four metal atoms. Comparing the different systems, it can be noted that copper forms stronger bonds with ammonia than silver or gold. The bond interaction between Ag_n and ammonia is the weakest of all the systems.

For silver clusters the bond distances are significantly bigger than for the other metals, owing to a large atomic radius of the silver atom compared with Cu and Au. For gold clusters, the bond distances are between those of copper and silver clusters. Although electrons occupy up to the 5d and 6s orbitals in gold atoms, the radii of the 6s and 5d orbitals is contracted due to the strong relativistic effects. The result of this contraction is a small radii, compared with the silver atom.

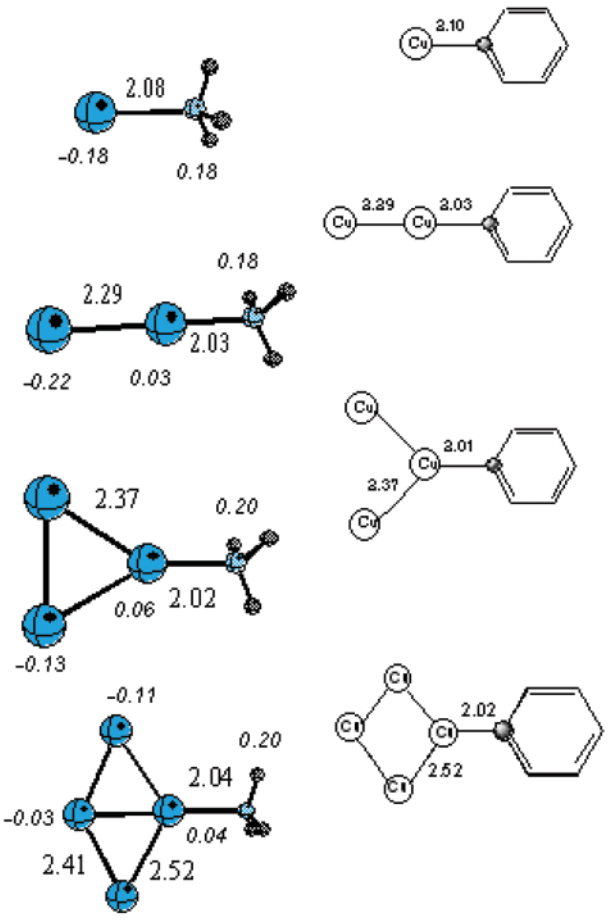

Figure 1. Optimized structures of Cu_n-NH_3 (n= 1 to 4). Bond distances in Å. Mulliken atomic charges in italics. For comparison, Cu_n-Py structures reported before are also shown. All the calculations with B3LYP/LANL2DZ.

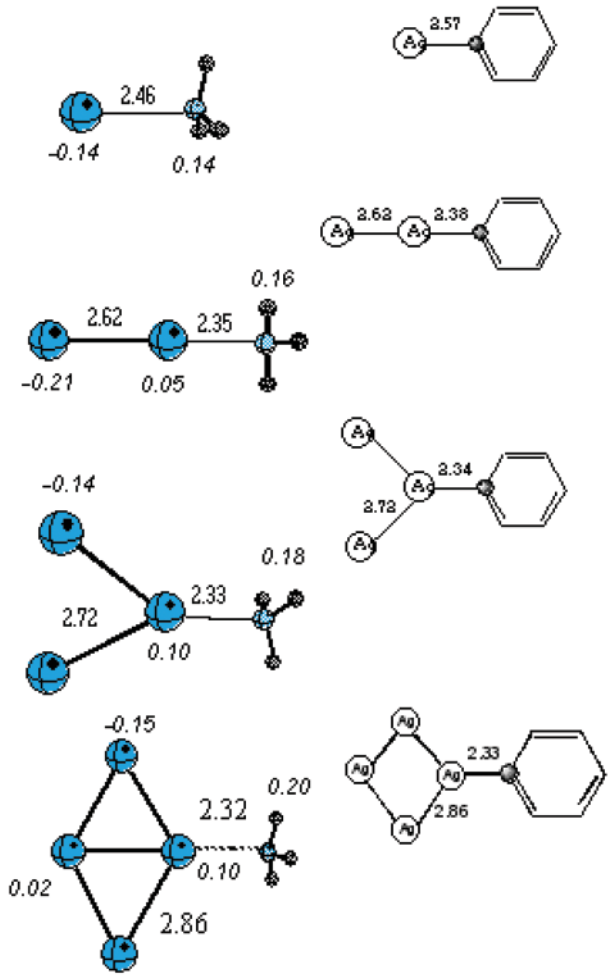

Figure 2. Optimized structures of Ag_n-NH_3 (n= 1 to 4). Bond distances in Å. Mulliken atomic charges in italics. For comparison, Ag_n-Py structures reported before are also shown. All the calculations with B3LYP/LANL2DZ.

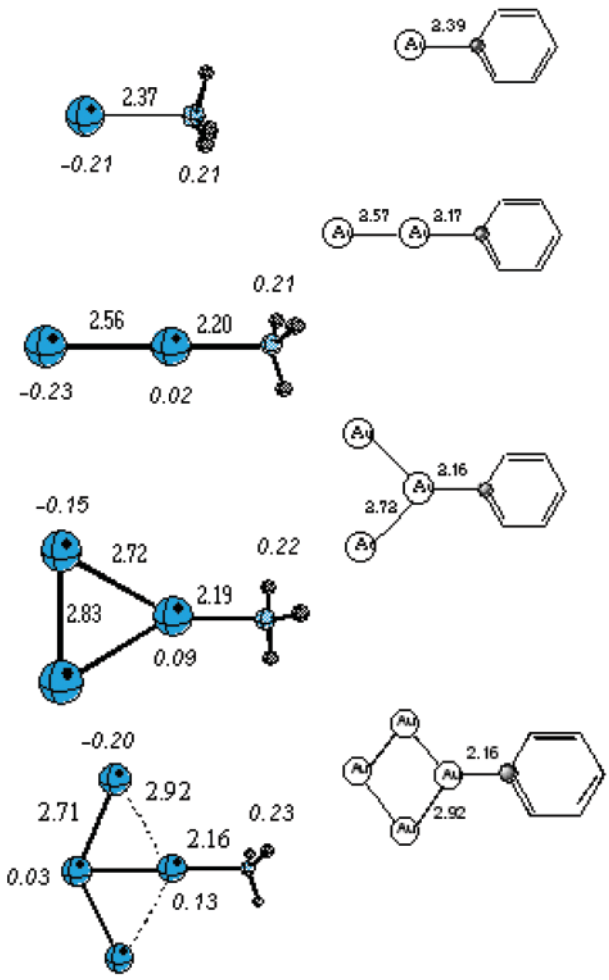

Figure 3. Optimized structures of Au_n-NH_3 (n= 1 to 4). Bond distances in Å. Mulliken atomic charges in italics. For comparison, Au_n-Py structures reported before are also shown. All the calculations with B3LYP/LANL2DZ.

Let us discuss the geometrical changes on the metal clusters due to the interaction with the ammonia molecule. Table 1 lists the bond length and bond angles of the bare metal clusters. The M-M bond distances of M_2 and M_3 clusters slightly increase owing to the lone-pair electrons dative to the antibonding orbitals of the M-M bonds. The strong interaction between the ammonia and the M_4 clusters results in a large change of the geometries of the cluster. For Cu_4, the M-M bond distance increases from 2.45 to 2.52 Å. For Ag_4 the bond length changes from 2.81 to 2.86 Å and from 2.77 to 2.92 Å for Au_4. These results indicate that the M-N bond leads to the large geometrical changes at the M-M bond distances of M_4.

The bond of the ammonia molecule to the metal clusters can be compared with the pyridine-M_n systems. As shown in Figures 1 to 3, the structures with ammonia are quite similar to those with pyridine. For Cu_n, Figure 1 indicates that the bonds distances are practically the same. The biggest

Table 1. Bond length (in Å) and angles (in °) of the bare metal clusters. All the calculations were obtained with LANDL2DZ and B3LYP

	Cu	Ag	Au
M_2	2.26	2.611	2.573
M_3	2.32	2.69	2.64
Angle	74 and 53	146 and 17	140 and 20
M_4	2.45	2.81	2.77
Angle	123 and 56	123 and 57	122 and 58

difference is for Cu-N, were the bond length changes from 2.08 Å with ammonia to 2.10 Å with pyridine. For silver in Figure 2, the distances for Ag_2, Ag_3 and Ag_4 are practically the same for both (ammonia and pyridine) but for the silver atom the M-N distance changes considerably, from 2.46 for ammonia to 2.57 Å for pyridine. As can be seen in Figure 3, for Au_n the behaviour is alike. Bond distances are similar, the biggest difference being on the M-N bond of Au, Au_2 and Au_3. From these results it is possible to say that pyridine and ammonia are comparable, and that their effects on the geometries of the clusters are the same. Both molecules present a donation interaction from the lone-pair of electrons of the nitrogen atom. This charge transfer process changes the geometry of the metal clusters. The similarity of the structures of Py-M*n* and NH_3- M*n* is a possible indication of the small back donation interaction from the *d* orbital to the fourth π type antibonding orbital of pyridine. This back donation does not affect the bond between the metal and the N atom of pyridine.

The photoelectron diffraction technique for pyridine absorbed on Cu(110) reveals a N-Cu bond distance equal to 2.00 Å.[30] This value is also similar to the calculated N-Cu bond distance of ammonia. For silver and gold there are no direct experimental data for comparison. The calculated bond distances for Py-M_n are fairly similar to the values of NH_3-M_n. Both values are probably close to the experimental values of chemisorption states. However, since the M-N bond distances are practically the same for both, pyridine and ammonia, the bond distance is not enough to distinguish between the absorbate species.

Harmonic vibrational frequencies (Table 2) have been obtained for the most stable structures. The M-N stretching vibrational mode is also indicated in the Table. The structures are minimum on the potential energy surfaces. For Cu_4NH_3, Au_3NH_3 and Au_4NH_3, one small imaginary frequency was found (equal to *17i*, *64i* and *32i* cm^{-1} respectively, see Table 2). Similar results were reported by Mierzwicki *et al.*[31] for Li atom, and Hashimoto *et al.*[32] for $Na(NH_3)_2$ and $Na(NH_3)_3$ complexes, where NH_3 molecules could rotate almost freely around the M-N bonds. The imaginary frequency of Cu_4NH_3, Au_3NH_3 and Au_4NH_3 also

Table 2. Harmonic vibrational frequencies (in cm^{-1}) for the most stable structures. The M-N stretching vibrational mode is underlined. The M-N stretching vibrational mode connected with the distorsion of the metal cluster is indicated in ***bold-italic***

$CuNH_3$	Cu_2NH_3	Cu_3NH_3	Cu_4NH_3
322, 500, 504, 1088, 1684, 1685, 3416, 3599, 3600	66, 67, ***226***, 380, 559, 561, 1134, 1696, 1696, 3447, 3612, 3612	20, 31, 66, 125, 146, ***213***, 399, 580, 594, 1163, 1699, 1700, 3460, 3617, 3619	*17i*, 52, 64, 74, 103, 117, 142, 217, ***225***, 398, 591, 592, 1155, 1699, 1700, 3468, 3623, 3630
$AgNH_3$	Ag_2NH_3	Ag_3NH_3	Ag_4NH_3
225, 418, 421, 936, 1684, 1684, 3474, 3669, 3670	67, 68, ***168***, 281, 509, 510, 1047, 1695, 1695, 3478, 3655, 3656	33, 47, 63, 73, 103, ***153***, 291, 532, 543, 1084, 1699, 1699, 3481, 3651, 3652	28, 32, 54, 61, 73, 83, 99, 152, ***164***, 297, 543, 549, 1082, 1698, 1699, 3485, 3653, 3657
$AuNH_3$	Au_2NH_3	Au_3NH_3	Au_4NH_3
248, 516, 523, 985, 1679, 1680, 3483, 3672, 3673	57, 59, ***165***, 354, 667, 668, 1190, 1698, 1699, 3464, 3620, 3622	*64i*, 37, 50, 82, 86, ***145***, 358, 673, 684, 1209, 1699, 1700, 3467, 3619, 3619	*32i*, 11, 29, 43, 54, 64, 90, 146, ***153***, 367, 684, 689, 1207, 1699, 1701, 3471, 3622, 3625

corresponds to the rotation of the NH_3 molecule around the M-NH_3 bond. The Potential Energy Surface is very flat and the imaginary frequency could be an artificial result due to numerical errors. Therefore, it is safe to assume that the geometries presented in Figures 1-3 and the energies of these structures are quite similar to the minimum on the potential energy surface.

Table 3 shows the M-N stretching vibrational mode of NH_3-M_2 together with pyridine-M_2 systems, previously reported by Wu *et al.*[13] Although the bond distances are quite similar, all the values for pyridine systems are smaller than those with ammonia due to the differences on the structures of the ligands. These harmonic frequencies can be used to differentiate the ligand that is bonded to the surface.

Table 3. M-N stretching vibrational mode (in cm^{-1}) of NH_3-M_2 and pyridine-M_2, previously reported by Wu *et al.*[13] Experimental values of pyridine adsorbed on the corresponding metal surface are 244, 235 and 260 cm^{-1}, for copper, silver and gold, respectively

Cu_2NH_3	Ag_2NH_3	Au_2NH_3
225, 380	167, 281	164, 354
Cu_2Py	Ag_2Py	Au_2Py
154, 276	107, 192	137, 199

Energetics, atomic charges and molecular orbitals

The binding energies for $M_n + NH_3 \rightarrow M_nNH_3$ are reported in Table 4. In all cases, the products of the reaction are more stable than the reactants. For comparison, other theoretical predictions and available experimental results[15] are shown. The binding energies for monoligand complexes of ammonia with metal atoms and clusters (M_n, with n from 1 to 4 atoms) are similar to those calculated by other authors. In general, the theoretical values overestimate the binding energies.

Table 4. Binding energies (kcal mol^{-1}) for monoligand complexes of ammonia with metal atoms and clusters (from 2 to 4 atoms). For comparison, other theoretical predictions and available experimental results are shown. Pyridine-Mn previous results are included. All calculations with B3LYP and LANL2DZ

System	This work	Experiment[15]	Other theoretical values[14,17]	Pyridine-M_n[13]
$CuNH_3$	16.8	Ω 11	13.1	
Cu_2NH_3	24.6	20 ±1	23.5	Cu_2-Py 21.4
Cu_3NH_3	29.5		28.4	Cu_3-Py 26.9
Cu_4NH_3	29.8		27.5	Cu_4-Py 26.7
$AgNH_3$	9.0	Ω 9.5	9.0	
Ag_2NH_3	16.8	15 ±1	16.8	Ag_2-Py 11.5
Ag_3NH_3	19.1		19.1	Ag_3-Py 13.8
Ag_4NH_3	21.6		21.6	Ag_4-Py 16.3
$AuNH_3$	9.2		13.9	
Au_2NH_3	30.9			Au_2-Py 25.7
Au_3NH_3	29.8			Au_3-Py 25.2
Au_4NH_3	32.1			Au_4-Py 27.6

The binding energy increases with cluster size from MNH_3 to M_4NH_3, with the exceptions of Cu_3NH_3 and Cu_4NH_3, and Au_2NH_3 and Au_3NH_3, where the values are roughly equal. Copper atom forms stronger bonds with ammonia than silver or gold. The bond interaction between Ag_n and ammonia is the weakest of all the systems. For the dimers, gold forms stronger interactions with ammonia than copper, whereas the trimers present similar binding energies. For the tetramers, gold presents stronger interactions than copper. There is a correlation between the equilibrium M-N bond length and the binding energy. For each system, the M-N bond distance decreases as the strength of the bond increases. Also in Table 4, the binding energies for pyridine-M_n systems are reported. They are smaller than the corresponding for ammonia, indicating that the metal-ammonia bond is stronger than the metal-pyridine bond. Also for metal-pyridine systems, the

binding energy increases with cluster size from M_2NH_3 to M_4NH_3, with some exceptions. The results for Cu_3-Py and Cu_4-Py are roughly equal, and the same is true for Au_2-Py and Au_3-Py. The bond interaction between Ag_n and pyridine is the weakest of all the systems. For the dimers, gold forms stronger interactions with ammonia than copper, whereas Cu_3 presents a larger binding energy than Au_3. For the tetramers, gold presents stronger interactions than copper. In general, the binding energies of metal atoms and clusters with pyridine and ammonia are similar.

Figure 1 to 3 show the net atomic charges from Mulliken population analyses. The analysis of the NH_3-M_n (M=Cu, Ag, Au; n=1-4) compounds shows that there is a small charge transfer process from the NH_3 molecule to the metal atom or cluster, suggestive of a dative bond formation. The analysis of the bond distances shows that the charge transfer from NH_3 to M_n weakens the M-M bond. As a consequence, the M-M bond is shorter when ammonia molecules are absent.

The metal atoms that are not connected to the N present a negative charge. Binding of NH_3 to Cu_3, Ag_3 and Au_3 results in a small charge transfer from the ligand to the cluster, and a redistribution of the charges within the cluster. For Cu_4, Ag_4 and Au_4, the two atoms at the end of the short diagonal carry positive charge while corresponding negative charges reside on the two atoms of the long diagonal. The N atom is negatively charged in free NH_3. Again, binding of NH_3 to Cu_4, Ag_4 and Au_4 results in a small charge transfer from the ligand to the cluster, and a redistribution within the cluster. Natural population atomic charges reported before for M_4NH_3 (M=Cu and Ag) reaches the same general conclusions.[17]

Little charge transfer is found for the interaction with the Au(111) surface. As far as it can be seen from this analysis, there is a small charge transfer from the ammonia molecule to the metal clusters. As a consequence, the metal clusters present a redistribution of the charge and this could be important for the stabilization of the system. In a surface, the redistribution of the charge should be less significant. In this sense, the use of metal clusters as a model of the surface may be an inadequate model. Besides, there are size dependent properties on clusters (such as binding energies and structures), that make these systems very interesting but interfere with the idea of a model for bulk properties, where there is not such dependence. The chemistry of the metal clusters is interesting by itself since their study is useful for the understanding of the chemical reactivity. Clusters as a model of the surface are useful to identify vibrational frequencies, but caution is required when we want to analyse different situations, like the charge transfer process.

The molecular orbital pictures of MNH_3, Cu_2NH_3 and Cu_3NH_3 are shown in Figures 4 and 5. The general appearance of the molecular orbitals is quite similar for all of the systems. For this reason, the other molecular orbitals are not reported (they are available upon request). For all the systems, the lowest unoccupied molecular orbital (LUMO) is a nonbonding orbital of the ammonia molecule.

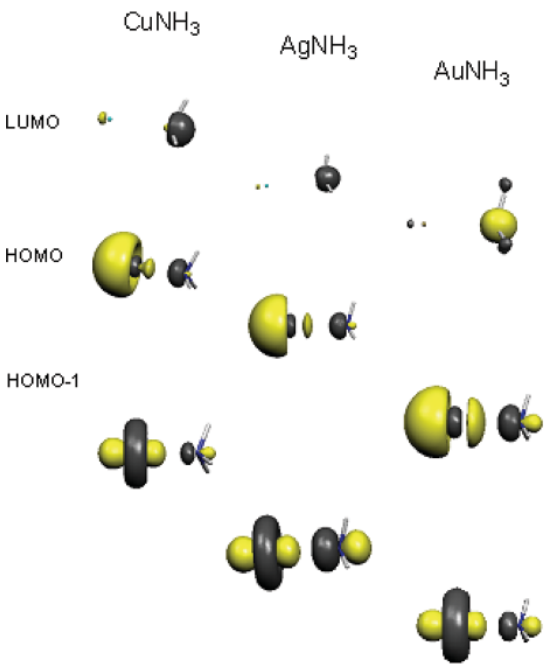

Figure 4. Representative molecular orbitals picture of $CuNH_3$, $AgNH_3$ and $AuNH_3$.

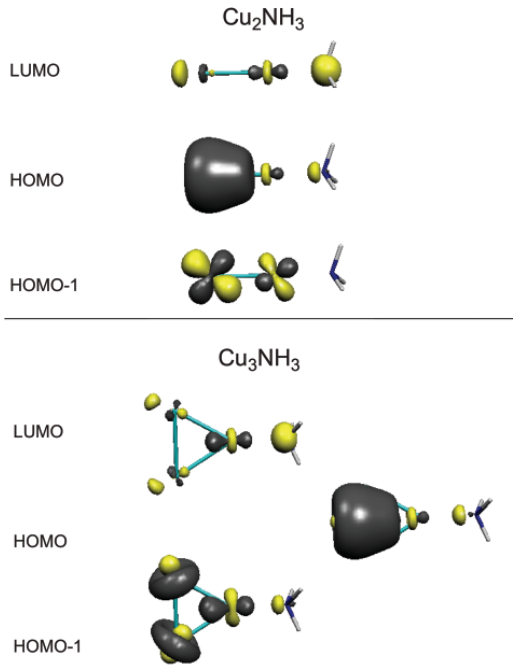

Figure 5. Representative molecular orbitals picture of Cu_2NH_3 and Cu_3NH_3.

In Figure 4 is possible to see that the highest occupied molecular orbital (HOMO), is an antibonding orbital between the N and the metal atom. In Figure 5, the HOMO for Cu_2NH_3 and Cu_3NH_3 is an antibonding orbital between nitrogen and the metal atom, and a σ bonding orbital between the metal atoms. The same results were found for silver and gold dimers and trimers. Removing an electron from these systems must reduce the bond distances between N and metal atoms, and increase the M-M bond length. As a general conclusion, the HOMO orbital is an antibonding orbital between the metal cluster and the ammonia molecule, and a bonding interaction in the cluster.

Cationic systems

Table 5 presents the results for the optimized cationic systems. Bond distances and adiabatic ionizations potential in eV are included. It is possible to see that the M-N bond distances of the cationics are smaller than for the neutral systems, whereas the M-M bond length of the cations is larger than for the neutral. This agrees with the molecular orbital pictures, were the HOMO is an antibonding orbital between the N and the metal atoms, and a bonding orbital between the metal atoms of the cluster. When one electron is removed from this orbital, the antibonding is diminished whereas the bonding interaction between the metal atoms is increased. The ionization potential of these systems is a size dependent property, as can be seen in Table 5. For the metal atoms is smaller than for the dimer. For the trimer is again smaller than for the dimer, and for the tetramer it is larger than for the trimer. The maximum ionization energy is for the dimer. Furthermore, the ionization energy of the gold systems is the larger among all the clusters, due to the strong relativistic effects. For copper and silver, the ionization energy is similar.

Table 5. Optimized cationic systems. Bond distances in Å and adiabatic ionizations potential in eV are reported

CATIONS	M-N	M-M	Addiabatic ionization energy
$CuNH_3$	1.96		5.7
Cu_2NH_3	1.99	2.44	6.7
Cu_3NH_3	2.01	2.44, 2.33	5.0
Cu_4NH_3	2.02	2.52, 2.40	5.9
$AgNH_3$	2.23		5.9
Ag_2NH_3	2.26	2.79	6.7
Ag_3NH_3	2.27	2.78, 2.69	5.0
Ag_4NH_3	2.29	2.88, 2.77	5.9
$AuNH_3$	2.09		6.9
Au_2NH_3	2.12	2.69	8.2
Au_3NH_3	2.15	2.75, 2.63	6.3
Au_4NH_3	2.17	2.86, 2.71	7.2

Conclusions

The bond of the ammonia molecule to the metal clusters can be compared with the pyridine-M_n systems. The structures with ammonia are quite similar to those with pyridine. The bonds distances are practically the same. Both molecules present a donation interaction from the lone-pair of electrons on nitrogen atom. This charge transfer process changes the geometry of the metal clusters. The similarity of the structures of Py-M*n* and NH_3- M_n is a possible indication of the small back donation interaction from the *d* orbital to the fourth π type antibonding orbital of pyridine. This back donation does not affect the bond between the metal and the N atom of pyridine.

The binding energy increases with cluster size from MNH_3 to M_4NH_3, with some exceptions. For each system, the M-N bond distance decreases as the strength of the bond increases. The binding energy for pyridine-M_n systems is smaller than the corresponding for ammonia. As a general conclusion, the HOMO orbital is an antibonding orbital between the metal cluster and the ammonia molecule, and a bonding interaction in the cluster.

Mulliken atomic charges show a small charge transfer from the NH_3 molecule to the metal atom or cluster, suggestive of a dative bond formation. As a consequence, the M-M bond is shorter when ammonia molecules are absent. After the charge transfer from the ammonia molecule, the metal clusters undergo a redistribution of the charge and this could be important for the stabilization of the system. In a surface, the redistribution of the charge should be less significant. In this sense, the use of metal clusters as a model of the surface may be an inadequate model.

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