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Origin of the Unusual Properties of Au_n(BO₂) Clusters

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We report the discovery of a new class of clusters consisting of $Au_n(BO_2)$ that forms during the oxygenation of gold clusters when boron nitride is used as insulation in a pulsed-arc cluster ion source (PACIS). Photoelectron and mass spectroscopy of these clusters further revealed some remarkable properties: instead of the expected Au_nO_m peaks, the mass spectra contain intense peaks corresponding to $Au_n(BO_2)$ composition. Some of the most predominant features of the electronic structure of the bare Au clusters, namely even–odd alternation in the electron affinity, are preserved in the $Au_n(BO_2)$ species. Most importantly, $Au_n(BO_2)$ [odd n] clusters possess unusually large electors.

1. Introduction

Herein we report the observation of a new class of unusually stable clusters consisting of Au atoms interacting with BO₂ molecules that have unique properties. Au, clusters retain their geometrical structure and electronic properties in spite of their strong interaction with the BO₂ molecule. Our observation of the unusually stable Au_n(BO₂) clusters was a result of serendipity. During a study of the interaction of Au clusters with oxygen in a pulsed-arc cluster ion source (PACIS)^[1] we observed a series of intense peaks in the mass spectra only when the sputter arc source was insulated with boron nitride and oxygen was added to the carrier gas. It is known that when boron nitride is heated, its surface becomes nitrogen-rich as boron is released. We hypothesized that these peaks could be explained if the released boron atoms interact with oxygen and form BO₂ which then bind to the Au_n clusters. Further experimentation involving anion photoelectron spectroscopy (PES) revealed even more dramatic results. The electron affinities of $Au_n(BO_2)$ [n = 2 and 4] clusters were substantially larger than any atom in the periodic table. To confirm these ideas, we carried out first-principles calculations of their structure, stability, and electron affinities. Excellent agreement with experimental data not only validates the structure of these clusters, but also provides a new pathway to design a new class of salts where $Au_n(BO_2)^-$ cluster anions can be counterbalanced with suitable cations.

Our interest in studying the reaction of Au clusters consisting of 20 atoms or fewer with oxygen was initially motivated by their outstanding catalytic and structural properties.^[2] While bulk gold is a noble metal it is reactive at the nanoscale. Bare Au clusters, as well as their charged counterparts, possess exceptional structural properties, for example, the anions prefer a planar two-dimensional structure up to a size of 11 atoms, although for most other metal clusters three-dimensional comtron affinity values for a closed-shell cluster, ranging from 2.8– 3.5 eV. The open-shell $Au_n(BO_2)$ [even *n*] clusters on the other hand, possess electron affinities exceeding that of F, the most electronegative element in the periodic table. Using calculations based on density functional theory, we trace the origin of these species to the unusual stability and high electron affinity of the BO₂ moiety. The resulting bond formed between BO₂ and Au_n clusters preserves the geometric and electronic structure of the bare Au_n clusters. The large electron affinity of these clusters is due to the delocalization of the extra electron over the Au_n cluster.

pact structures are by far more stable.^[3] Au clusters exhibit hollow cage structures in the size range of 14 to 16 atoms and Au₂₀ assumes a compact pyramidal form.^[4] The electronic structure of these species is even more amazing. Au clusters exhibit the most pronounced even-odd alternation of the electronic structure of any cluster with the change in the electron affinity (EA) between Au_2 and Au_3 being more than 1.5 eV.^[5] $Au_{6\prime}$ Au_8 and Au_{20} have large HOMO–LUMO (H–L) gaps making them stable and therefore possibly suitable as building blocks for new materials. The interaction of Au_n clusters with O₂ studied using anion photoelectron spectroscopy and density functional calculations show that the geometric and electronic structures are altered considerably by this interaction, although the O₂ molecule is not bound strongly.^[6] The geometric and electronic structure of Au clusters is also dramatically altered by their interaction with a single hydrogen atom.^[7] Since such small clusters are strongly altered by the interaction with an atom or a molecule, one wonders whether they might survive the conditions of real catalysis.

Herein we demonstrate that small Au clusters consisting of up to five atoms preserve their structural and electronic prop-

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erties in spite of the strong ionic interaction with BO₂. The geometric structure is basically unchanged and the electronic structure keeps its most predominant feature, the even-odd alternation. In addition, because of the electrostatic forces the electron affinity is increased dramatically.

2. Results and Discussion

Figure 1 displays a part of a typical mass spectrum of Au_n^- cluster anions reacted with O_2 in our PACIS insulated with BN. The spectrum is dominated by intense mass peaks of the $Au_n(BO_2)^-$ series. No clusters containing N were detected. For the Au monomer, the $Au(BO_2)_2^-$ line is more intense than that of the regular $Au(BO_2)^-$ peak. Similarly, $Au_2(BO_2)^-$ peak is more intense than the $Au(BO_2)^-$ peak is similar to that of the Au(BO_2)^- peak. The main progression can be detected up to n=30, beyond which the mass resolution of our apparatus is no longer sufficient to separate $Au_nO_2^-$ and $Au_nO_3^-$ from $Au_n(BO_2)^-$. The mass spectrum suggests the high stability of the $Au_n(BO_2)^-$ species.

Figure 2 displays a comparison of the photoelectron spectra of bare Au_n^- clusters with those of



Figure 1. Section of a mass spectrum of Au_n^- cluster anions reacted with boron nitride and O_2 .

Au_n(BO₂). In some cases the electron affinity increases dramatically, although retaining the even-odd alternation. Besides these general trends, there are peculiar similarities and differences between the two sets of spectra. From the experimental data, the threshold energies and the vertical detachment energies can be estimated. The threshold energy is determined by fitting the signal increase at low binding energy to a linear function whose intersection with the zero is taken as the threshold energy. If the change in the ground-state geometry between the anion and the neutral is not too large, the threshold energy can be compared to the calculated EA, which is the energy difference between the ground states of the anion and corresponding neutral. If the geometry of anion and neutral differ significantly, then the threshold energy is compared to the calculated adiabatic detachment energies (ADE). The verti-



Figure 2. Comparison of photoelectron spectra of bare Au_n^- clusters with ones reacted with BO₂. The photon energy is 7.9 eV and the experimental uncertainty of the binding energy is +/-0.1 eV.

cal detachment energy (VDE) is taken as the binding energy of the first maximum at lowest binding energy and measures the energy difference between the ground state of the anion and its corresponding neutral at the anion ground state geometry. The values are listed in Table 1.

Table 1. The experimental and theoretical adiabatic detachment energies				
(ADE) and vertical detachment energies (VDE) of $Au_n(BO_2)$ clusters. For				
comparison, the EA of Au_n clusters for $n = 1, 2, 3, 4$, and 5 are respectively				
2.3, 2.0, 3.9, 2.8, and 3.1 eV. The experimental uncertainty is $\pm/-0.1$ eV.				

Clusters	ADE [eV] Expt. (Theory)	VDE [eV] Expt. (Theory)
$\begin{array}{l} Au_{1}(BO_{2})\\ Au_{2}(BO_{2})\\ Au_{3}(BO_{2})\\ Au_{4}(BO_{2})\\ Au_{5}(BO_{2})\end{array}$	2.8 (3.06) 4.7 (4.66) 3.1 (3.00) 4.7 (4.46) 3.5 (3.00)	3.0 (3.34) 4.8 (4.80) 3.2 (3.36) 4.9 (4.82) 3.7 (3.66)

As is obvious from the values of the ADEs, the even-odd alternation is inverted with respect to that of the bare Au_n^- clusters. A gold cluster with a relatively low ADE (e.g. Au_2^- with 2 eV) has a high electron affinity if bound to BO₂ (e.g. $[Au_2(BO_2)]$ with 4.7 eV). For the bare species with high electron affinities (e.g. Au_3 with 3.9 eV) there is only a slight increase or even a decrease (e.g. $[Au_3(BO_2)]$ with 3.1 eV).

The above experimental observation raises some interesting questions: 1) Why are the B-containing peaks mostly associated with two O atoms? 2) Why are $[Au_n(BO_2)]^-$ peaks in the mass spectra so intense compared to Au_n^- peaks? Is the origin

of these intense peaks due to the high thermodynamic stability of these species, or is it governed by kinetic considerations? 3) Why is the $[Au_2(BO_2)]^-$ peak more intense than that of either the $[Au(BO_2)]^-$ or $[Au_3(BO_2)]^-$ peak? 4) How are the Au atoms attached to the $(BO_2)^-$ moieties? 5) Why are the electron affinities of some of the clusters so much larger than those in pure Au_n clusters? 6) Where does the extra electron reside?

To answer the above questions and to understand the structure and bonding of Au_n to BO_2 , we have carried out calculations based on density functional theory and generalized gradient approximation (GGA) exchange-correlation energy functional. We used the B3LYP functional and 6-311 + +G(3df)basis set for B and O atoms and the SDD basis for Au atoms as implemented in the Gaussian 03 code.^[8] The latter basis set includes scalar relativistic corrections for Au. The equilibrium geometries of neutral and anionic BO_n and Au_n(BO₂) [n = 1-5] clusters were calculated by optimizing various initial structures with and without any symmetry constraints. In the geometry optimization procedure, the convergence criterion for energy was set to 10^{-9} hartree, while the gradient was converged to 10⁻⁴ hartree Å⁻¹. The reliability and accuracy of the functional form and the basis sets used in this study has been established previously.^[6, 9] The stability of these clusters was confirmed by analyzing their normal mode frequencies, which are all positive. In the following, we discuss the structure and properties of these clusters and examine the source of their stability.

2.1. Neutral and Anionic BO_n (n = 1-3)

The origin of the unexpected properties of $Au_n(BO_2)$ clusters and, in particular, why the B-containing peaks are associated mostly with two O atoms can be understood by examining the structure and relative stability of neutral and anionic BO_n . The equilibrium geometries of neutral and anionic BO_n (n = 1-3) molecules are given in Figure 3. The neutral and anionic BO_2 molecules are linear, with the B–O bond lengths nearly identical at 1.26 and 1.27 Å, respectively. However, for BO₃, the neutral and anionic structures differ significantly from each other. Neutral BO₃ is a bent structure (C_s), with two O atoms forming a quasi-molecular structure, which in turn is bonded to BO. The O–O bond length in this structure is 1.35 Å, which is larger than the corresponding bond length in O₂ molecule (1.20 Å). The anionic BO₃ cluster, on the other hand, forms a C_{2v} struc-

EA: 2.58 eV

EA: 4.32 eV

EA: 3.91 eV

Neutral 1.20 Å

1.26 Å

1.20 Å



Anion

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ture, where there are two types of B–O bonds (1.26 and 1.42 Å) and no O–O bond.

Our calculated EAs of BO (2.58 eV) and BO₂ (4.32 eV) are in excellent agreement with the previously reported [10] experimental values of 2.51 ± 0.015 eV and 4.46 ± 0.03 eV, respectively. Thus, the EA of BO₂ is larger than that of the F, Cl, and Au atoms, which are 3.4 eV, 3.6 eV, and 2.3 eV, respectively. It is also substantially larger than the electron affinity of BO. The large electron affinity of BO₂ is consistent with the octet rule. Note that the BO₂ cluster has seven valence electrons and is lacking one electron to become a closed-shell species like a noble gas atom. The unusual stability of BO₂⁻ can also be understood by realizing that BO₂⁻ is isoelectronic with CO₂ which is a stable molecule. BO2 can also be viewed as a superhalogen.^[10] Almost three decades ago, Gutsev and Boldyrev^[11] had shown that a cluster or a molecule consisting of a metal atom at the center surrounded by peripheral halogen and oxygen atoms can be a superhalogen if they have the formula unit $MX_{(n+1)/m}$, where n is the maximal formal valence of the metal atom M and m is the valence of the halogen/oxygen atom. The superhalogens have EAs larger than those of the halogen atoms and this arises as the extra electron is distributed over more than one electronegative atom. In the case of BO₂, n=3and m=2 and thus the superhalogen requirement is satisfied by BO₂ moiety. On comparing the natural bond orbitals (NBO) charges of neutral and anionic BO₂, it was revealed that the extra electron in the anion is distributed over both O atoms. The EA of BO₃, namely 3.91 eV, is also larger than that of any halogen atom.

In order to further establish the thermodynamic stability of BO_2 among the BO_n (n = 1-3) molecules, we have calculated the relative stability of BO_n with respect to sequential addition of oxygen atoms as shown in Equations (1)–(3):

$$\Delta E^{\text{neutral}} = -[E(BO_n) - E(BO_{n-1}) - E(O)]$$
(1)

$$\Delta E_1^{\text{anion}} = -[E(BO_n^{-}) - E(BO_{n-1}^{-}) - E(O)]$$
(2)

$$\Delta E_{2}^{\text{anion}} = -[E(BO_{n}^{-}) - E(BO_{n-1}) - E(O^{-})]$$
(3)

Here $E(BO_n)$ and $E(BO_n^-)$ are the total energies of the neutral and anionic BO_n molecules, respectively. $\Delta E_1^{\text{anion}}$ and $\Delta E_2^{\text{anion}}$ yield the stability of the BO_n^- species against dissociation into O and O⁻ respectively. The least positive values indicate the preferred channel. The results are given in Table 2. We see that

Table 2. The relative stability of neutral and anionic BO _n $[n = 1-3]$ and Au _n (BO ₂) $[n = 1-5]$ clusters [see Eqs. (1)–(6) for definitions].						
Clusters	$\Delta E^{ m neutral}$	ΔE_1^{anion}	ΔE_2^{anion}			
BO	8.48	11.42	9.46			
BO ₂	5.90	7.64	8.61			
BO₃	2.05	1.65	4.63			
Au ₁ (BO ₂)	2.10	0.84	2.95			
Au ₂ (BO ₂)	1.44	1.78	4.15			
Au ₃ (BO ₂)	3.25	1.92	2.69			
Au ₄ (BO ₂)	2.57	1.81	3.30			
Au ₅ (BO ₂)	2.95	1.64	2.90			

the binding energies of both neutral and anionic BO are rather large and demonstrate why they are readily formed in the presence of oxygen. However, the binding energy increases even further when the second O is introduced. Neutral BO₂ gains 5.90 eV while anionic BO₂ gains 7.64 eV. The corresponding energy gains when the third O is attached are considerably less, namely 2.05 eV and 1.65 eV. In an oxygen-rich and boronpoor environment, as is the case in our experiment, BO₂ and BO₂⁻ are the most preferred products when B interacts with O. In addition, the binding energy of BO₂ is much larger than the binding energies of Au_n clusters with oxygen. Thus, based on

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thermodynamics criteria alone, one can see that BO_2 molecules formed during the arc discharge preferentially bind to Au_n clusters, and hence give rise to an abundance of $Au_n(BO_2)$ clusters. This explains the intense BO_2 containing peaks in Figure 1.

The stability and formation of BO_2^- and $Au_nBO_2^-$ can be also understood by taking the kinetics rather than thermodynamics into consideration. However, the relative concentration of boron in our experiment is much lower than that of oxygen, because boron is an impurity created by the unwanted erosion of the BN insulation. In contrast, oxygen is injected into the source through a pulsed valve. There should be at least an order of magnitude lower partial pressure of boron than of oxygen present in the He carrier gas. As the $Au_n(BO_2)$

2.2. Neutral and Anionic Au_n(BO₂) Clusters

We calculated the total energies of different isomers of $Au_n(BO_2)$ (n = 1-5) clusters by allowing the Au atoms to bind to different O atoms as well as to the B atom. Figures 4 and 5 show the geometries of the ground state and those of the low-lying isomers of anionic and neutral clusters, respectively. We note from these geometries that the structure of the BO₂ moiety remains unchanged. The structures of Au_n in $Au_n(BO_2)$ clusters are also similar to those of the corresponding pure Au_n clusters. In neutral $Au_n(BO_2)$ clusters, it is expected that the



Figure 4. Ground-state geometries of $Au_n(BO_2)^-$ [n = 1-5] clusters. B atoms are grey, O atoms are dark grey, and Au atoms are white.

mass peaks are more intense than the Au_nO_m mass peaks we believe that this is an indication for the high stability of the BO_2^- and $Au_nBO_2^-$ anions.

Thus, we can visualize the formation process of $Au_n(BO_2)$ clusters as follows: B atoms are released from the boron nitride insulation during arc discharge and react with O to form BO_2 molecules. BO_2^- species formed after electron attachment bind to neutral Au_n clusters to form $Au_n(BO_2)^-$. During photodetachment, an electron is removed from the Au_n portion of the cluster rather than from BO_2^- , hence the even–odd alternation follows the pattern expected based on the neutral Au_n ionization potentials. One can also view the formation process of $Au_n(BO_2)$ clusters in another way. Due to the large electron affinity of BO_2 , they bind to Au_n clusters by drawing electrons from Au_n and the resulting $Au_n(BO_2)$ clusters are stabilized by bonding between the Au_n^+ and BO_2^- species. We show in the following that it is this superhalogen property of BO_2 that drives the structure of $Au_n(BO_2)$ clusters.



Figure 5. Ground-state geometries of neutral $Au_n(BO_2)$ [n=1-5] clusters. B atoms are grey, O atoms are dark grey, and Au atoms are white.

Au_n clusters would lose charge to the BO₂ moiety, thus forming an ionic-like bond between Au_n⁺ and BO₂⁻. This is confirmed from the NBO charge analysis. The NBO charges on Au_n clusters in neutral AuBO₂, Au₂BO₂, and Au₃BO₂ are +0.676*e*, +0.6*e*, and +0.791*e*, respectively.

When an extra electron is added to neutral Au_n(BO₂) clusters this charge would be localized on the positively-charged Au_n portion of the cluster. NBO charge analysis indeed confirms this and the Au atom in AuBO₂⁻ gains a charge of -0.7845e, while in Au₂BO₂⁻ and Au₃BO₂⁻ clusters a gain of -0.72e and -0.914e is observed for the Au_n part of the cluster. Because the extra electron in the anion is localized mostly on Au_n, the even-odd alternation in the electron affinity remains, except that they are shifted by one, that is, even Au_n(BO₂) clusters have a larger electron affinity than odd Au_n(BO₂) clusters, while the reverse is the case with bare Au_n clusters.

In Table 1 we compare our calculated vertical detachment energies and electron affinities with experiment. The excellent agreement validates the computed structures of $Au_n(BO_2)$ clusters. We also note that the electron affinities of $Au_n(BO_2)$ clusters are larger than those of the corresponding Au_n clusters and in some cases these values are as large as those in the superhalogens. However, the reason for these large electron affinities is different from that described for conventional superhalogens. Here the anionic cluster is stabilized as the extra electron goes to the positively charged Au_n portion of the cluster.

We now turn to the chemical stability of Au_n(BO₂) clusters. Among these clusters, AuBO₂, Au₃BO₂, and Au₅BO₂ clusters are closed-shell species (2S + 1 = 1). The H–L gaps of these neutral clusters are high, ranging from 3.01 eV in AuBO₂ to 3.56 eV in Au₅BO₂. The large H-L gaps indicate the kinetic stability of these neutral clusters. Closed-shell neutral clusters with such a large H-L gap are generally expected to have low VDE and EA values. This is not the case here. Surprisingly, their anionic counterparts, which are open-shell clusters are also stable. In fact, VDE, the lowest electron detachment energy from the anion, is unusually high for an open-shell cluster, especially when compared to the corresponding open-shell bare Au clusters. For example, the VDE values of open-shell bare Au₂⁻ and Au₄⁻ are 2 and 2.5 eV, respectively, while the VDE values of $AuBO_2^{-},\ Au_3BO_2^{-},\ and\ Au_5BO_2^{-}$ clusters are respectively 3.0, 3.2, and 3.7 eV. As mentioned above, in neutral clusters, the Au_n and BO₂ form an ionic-like bond, due to charge transfer from Au, to BO₂. Thus, in case of the anionic cluster, the charge of the extra electron is delocalized over the positively charged Au_n portion of the cluster and hence the VDE of $[Au_n(BO_2)]^-$ becomes larger than those of corresponding bare Au clusters.

In order to further see if the unusually large EA values for a closed-shell species is unique to $Au_n(BO_2)$ clusters, we have compared the EA values of similar ionic-species, namely, AuF, Na(BO₂), and Na₃(BO₂) with that of the Au_n(BO₂) clusters. The calculated EA value of AuF dimer is 2.46 eV, which is lower than the EA of Au(BO₂) cluster (3.06 eV), thereby further reflecting the superhalogen character of BO₂. On the other hand, if the bonding between the Au_n and BO₂ has a routine ionic-like

nature, then the EA values of Au(BO₂) and Au₃(BO₂) should be comparable to that of the corresponding Na_n(BO₂) clusters. The calculated EAs of Na(BO₂) and Na₃(BO₂) are respectively 1.16 eV and 0.98 eV, which are significantly lower than that of the EA values of Au(BO₂) and Au₃(BO₂), again establishing the unique character of closed-shell Au_n(BO₂) clusters. The unusually high EA values of closed-shell Au_n(BO)₂ clusters reflects more complex bonding between BO₂ and the Au_n cluster, involving both ionic and covalent character.

The remaining neutral $Au_n(BO_2)$ clusters in this series, namely Au_2BO_2 and Au_4BO_2 are open-shell species preferring a doublet spin multiplicity (2S + 1 = 2). These clusters have an unusually high EA value of 4.7 eV, which is greater than the EA of the chlorine atom. The large EA value of these clusters, as discussed earlier, are a consequence of the charge transfer from the Au_n part of the cluster to the BO_2 moiety and the subsequent delocalization of the extra electron onto the positively charged Au_n . On the other hand, the anionic counterparts of these clusters, namely $Au_2BO_2^-$ and $Au_4BO_2^-$ are closed-shell clusters, with large H–L gaps of 3.94 eV and 3.00 eV, respectively. We have calculated the binding energy of the neutral and anionic $Au_n(BO_2)$ clusters as shown in Equations (4)–(6):

$$\Delta E^{\text{neutral}} = -[E(Au_n BO_2) - E(BO_2) - E(Au_n)]$$
(4)

$$\Delta E_1^{\text{anion}} = - \left[E(\operatorname{Au}_n \operatorname{BO}_2^{-}) - E(\operatorname{BO}_2^{-}) - E(\operatorname{Au}_n) \right]$$
(5)

$$\Delta E_2^{\text{anion}} = - \left[E(\operatorname{Au}_n \operatorname{BO}_2^{-}) - E(\operatorname{BO}_2) - E(\operatorname{Au}_n^{-}) \right]$$
(6)

Equation (5) yields the energy needed for dissociation into BO_2^- and Au_n , while Equation (6) yields energy needed into dissociation into BO_2 and Au_n^- . The results are given in Table 2. Note that the binding energies exhibit even-odd alternation as seen in the electron affinities.

It is interesting to compare our current results with similar studies performed by Zubarev et al. ^[9] on Au_n(BO)⁻ (n = 1-3) clusters. BO⁻ is isoelectronic with CO, while BO₂⁻ is isoelectronic with CO₂. However, in our experiments we did not observe the Au_n(BO)⁻ species seen by Zubarev et al.^[9] One reason could be the experimental conditions. In our study boron is an impurity while in the study conducted by Zubarev et al.^[9] oxygen is an impurity. Curiously, the Au_n(BO₂)⁻ clusters are observed under O₂-rich conditions. However, the electronic structure of Au_n clusters namely even-odd alternation seems to be unaffected by whether Au_n clusters bind to BO⁻ or BO₂⁻.

3. Conclusions

We observed a new class of $Au_n(BO_2)$ clusters which formed when Au clusters were allowed to interact with oxygen in a PACIS insulated with BN. These clusters possess rather unusual properties both in terms of their stability and electronic properties. To summarize: 1) The intensity of the $Au_n(BO_2)$ cluster peaks in the mass spectra are much more pronounced than those of Au_n clusters. Calculations based on density functional theory enable us to trace the origin of their stability. 2) B atoms, released from the BN insulation during arc discharge, interact with oxygen atoms and form BO_n molecules. Among these, BO₂ molecules are the most stable and highly electronegative. BO₂, due to its large electron affinity, namely 4.32 eV, belong to the class of superhalogens where energy is considerably lowered when the extra electron is delocalized over two or more electronegative atoms, in this case O. 3) BO₂ binds to Au_n clusters in the PACIS to form the observed $Au_n(BO_2)$ clusters. The large electron affinity of BO₂ moiety causes electrons to transfer from Au_n clusters when $Au_n(BO_2)$ clusters form. The resulting bond between BO_2^- and Au_n^+ is what gives $Au_n(BO_2)$ clusters their unusual stability. 4) In the anionic $Au_n(BO_2)^-$ clusters, the extra electron goes to the Au_n portion of the cluster which is positively charged. Consequently, Aun(BO2) clusters possess larger electron affinity than the corresponding pure Au_n clusters. In some cases the electron affinities can be even larger than that of Cl. Thus, one could classify these $Au_n(BO_2)$ clusters as superhalogens. However, as mentioned before, the traditional definition of a superhalogen is that of a central atom, typically a metal, which is surrounded with halogen and/ or oxygen atoms. In this sense BO₂ is a traditional superhalogen while $Au_n(BO_2)$ clusters with electron affinities larger than those of Cl are not. 5) The electron affinity of the $Au_n(BO_2)$ clusters exhibit even-odd alternation as seen in pure Au_n clusters with one exception: the odd-n clusters have lower electron affinity than the even-*n* clusters. In addition, Au_n clusters interacting with BO₂ moieties retain their structural identity in spite of their open-shell structures. 6) Closed-shell clusters are supposed to have small electron affinities. That is not the case in these $Au_n(BO_2)$ [n = 1,3,5] clusters, which have electron affinities as high as 3.5 eV. 7) The properties of $Au_n(BO_2)$ clusters are different from those of Na_n(BO₂) clusters, even though the bonding in both cases is due to charge transfer from the metal clusters to the BO_2 moiety. This sets apart the interactions of Au_n clusters with BO₂ from other metals.

The fact that the electron affinities of Au_n clusters can be substantially enhanced by reacting them with other species provides a scheme for synthesizing new materials with novel electronic and magnetic properties. We are currently exploring these possibilities.

Experimental Section

The photoelectron spectroscopy (PES) experiment was conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy. Our apparatus, which has been described previously,^[7] consists of a PACIS, a time-of-flight mass spectrometer for mass analysis and mass selection, an excimer laser operating at 7.9 eV for photodetachment, and a magnetic bottle electron energy analyzer. In a PACIS source, a discharge is struck between an anode and a grounded, metallic sample cathode, while helium gas from a pulsed valve flows through the discharge region. The electrodes are mounted in a boron nitride cube with the bore perpendicular to the electrodes to allow the helium to flow through the gap between the electrodes.

When oxygen is added to the carrier gas, we observed a strong progression of $Au_n(BO_2)^-$ clusters in addition to the signals of the $Au_nO_m^-$ clusters. The boron nitride of the cube is eroded by the O_2 -containing plasma. Without oxygen, no boron contamination is observed in the mass spectra. We never saw any nitrogen contamination, although our mass resolution is sufficient to distinguish nitrogen from oxygen compounds for the small clusters with less then five Au atoms. The resulting anions were then subjected to extraction and mass analysis/selection.

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