# An Ab Initio Theoretical Investigation on the Geometrical and Electronic Structures of $BAu_n^{-/0}$ (n = 1-4) Clusters

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Received 23 October 2010; accepted 28 October 2010 Published online 18 January 2011 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/qua.22993

**ABSTRACT:** An *ab initio* theoretical investigation on the geometrical and electronic structures and photoelectron spectroscopies (PES) of  $BAu_n^{-/0}$  (n = 1-4) auroboranes has been performed in this work. Density functional theory and coupled cluster method (CCSD(T)) calculations indicate that  $BAu_n^{-/0}$  (n = 1-4) clusters with n-Au terminals possess similar geometrical structures and bonding patterns with the corresponding boron hydrides  $BH_n^{-/0}$ . The PES spectra of  $BAu_n^-$  (n = 1-4) anions have been simulated computationally to facilitate their future experimental characterizations. In this series, the T<sub>d</sub>  $BAu_4^-$  anion appears to be unique and particularly interesting: it possesses a perfect tetrahedral geometry and has the highest vertical electron detachment energy (VDE = 3.69 eV), largest HOMO-LUMO gap ( $\Delta E_{gap} = 3.0 \text{ eV}$ ), and the highest first excitation energy ( $E_{ex} = 2.18 \text{ eV}$ ). The possibility to use the tetrahedral  $BAu_4^-$  unit as the building block of Li<sup>+</sup>[ $BAu_4$ ]<sup>-</sup> ion-pair and other [ $BAu_4$ ]<sup>-</sup>-containing inorganic solids is discussed. ©2011 Wiley Periodicals, Inc. Int J Quantum Chem 111: 4418–4424, 2011

**Key words:** auroboranes; *ab initio* calculations; geometrical structures; electronic structures; photoelectron spectroscopy

## **1. Introduction**

Ithough Au, Cu, and Ag all belong to the same column in the Periodic Table, gold dif-

fers dramatically from other coinage metals because of its strong relativistic effect [1, 2] which stabilizes the Au 6s orbital and destabilizes Au 5d [3]. Au possesses the highest electronegativity (2.4) in all metals, which is comparable with that of H (2.2). Since the surprising experimental

International Journal of Quantum Chemistry, Vol 111, 4418–4424 (2011) © 2011 Wiley Periodicals, Inc.

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discovery of H/AuPR<sub>3</sub> analogy [4], various compounds with 2c-2e N-Au and B-Au bonds have been reported [5, 6]. More recently, the H/Au isolobal relationship in silicon aurides  $T_d SiAu_4^{0/-}$  [7],  $C_{2v}$  Si<sub>2</sub>Au<sub>2</sub><sup>0/-</sup>, and  $C_{2h}/C_{2v}$  Si<sub>2</sub>Au<sub>4</sub><sup>-</sup> [8] and hepta-boron auride  $C_{2v}$  B<sub>7</sub>Au<sub>2</sub><sup>0/-</sup> [9] were confirmed by joint photoelectron spectroscopy (PES) and density functional theory investigations. Cage-like  $B_n A u_n^{2-}$  (*n* = 5–12) with n-Au terminals were predicted stable recently in theory [10]. Relativistic pseudopotential calculations on the X-centered XAu<sub>n</sub><sup>m+</sup> cluster cations (X = B-N, Al-S, n = 4-6) and Au-bridged X…Au-Y Lewis acid-base pairs were also reported [11]. Very recently, our group presented an *ab initio* investigation on bridging gold atoms in diboron aurides  $B_2Au_n^{-/0}$  (n = 1, 3,5) and their  $B_2H_mAu_n^-$  mixed analogues (m + n =3, 5) [12].

In this work, we present a detailed *ab initio* investigation on the geometrical electronic structures of  $BAu_n^{0/-}$  series (n = 1-4) at both density functional theory and wave function theory levels. The PES spectra of the anions are computationally simulated to facilitate their future experimental characterizations. In the  $BAu_n^-$  anions (n = 1-4), the perfect tetrahedral  $T_d BAu_4^-$  proves to have the highest vertical electron detachment energy, the largest HOMO-LUMO gap, and the biggest first excitation energy. The possibility to use the tetrahedral  $BAu_4^-$  unit as the building block of Li<sup>+</sup>[BAu\_4]<sup>-</sup> ion-pair and other inorganic solids is discussed.

## **2. Theoretical Methods**

Structural optimizations and vibrational analyses were comparatively carried out using the hybrid B3LYP [13] and PBE1PBE [14] methods. PBE1PBE and B3LYP produced similar groundstate structures and relative energies with slightly different bond parameters. Relative energies for the lower-lying isomers were further refined using the coupled cluster method with triple excitations (CCSD(T)) [15] at B3LYP structures. Natural resonance theory (NRT) was used to calculate the bond orders and bond polarities. The Stuttgart quasi-relativistic pseudo-potential and the basis set augmented with two f-type polarization functions and one g-type polarization function (Stuttgart\_rsc\_1997\_ecp+2f1g ( $\alpha$ (f) = 0.498,  $\alpha$ (f) =

1.464, and  $\alpha(g) = 1.218$  [16] were used for Au and the augmented Dunning's correlation consistent basis sets aug-cc-pvTZ [17] for B, H, and Li. The low-lying isomers of  $BAu_n^-$  anions and the ground-state structures of BAu<sub>n</sub> neutrals (n = 1-4) are depicted in Figures 1 and 2, respectively. The calculated bond orders and natural atomic charges of  $BAu_n^-$  (n = 1-4) and LiBAu<sub>4</sub> were tabulated in Table I, with the ADE and VDE values of  $BAu_n^-$  anions summarized in Table II. ADE values were calculated as the energy differences between the anion and its neutral molecule at their ground-state structures, whereas VDEs calculated as the energy differences between the anion and the neutral at the ground-state structure of the anions. The valence molecular orbitals of  $[BAu_4]^-$  and  $[BH_4]^-$  are compared in Figure 3. The simulated PES spectra of  $BAu_n^-$  (n = 1-4) obtained by using the time-dependent DFT method (TDDFT) were shown in Figure 4. Figure 5 depicts the optimized structures of LiBAu<sub>4</sub> and LiBH<sub>4</sub>. All the calculations in this work were performed using the Gaussian 03 program [18]. The NBO5.0 [19] program was used to calculate the bond orders and atomic charges.

## **3. Results and Discussion**

# 3.1. GEOMETRIES AND BONDING PATTERNS OF $BAu_n^{-/0}$ (n = 1-4)

As shown in Figures 1 and 2, the BAu<sub>n</sub><sup>-/0</sup> (n =1-4) clusters with n-Au terminals possess similar geometrical structures with the corresponding boron hydrides  $BH_n^{-/0}$  [20–22]. Low-spin electronic states are found to be consistently favored in  $BAu_n^{-/0}$  (n = 1–4). The ground state of the  $BAu^$ anion  $(^{2}\Sigma^{+}, 1)$  has the bond length of  $r_{\text{B-Au}} =$ 1.99 Å and lies 1.42 eV lower than its quartet isomer ( ${}^{4}\Sigma^{+}$ , 2) at CCSD(T), whereas the ground state of the BAu neutral ( ${}^{1}\Sigma^{+}$ , **12**) possesses actually a B≡Au triple bond with the bond length of  $r_{\text{B-Au}} = 1.93$  Å which is close to the sum (1.96 Å) of the proposed triple-covalent radii of B and Au [23]. BAu2 possesses a ground state of  $C_{2v}$  BAu<sub>2</sub><sup>-</sup> (<sup>1</sup>A<sub>1</sub>) (3), which lies 0.98 eV and 1.98 eV lower than the singlet  $C_{\infty v}$  BAu<sub>2</sub><sup>-(1</sup> $\Sigma_{\sigma}^{+}$ ) (4) and triplet  $C_{2v}$   $BAu_2^-$  ( ${}^3B_1$ ) (5) at  $CCSD(\tilde{T})$  level, respectively. On  $BAu_3^-$ , the slightly offplaned  $C_{3v} BAu_3^-$  (<sup>2</sup>A<sub>1</sub>) (6) is the ground state, while the perfect planar  $D_{3h} BAu_3^-$  (8) is a transition state due to Jahn-Teller effect. The second

LI AND LI



**FIGURE 1.** Low-lying isomers of  $BAu_n^-$  anions (n = 1-4) at B3LYP with energies ( $\Delta E$ ) relative to the ground states indicated in eV at CCSDT//B3LYP. Bond lengths are in angstroms and angles in degrees. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 2.** Ground-state geometries of BAu<sub>n</sub> neutrals at B3LYP level. Bond lengths are indicated in angstroms and angles in degrees. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I

Full valency, covalency, and electrovalency indexes, the covalent percentages, and natural atomic charges (q/|e|) calculated for BAu<sub>n</sub><sup>-</sup> anions and LiBAu<sub>4</sub> neutral.

Isomers	Atom	Valency	Covalency	Electrovalency	Covalent percentage	q
<b>1</b> $C_{\infty v}$ BAu <sup>-</sup> ( <sup>2</sup> $\Sigma^+$ )	В	1.53	0.62	0.91	0.41	-0.66
	Au	1.53	0.62	0.91	0.41	-0.34
<b>3</b> C <sub>2v</sub> BAu <sub>2</sub> <sup>-</sup> ( <sup>1</sup> A <sub>1</sub> )	В	2.07	1.30	0.77	0.63	-0.50
	Au	1.04	0.65	0.39	0.63	-0.25
6 C <sub>3v</sub> BAu <sub>3</sub> <sup>-</sup> ( <sup>2</sup> A <sub>1</sub> )	В	3.50	2.49	1.01	0.71	-0.74
	Au	1.17	0.83	0.34	0.71	-0.09
<b>9</b> T <sub>d</sub> BAu <sub>4</sub> <sup>-</sup> ( <sup>1</sup> A <sub>1</sub> )	В	4.00	3.87	0.13	0.97	-1.22
	Au	1.00	0.97	0.03	0.97	-0.06
<b>16</b> C <sub>3v</sub> LiBAu <sub>4</sub> ( <sup>1</sup> A <sub>1</sub> )	В	3.89	3.57	0.32	0.92	-1.39
	Au	1.00	0.81	0.19	0.81	+0.23
	Au′	0.99	0.92	0.07	0.93	+0.11
	Li	0.07	0.00	0.07	0.00	+0.83

lowest-lying isomer  $C_s$  (<sup>2</sup>A') (7) lies 0.72 eV higher in energy. As expected, the ground state of D<sub>3h</sub> BAu<sub>3</sub> neutral (14) indeed possesses a perfect triangular structure similar that of BH<sub>3</sub> [20] with a sp<sup>2</sup> hybridized B at the center. Most interestingly, the ground state of  $BAu_4^-$  (9) proves to be a perfect tetrahedron with a T<sub>d</sub> symmetry similar to T<sub>d</sub> BH<sub>4</sub><sup>-</sup>. Our optimized B-Au bond length of  $r_{\text{B-Au}} = 2.05$  Å, which appears to be close to the sum (2.09 Å) of the proposed singlebond covalent radii of the B and Au [23], is about 0.08 Å shorter than the corresponding value of  $r_{\text{B-Au}} = 2.137$  Å predicted at Hartree-Fock level [11(a)].  $T_d BAu_4^-$  (9) is separated by 0.55 eV from the second lowest-lying isomer of  $C_{2v}$  BAu<sub>4</sub><sup>-(1</sup>A<sub>1</sub>) (10) and has the biggest HOMO-LUMO energy gap of  $\Delta E_{gap} = 3.0$  eV in the  $BAu_n^-$  series.

As shown in Table I, the covalent contributions to the B-Au interactions increase constantly in the BAu<sub>n</sub><sup>-</sup> series from n = 1 to n = 4. B-Au bonds in T<sub>d</sub> BAu<sub>4</sub><sup>-</sup> have the highest percentage of covalency (97%). The B-Au bonds in  $BAu_3^-$  and  $BAu_2^-$  have the covalent contributions of 71 and 63%, respectively. Obviously, these B-Au bonds can be viewed as mainly covalent. However, the B-Au bond in BAu<sup>-</sup> has the covalent component of 41% and electrovalent contribution of 59%, indicating that the B-Au interaction in BAu<sup>-</sup> is mainly ionic. This situation can be understood based on that fact that Au atom carries about one third (q = -0.34 | e |, see Table I) of the negative charge the BAu<sup>-</sup> anion possesses.

In the BAu<sup>-</sup><sub>n</sub> series, the perfect tetrahedral T<sub>d</sub> BAu<sub>4</sub><sup>-</sup> appears to be unique and particularly interesting. Figure 3 shows its four valence molecular orbitals, which contains a triply degenerate HOMO (t<sub>2</sub>) and a singlet HOMO-1 (a<sub>1</sub>).  $T_d BAu_4^-$  has a bonding pattern similar to that of T<sub>d</sub> BH<sub>4</sub><sup>-</sup>, with a sp<sup>3</sup> hybridized B center surrounded by four Au atoms to form four equivalent  $\sigma$  single bonds. However, there are subtle differences in orbital compositions between B-Au and B-H  $\sigma$  bonds in  $T_d BAu_4^-$  and  $T_d BH_4^-$  due to the obvious relativistic effects in Au. T<sub>d</sub> BAu<sub>4</sub><sup>-</sup> possesses the orbital hybridization of  $MO_{B-Au} = 0.707(sp^3)_B$ +0.708(sd<sup>0.13</sup>)<sub>Au</sub> and the corresponding atomic contribution of 49.9%B + 50.1%Au, with Au 6s

#### TABLE II

Calculated ADEs (eV) and VDEs (eV) of  $BAu_n^-$  anions (n = 1-4) at B3LYP and CCSD(T)//B3LYP levels. ADEs of the anions are equivalent to the electron affinities of the corresponding neutrals.

		<b>B3LYP</b>	CCSD(T)//B3LYP
<b>1</b> $C_{\infty v}$ BAu <sup>-</sup> ( <sup>2</sup> $\Sigma$ <sup>+</sup> )	ADE	0.87	0.66
	VDE	0.89	0.68
<b>3</b> C <sub>2v</sub> BAu <sub>2</sub> <sup>-</sup> ( <sup>1</sup> A <sub>1</sub> )	ADE	1.84	1.86
2 · · ·	VDE	2.15	2.20
6 C <sub>3v</sub> BAu <sub>3</sub> <sup>-</sup> ( <sup>2</sup> A <sub>1</sub> )	ADE <sup>a</sup>	1.52	1.28
0.0	VDE	1.79	1.65
<b>9</b> T <sub>d</sub> BAu <sub>4</sub> <sup>-</sup> ( <sup>1</sup> A <sub>1</sub> )	ADE <sup>b</sup>	3.12	3.06
	VDE	3.57	3.69

<sup>a</sup> The final state corresponds to  $D_{3h} BAu_3(^{1}A'_1)$ .

<sup>b</sup> The final state corresponds to  $D_{2d}$  BAu<sub>4</sub>(<sup>2</sup>B<sub>2</sub>).

#### LI AND LI

T<sub>d</sub> [BAu<sub>4</sub>]



**FIGURE 3.** Comparison of the four valence MOs responsible for the four equivalent  $\sigma$ -bonds in T<sub>d</sub> [BAu<sub>4</sub>]<sup>-</sup>(<sup>1</sup>A<sub>1</sub>) and T<sub>d</sub> [BH<sub>4</sub>]<sup>-</sup> (<sup>1</sup>A<sub>1</sub>) at B3LYP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contributing 90.4% and Au 5d 9.3% to the Aubased orbital, whereas  $T_d BH_4^-$  has the orbital hybridization of B-H =  $0.681(sp^3)_B + 0.732s_H$  and the corresponding atomic contribution of 46.4%B + 53.6%H, with the H-based orbital containing pure H 1s contribution. Au 5d makes about 10% contribution to the Au-based orbitals in BAu<sup>-</sup>, BAu<sup>-</sup><sub>2</sub>, and BAu<sup>-</sup><sub>3</sub>, too. The 10% Au 5d contribution to the Au-based orbitals in BAu<sup>-</sup> series (n = 1-4) generally agrees with the situation previously observed in diboron aurides  $B_2Au_n^{-/0}$  (n = 1, 3, 5) [12].

#### 3.2. ELECTRON DETACHMENT ENERGIES AND B-AU SYMMETRICAL STRETCHING VIBRATIONAL FREQUENCIES

As can be seen from Table II, B3LYP and CCSD(T)//B3LYP methods agree well in predicting the one-electron detachment energies of  $BAu_n^-$  anions. For  $BAu^-$ ,  $BAu_2^-$ , and  $BAu_3^-$ , the calculated ADEs and VDEs at CCSD(T) level lie between 0.66 eV and 2.20 eV, whereas for  $BAu_4^-$ , the corresponding values are ADE = 3.06 eV and VDE = 3.69 eV, respectively. Obviously,  $T_d BAu_4^-$  has the highest one-electron detachment energy

and, therefore, possesses the highest electronic stability in this series. The high stability of the closed-shell T<sub>d</sub> BAu<sub>4</sub><sup>-</sup> is clearly related with the fact it has the same number of valence electrons with the well-known methane T<sub>d</sub> CH<sub>4</sub>. The electronic binding energies of  $BAu_n^-$  anions fall within the energy range of the conventional excitation laser (266 nm, 4.661 eV) in PES measurements [7-9]. To facilitate future experiments, we also simulated the PES spectra of  $BAu_n^-(n = 1-4)$  by using TDDFT. As shown in Figure. 4,  $T_d BAu_4^-$  has a unique PES pattern in these anions: it has the highest X-band (<sup>2</sup>T<sub>2</sub>) at 3.69 eV followed by a group of closely-lying bands (A-E) between 5.8 and 6.6 eV, with an exceptionally wide X-A energy gap of  $E_{ex} = 2.18$  eV which corresponds to the first excitation energy of the BAu<sub>4</sub> neutral, further supporting the high stability of T<sub>d</sub> BAu<sub>4</sub>. The highly symmetrical C<sub>3v</sub> BAu<sub>3</sub><sup>-</sup> also possesses a considerable X-A energy gap of  $E_{ex} = 1.81$  eV. The calculated Au-B symmetrical stretching vibrational frequencies appeared to lie at 635, 801, 711, and 623 cm<sup>-1</sup> for  $C_{\infty v}$  BAu (<sup>1</sup> $\Sigma^+$ ),  $C_{2v}$  BAu<sub>2</sub> (<sup>2</sup>A<sub>1</sub>),  $D_{3h}$  BAu<sub>3</sub> (<sup>1</sup>A<sub>1</sub>), and  $D_{2d}$  BAu<sub>4</sub> (<sup>2</sup>B<sub>2</sub>), respectively. These calculated values may help indentify these





**FIGURE 4.** PES spectra of  $BAu_n^-$  (n = 1-4) anions simulated at TDDFT level.

auroboranes in future infrared and PES measurements.

#### 3.3. BAu<sub>4</sub><sup>-</sup> UNIT IN LIBAu<sub>4</sub> NEUTRAL

To further evaluate the stability of  $BAu_4^-$ , we compare its atomization energy (AME) with the corresponding value of  $BH_4^-$  at CCSD(T):

$$\begin{split} BAu_4^-(T_d{}^1A_1) &\to 4Au({}^2S) + B^-({}^3P) \\ &\Delta E = 271.7\,kcal/mol \\ BH_4^-(T_d{}^1A_1) &\to 4H({}^2S) + B^-({}^3P) \\ &\Delta E = 362.9\,kcal/mol \end{split}$$

The choice of B<sup>-</sup> monoanion is based upon the fact that the B centers carry the extra electron in both  $BAu_4^-$  and  $BH_4^-$  monoanions. Our CCSD(T) values indicates that  $T_d BAu_4^-$  possesses the positive atomization energy of AME = 271.7 kcal/mol and, therefore, should be thermodynamically stable (though less stable than the well-known  $BH_4^-$  [22] which has an AME = 362.9 kcal/mol at the same theoretical level). A closed-shell tetrahedral  $BAu_4^-$  unit is expected to be further stabilized when incorporated in solids with suitable counterions (like Li<sup>+</sup>) [24].

In the simplest case, it is true that the ground state  $C_{3v}$  LiBAu<sub>4</sub> (**16**) has a very similar geometry with that of  $C_{3v}$  LiBH<sub>4</sub> (**17**). The tetrahedral BAu<sub>4</sub><sup>-</sup> unit is well maintained in  $C_{3v}$  LiBAu<sub>4</sub>. The calculated natural atomic charge of  $q_{Li} = +0.83 |e|$  indicates that the Li atom donates its valence  $2s^1$  electron almost completely to the BAu<sub>4</sub><sup>-</sup> anionic unit, and the interaction between Li<sup>+</sup> and BAu<sub>4</sub><sup>-</sup> unit is basically ionic. Thus, LiBAu<sub>4</sub> can be viewed essentially as a Li<sup>+</sup>[BAu<sub>4</sub>]<sup>-</sup> ion-pair, presenting the possibility of synthesizing LiBAu<sub>4</sub> and other [BAu<sub>4</sub>]<sup>-</sup> containing inorganic solids in future experiments.

# 4. Summary

The structures and electronic characters of a series of auroboranes  $BAu_n^{-/0}$  (n = 1–4) with one B



**FIGURE 5.** Ground-state structures of LiBAu<sub>4</sub> and LiBH<sub>4</sub> at B3LYP. Bond lengths are indicated in angstroms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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atom at the center have been investigated at *ab initio* theoretical level. NRT analyses showed that the B-Au interactions in  $BAu_n^{-/0}$  clusters (n = 2-4) are mainly covalent. The PES spectra of the  $BAu_n^-$  anions and the Au-B stretching vibrations of the BAu<sub>n</sub> neutrals (n = 1-4) are calculated. Based on the Au/H analogy, an interesting structural link between LiBAu<sub>4</sub> and LiBH<sub>4</sub> is established. A tetrahedral BAu<sub>4</sub><sup>-</sup> unit is predicted to serve as the building block of Li<sup>+</sup>[BAu<sub>4</sub>]<sup>-</sup> air-pair and other [BAu<sub>4</sub>]<sup>-</sup>-containing inorganic solids.

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