Photoelectron spectroscopy of aromatic compound clusters of the B$_{12}$ all-boron benzene: B$_{12}$Au$^{-}$ and B$_{12}$(BO)$^{-}$

Hui Bai,$^{a}$ Hua-Jin Zhai,$^{a,b}$ Si-Dian Li$^{a}$ and Lai-Sheng Wang$^{a,b}$

We report a photoelectron spectroscopy and density-functional theory study of the B$_{12}$Au$^{-}$ and B$_{13}$O$^{-}$ clusters and their neutrals, which are shown to be six $\pi$ electron aromatic compounds between the quasi-planar all-boron B$_{12}$ benzene-analogue and a monovalent Au or BO ligand. Electron affinities of B$_{12}$Au and B$_{13}$O are measured to be 3.48 $\pm$ 0.04 and 3.90 $\pm$ 0.04 eV, respectively. Structural searches are performed for B$_{12}$Au$^{-}$ and B$_{13}$O$^{-}$, which are compared with the isovalent B$_{13}$H$^{-}$ cluster. The global minima of B$_{12}$Au$^{-}$ and B$_{13}$O$^{-}$ both feature an almost intact B$_{12}$ cluster with the Au and BO ligands bonded to its periphery, respectively. For B$_{13}$O$^{-}$, a low-lying isomer is also identified, which is only 0.4 kcal mol$^{-1}$ above the global minimum, in agreement with the experimental observation of a weakly populated isomer in the cluster beam of B$_{13}$Au$^{-}$. These aromatic compound clusters provide new examples for the Au/H isovalanol and the boronyl (BO) chemistry.

1. Introduction

In contrast to bulk boron where three-dimensional B$_{12}$ cage units dominate, elemental boron clusters exhibit planar or quasi-planar structures up to very large sizes$^{1-14}$ that are unparalleled in any other elements in the periodic table. The critical size for two-dimensional (2D) to three-dimensional (3D) transition is established to be B$_{16}$ for cations,$^{13}$ B$_{20}$ for neutrals,$^{10}$ and beyond B$_{32}$ for anionic clusters,$^{6-11}$ for which the exact size for 2D-to-3D transition is yet to be determined. Among all boron clusters characterized so far, the B$_{12}$ neutral shows unique electronic and structural properties.$^6$ As revealed from the B$_{12}^-$ anion photoelectron spectra, the B$_{12}$ cluster possesses a 2.0 eV energy gap between its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the greatest of all B$_n$ ($n = 3-23$) clusters.$^6-11$ Both B$_{12}$ and B$_{13}$ adopt quasi-planar structures with a circular shape,$^6$ as does their cationic counterpart, B$_{12}^+$. Bonding analysis shows that B$_{12}$ is an aromatic system with six $\pi$ electrons and may be considered as a prototypical all-boron benzene, similar to the “magic” B$_{13}$ cluster in prior mass spectrometric studies.$^3,4,14$ Computational “design” of a fluxional B$_{12}$C$_3^+$ molecular wheel,$^{14}$ which is isoelectronic to B$_{12}$, was also reported, albeit such B$_{6}$C$_3$ wheel is not the global minimum structure. The quasi-planarity of B$_{13}$ was recently found to be entirely due to a “mechanical” effect to fit three boron atoms in a B$_9$ ring, as revealed from isoelectronic substitution by Al in B$_{13}$Al.$^{16}$

Compound clusters based on B$_{12}$, in particular its hydrogenation, have also been actively pursued lately.$^{17-22}$ A primary motivation of these studies was to address the planar to cage structural transition in B$_{12}$H$_6$ as a function of hydrogen content, as the dodecaborane dianion B$_{12}$H$_{12}^-$ is known to be a stable icosahedral cage. A planar D$_{18h}$ borozene molecule B$_{12}$H$_6$ was proposed initially,$^{17}$ and its potential as a building block for large aromatic compounds explored.$^{18}$ Subsequent systematic computational data on B$_{12}$H$_n$ ($n = 1-8$) showed, however, that the proposed borozene B$_{12}$H$_6$ structure is not the global minimum and instead a cage-like structure was found to be substantially lower in energy by 35 kcal mol$^{-1}$ at the CCSD(T) level.$^{19}$ Computational data also revealed that in B$_{12}$H$_n$ and B$_{13}$H$_n$ clusters the cage-like structures gradually gain stability relative to the planar ones with increasing $n$, and a planar-to-cage structural transition...
occurs at around \( n = 4 \).\(^{19-21}\) Experimentally, \( \text{B}_{12}\text{H}_n^+ \) clusters were generated in ion-molecule reactions in an ion trap, revealing \( \text{B}_{12}\text{H}_4^+ \) as the most abundant species. However, spectroscopic characterizations of these hydride clusters were not possible due to isotopic mass mixing.\(^{22}\)

In the current work, we investigate the \( \text{B}_{12}\text{Au}^- \) and \( \text{B}_{13}\text{O}^- \) clusters and their neutral species. These clusters turn out to be aromatic compounds between the quasi-planar \( \text{B}_{12} \) cluster and a monovalent Au and BO ligand, respectively, which are isovalent to the \( \text{B}_{12}\text{H}_n^- \) and \( \text{B}_{12}\text{H}_n^+ \) clusters. The current results extend the Au/H isosbestic analogy\(^{23-26}\) and the boron boronyl chemistry.\(^{27-30}\) The structural and bonding analogy between a bare gold atom and H was discovered in gas-phase binary Au clusters, such as Si–Au clusters, where \( \text{SiAu}_n \) \( (n = 2, 3) \), Si\(_2\)Au\(_n \) \( (n = 2, 4) \), and Si\(_3\)Au\(_n \) were demonstrated to possess structures and bonding similar to the \( \text{SiH}_4 \) silane, \( \text{SiH}_4 \), \( \text{Si}_2\text{H}_6 \), and \( \text{Si}_3\text{H}_8 \), respectively.\(^{24}\) A subsequent study\(^{25}\) showed that the B–Au bonding in \( \text{B}_{12}\text{Au}^- \) cluster is highly covalent and similar to the B–H bonding in the \( \text{B}_{12}\text{H}_3^- \) cluster.\(^{26}\) The \( \text{B}_{10}\text{Au}^- \) cluster\(^{20}\) served as another example of the Au/H analogy in Au-doped boron clusters. The concept of Au/H analogy also has an analogous role in terms of the isovalent boronyl (BO) group.\(^{31}\) Similar to the SiH\(_4\) silane, SiH\(_4\), Si\(_2\)H\(_6\), and Si\(_3\)H\(_8\), respectively.\(^{24}\) We also studied the \( \text{B}_{12}\text{H}_n^- \) and \( \text{B}_{12}\text{H}_n^+ \) clusters. The potential energy surfaces of \( \text{B}_{12}\text{Au}^- \) and \( \text{B}_{13}\text{O}^- \) were performed initially at the hybrid B3LYP level\(^{18}\) with the 3-21G basis set,\(^{19}\) using the Coalescence Kick (CK) global minimum search program.\(^{8,40}\) The top 12 low-lying candidate structures were then fully optimized at the B3LYP level with the 6-311G(d,p) basis set\(^{41}\) for \( \text{B}, \text{O}, \) and H and the Stuttgart relativistic small-core pseudopotential and valence basis sets augmented with two \( f \) and one \( g \) functions for Au \([ z(f) = 0.498, 1.461; z(g) = 1.218] \),\(^{42}\) denoted hereafter as Stuttgart_rsc_1997_ecp+2fg. Relevant low-lying neutral structures were also optimized. For the purpose of comparison, the same set of structures was also calculated for \( \text{B}_1\text{H}_4^+ \) and \( \text{B}_1\text{H}_4^- \). Frequency calculations were done to confirm that the obtained structures are true minima, unless stated otherwise. Excitation energies of the neutral clusters were calculated with the time-dependent DFT (TD-DFT) method\(^{43}\) at the ground-state structures of the anions. Additional single-point CCSD(T)\(^{44}\) calculations were done at the B3LYP/B,O,H/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2fg geometries to further evaluate the relative energies of the top four low-lying anion structures, which were calculated with the time-dependent DFT (TD-DFT) method\(^{45}\) at the ground-state structures of the anions. The ADEs and VDEs were calculated using the Gaussian 03 package.\(^{46}\)

3. Experimental results

3.1. \( \text{B}_{12}\text{Au}^- \)

The PES spectra of \( \text{B}_{12}\text{Au}^- \) are shown in Fig. 1 at two detachment energies. The 266 nm spectrum reveals two intense bands (X and A; Fig. 1a) and two additional weak features in between. The ground-state band X is relatively broad with a VDE of 3.39 eV (Table 1), as measured from the band maximum. Since no vibrational structures are resolved for band X, the ADE is estimated by drawing a straight line along the well-defined leading edge of band X and then adding the instrumental resolution to the intersection with the binding energy axis.
The ADE thus obtained is $3.48 \pm 0.04$ eV, which is also the electron affinity of B$_{12}$Au neutral. Band A at 4.55 eV is sharp, being separated from band X by a ~1.0 eV energy gap. Continuous weak signals, which are attributed to a minor isomer, are present in between bands X and A. Two bands are tentatively labeled: X' (~4.0 eV) and A' (~4.4 eV).

The 193 nm spectrum reveals numerous higher binding energy bands (Fig. 1b). Band B appears to be overlapping with band A, resulting in an intense and broad peak. The center of A/B peak (4.64 eV) should be viewed as the average of two VDEs. Beyond bands A/B, a broad band C (~5.5 eV) roughly covers the energy range from 5.2 to 5.7 eV and likely contains overlapping electronic transitions, as well. At higher binding energies, two relatively sharp bands are observed: D (5.89 eV) and E (6.12 eV).

### 3.2. B$_{13}$O$^-$

The 266 nm PES spectrum of B$_{13}$O$^-$ (Fig. 2a) shows a broad band X for the ground-state transition with an ADE and VDE of 3.90 ± 0.04 and 4.04 eV, respectively (Table 2). The ADE also represents the electron affinity of B$_{13}$O neutral. Following an energy gap of ~0.8 eV, four well-defined excited-state bands (A, B, C, and D; Fig. 2b) are observed in the 193 nm spectrum at VDEs of 4.84, 5.32, 5.74, and 6.15 eV, respectively. The relatively clean and well-resolved PES bands for B$_{13}$O$^-$ suggest that there is only one isomer present in the cluster beam.

### 4. Computational results

All cluster structures presented herein are at the B3LYP/B/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2f1g level of theory. The global minima and two low-lying structures of B$_{12}$Au$^-$ (1–3), B$_{12}$Au (13–15), B$_{13}$O$^-$ (16–18), and B$_{13}$O (28–30) are depicted in Fig. 3. Alternative optimized structures are summarized in Fig. S1 and S2 in the ESI† for B$_{12}$Au$^-$ (1–12) and B$_{13}$O$^-$ (28–30) neutral clusters. To aid the analysis of chemical bonding, a similar set of structures is also optimized for B$_{12}$H$^-$ (31–42) and B$_{12}$H (43–46) (Fig. S3 in ESI†). Nearly all these structures are true minima on their potential energy surfaces, except for structures 14, 26, and 40 which correspond to first or second order saddle points.

---

**Table 1** Experimental adiabatic and vertical detachment energies (ADEs and VDEs, in eV) from the photoelectron spectra of B$_{12}$Au$^-$, as compared with theoretical calculations based on the global minimum (1) and low-lying structures (2 and 3) at the B3LYP/B/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2f1g and TD-DFT levels.

<table>
<thead>
<tr>
<th>Feature</th>
<th>ADE (expt)</th>
<th>VDE (expt)</th>
<th>VDE (1)</th>
<th>VDE (2)</th>
<th>VDE (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>3.48 ± 0.04$^a$</td>
<td>3.59 ± 0.02</td>
<td>3.34 (3.40)$^b$</td>
<td>3.57 (3.66)$^b$</td>
<td></td>
</tr>
<tr>
<td>X'</td>
<td>4.0$^{d}$</td>
<td>3.76 (3.85)$^e$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A'</td>
<td>~4.4$^{d}$</td>
<td>4.27</td>
<td>4.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4.55 ± 0.01</td>
<td>4.51</td>
<td>4.51</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4.64 ± 0.05</td>
<td>4.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>~5.3$^{f}$</td>
<td>5.19</td>
<td>5.11</td>
<td>5.05</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>5.35</td>
<td>5.51</td>
<td>5.51</td>
<td>5.21</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>5.89 ± 0.03</td>
<td>5.76</td>
<td>5.82</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.12 ± 0.02</td>
<td>5.96</td>
<td>6.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Electron affinity of the neutral cluster. $^b$ Numbers in italic in the parentheses are from the single-point CCSD(T)/B3LYP/B/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2f1g calculations. $^c$ Calculated ADEs are 3.16 (3.24), 3.56 (3.59), and 3.46 (3.52) eV for structures 1, 2, and 3, respectively. $^d$ From minor isomer. $^e$ Center of the overlapping transitions.
4.1. B_{12}Au^+ and B_{12}Au

The top three low-lying structures of B_{12}Au^+ (1–3) (Fig. 3) and an additional higher-energy structure 5 (Fig. S1 in ESI†) are based on the global minimum of the B_{13} cluster with the Au atom bonded either to the outer B_9 or inner B_3 rings. Structure 1 (C_1, A) is the global minimum. However, structures 2 (C_{1e}, A') and 3 (C_{1e}, A') are competitive, which are within ~0.5 kcal mol\(^{-1}\) above the C_1 global-minimum structure at the single-point CCSD(T)//B3LYP/6-311G(d,p) level. All other anion structures as shown in Fig. S1 in the ESI† are considerably higher in energy.

Selected structures of B_{12}Au neutral cluster, corresponding to the top three anionic structures, are optimized (13–15; Fig. 1). Structure 13 is the lowest in energy and closely resembles the anionic global-minimum structure 1. Note that structures 14 and 15, which correspond to the low-lying anionic isomers 2 and 3, are located more than 10 kcal mol\(^{-1}\) above 13.

4.2. B_{13}O^- and B_{13}O

It is clear that all B_{13}O^- structures, of which the top three low-lying structures (16–18) are shown in Fig. 3 and higher energy structures (19–27) collected in Fig. S2 in the ESI† are not related to the bare B_{13} cluster.\(^6\) Instead, the boronyl BO unit is featured in all the B_{13}O^- structures. The global minimum 16 (C_{1e}, A') is based on the global minimum of B_{12} with a BO group bonded to an apex of the outer ring, closely resembling the global minimum of B_{12}Au^+ (1). The next lowest energy structure 17 (C_{1e}, A') of B_{13}O^- also resembles that of B_{12}Au^+ (2). The third lowest energy structure 18 (C_{1e}, A') of B_{13}O^- possesses a distorted B_{12} motif, which includes a planar hepta-coordinate boron center.\(^7\) Structures 17 and 18 are ~3 kcal mol\(^{-1}\) above the global minimum at the single-point CCSD(T)//B3LYP/6-311G(d,p) level. Note that owing to intramolecular coulomb repulsion, BO bonding to the B_{12} core appears to favor the low-coordinate apex sites as compared to the on-top site (Fig. S2 in ESI†), akin to CO chemisorption on nanogold.\(^46\) This makes the B_{13}O^- cluster structurally more selective, as shown in Fig. S4 in the ESI† Alternative optimized structures 19–27 of B_{13}O^- are ~7–48 kcal mol\(^{-1}\) higher in energy, where structure 19 corresponds to the low-lying structure 3 of B_{12}Au^+.

Again we optimized three neutral B_{13}O structures, 28–30 in Fig. 3, corresponding to the top three anionic structures. The neutral global minimum (28) is similar to its anion (16). Structure 29 is ~3.6 kcal mol\(^{-1}\) above 28, whereas isomer 30 is higher in energy by ~18 kcal mol\(^{-1}\).

5. Comparison between experiment and theory

We first use the well-characterized B_{12}^- cluster\(^6\) to benchmark the B3LYP/6-311G(d,p) method, which predicted the ground-state
VDE and second VDE for \( \text{B}_{12}\text{Au}^- \) as 2.16 and 4.14 eV, respectively. These VDEs compare well with the experimental data of 2.26 ± 0.04, and 4.31 ± 0.05 eV, reported previously, although the B3LYP method seems to underestimate the VDEs by 0.1–0.2 eV. Similar errors are anticipated for the \( \text{B}_{12}\text{Au}^- \) and \( \text{B}_{12}\text{O}^- \) clusters.

### 5.1. \( \text{B}_{12}\text{Au}^- \) : the global minimum

Structure 1 \((\text{C}_1, \text{A})\) is the global minimum for \( \text{B}_{12}\text{Au}^- \) at both the B3LYP/B/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2f1g and single-point CCSD(T)//B3LYP/B/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2f1g levels (Fig. 3). Its calculated VDEs and simulated PES spectrum are compared with experimental measurements in Table 1 and Fig. 4a, respectively, where the simulated PES spectrum was constructed by fitting the distribution of the calculated VDEs with unit-area Gaussian functions of 0.05 eV half-width and each doublet final state was assumed to have equal intensity. The calculated ground-state ADE/VDE (3.16/3.34 eV) at B3LYP are systematically lower than the experimental data (3.48/3.59 eV) by ~0.3 eV, consistent with the benchmarks of B3LYP via \( \text{B}_{12}\text{Au}^- \), as mentioned above.47,48 The single-point CCSD(T) data, 3.24/3.40 eV, are slightly improved. The simulated PES pattern is in excellent agreement with the main experimental features (Fig. 4a). Thus, the main PES bands for \( \text{B}_{12}\text{Au}^- \) (X and A–E) can be assigned reliably to the global minimum of \( \text{B}_{12}\text{Au}^- \) (Table 1). The overall agreement between the theoretical results and the experimental PES data suggest that the energetics of single-point CCSD(T) calculations is probably quite accurate.

### 5.2. \( \text{B}_{12}\text{Au}^- \) : the minor isomer

The observed weak features X’ and A’ of \( \text{B}_{12}\text{Au}^- \) (Fig. 1) are due to coexisting minor isomers. Our calculations yield two low-lying isomers 2 \((\text{C}_2, \text{A}')\) and 3 \((\text{C}_3, \text{A}'')\), which are within ~0.5 kcal mol\(^{-1}\) of the global minimum at the single-point CCSD(T) level (Fig. 3). The simulated PES spectrum of isomer 2 (Fig. 4b) shows the first two predicted VDEs at 3.76 and 4.27 eV, where the band intensity for isomer 2 (as well as that for isomer 3; Fig. 4c) was weighed roughly according to the experimental X’/X ratio. These predicted VDE values are in good agreement with the observed minor bands X’ (~3.40 eV) and A’ (~4.4 eV), considering the B3LYP errors of 0.1–0.3 eV. Again, the calculated VDE at single-point CCSD(T) level is 3.85 eV, in slightly better agreement with band X’.

Isomer 3 (Fig. 4c) predicts a ground-state VDE of 3.57 and 3.66 eV, respectively, at B3LYP and single-point CCSD(T) levels, which numerically match the experimental VDE for band X (3.59 eV). However, considering the above-mentioned errors of B3LYP, the simulated spectrum is subject to a similar overall shift to the blue in order to compare faithfully with experiment. Such corrections deteriorate the agreement between the experimental and simulated spectra. The simulated PES spectrum also fails to reproduce the broad experimental A/B bands. Furthermore, the simulation predicts only one transition in the 5.6–6.3 eV binding energy regime, in contrast to two well-resolved experimental bands (D and E). It is stressed that a “missing” PES band in the simulation is a clear indication of a “wrong” cluster structure. It may thus be concluded that the contribution of isomer 3 is small, if any, and its corresponding PES features are likely to be buried below those from the main isomer 1.

### 5.3. \( \text{B}_{13}\text{O}^- \)

The global minimum 16 \((\text{C}_4, \text{A}')\) of \( \text{B}_{13}\text{O}^- \) is considerably more stable than the other low-lying isomers 17 \((\text{C}_3, \text{A}')\) and 18 \((\text{C}_1, \text{A})\).
at the single-point CCSD(T)/B3LYP/6-311G(d,p) level, by 2.81 and 3.38 kcal mol\(^{-1}\), respectively. Indeed, in contrast to \(\text{B}_{12}\text{Au}^-\) (Fig. 1), no clear evidence is observed for any coexisting isomers for \(\text{B}_{13}\text{O}^-\) (Fig. 2). The calculated ground-state ADE/VDE (3.56/3.76 eV) at B3LYP/6-311G(d,p) compare well to the experimental values (3.90/4.04 eV), with the anticipated errors of \(\sim 0.3\) eV. The simulated PES spectrum from the global minimum displays peak-to-peak correspondence to the experimental data (Fig. 4d and Table 2). Isomers 17 and 18 can be ruled out on the basis of the energetics at the CCSD(T)/B3LYP/6-311G(d,p) level.

6. Discussion

6.1. Chemical bonding in \(\text{B}_{12}\text{Au}^-\) and \(\text{B}_{13}\text{O}^-\)

The above comparisons between experiment and theory establish the global-minimum structures of \(\text{B}_{12}\text{Au}^-\) (1) and \(\text{B}_{13}\text{O}^-\) (16) and their neutrals (13 and 28; Fig. 3). Basically, these structures are derived from the aromatic \(\text{B}_{12}\) and \(\text{B}_{12}\) clusters and are similar to \(\text{B}_{12}\text{H}^-\) (31) and \(\text{B}_{12}\text{H}\) (43) (Fig. S3 in ESI†). The simulated PES spectra based on 1, 16, and 31 are compared in Fig. S5 in the ESI.† The molecular orbitals of \(\text{B}_{12}\text{X}^-\) (\(\text{X} = \text{Au}, \text{BO}, \text{H}\)) are also compared with those of \(\text{B}_{12}\) in the ESI† (Fig. S6–S8). Alternatively, chemical bonding in these systems can be understood from the adaptive natural density partitioning (AdNDP) analyses, as shown in Fig. 5 for all three \(\text{B}_{12}\text{X}^-\) clusters. The \(\text{X}\) ligand is bonded to a peripheral B atom of \(\text{B}_{12}\) via a 2c-2e \(\sigma\) bond, whereas the bonding elements of the \(\text{B}_{12}\) motif are similar to bare \(\text{B}_{12}\) cluster, that is, nine 2c-2e \(\sigma\) bonds for the \(\text{B}_{9}\) peripheral ring, one 3c-2e \(\sigma\) bond for the inner \(\text{B}_{3}\) triangle, five 3c-2e \(\sigma\) bonds for bonding between the inner triangle and the outer \(\text{B}_{9}\) ring, and three delocalized \(\pi\) bonds. The \(\text{H}, \text{Au}, \text{and BO ligands}\) are all \(\text{s}\) radicals, which form a single \(\sigma\) bond with \(\text{B}_{12}\) using the extra electron, thus leaving the bonding in the \(\text{B}_{12}\) motif intact. It is expected that additional ligands to the \(\text{B}_{12}\) motif will start to break the B–B \(\sigma\) bonds on the peripheral \(\text{B}_{9}\) ring, leading to instability of the \(\text{B}_{12}\) motif and eventually to the anticipated 2D-to-cage structural transition.

6.2. Au–H isolobal analogy and boronyl chemistry

In recent years, we have found experimental and theoretical evidence that a single Au atom can act as H in alloy clusters such as the Si–Au and B–Au systems, which is an extension of the isolobal analogy between a gold phosphine (AuPH\(_3\)) unit and hydrogen in synthetic Au compounds. The present results show that \(\text{B}_{12}\text{Au}^-\) and \(\text{B}_{12}\text{Au}\) clusters are similar to \(\text{B}_{12}\text{H}^-\) and \(\text{B}_{12}\text{H}\) clusters in terms of structures and bonding. This provides another example of the Au/H analogy, due to the high covalency of the B–Au bonding. Indeed, natural bond orbital (NBO) analysis indicates little charge transfer within the Au–B bond: \(Q(\text{Au}) = -0.14\) \(|e|\) and \(Q(\text{B}) = -0.29\) \(|e|\) in \(\text{B}_{12}\text{Au}^-\) (1), and \(Q(\text{Au}) = +0.18\) \(|e|\) and \(Q(\text{B}) = -0.17\) \(|e|\) in \(\text{B}_{12}\text{Au}\) (13). The B–Au bond distances are 2.10 Å in 1 and 2.05 Å in 13, which are typical for a single bond.

Our prior systematic studies on boron oxide clusters have uncovered the structural and chemical robustness of the boronyl BO group as a key structural unit, and also established the close analogy between boron-rich oxide clusters and boranes. In the current \(\text{B}_{13}\text{O}^-\) (16) and \(\text{B}_{13}\text{O}\) (28) clusters, the BO group again governs their structural and chemical properties. Note that 16 and 28 bear little structural resemblance to the \(\text{B}_{13}\) or
B_{13} cluster.\textsuperscript{3,4,6,13} Although the latter cation is a well-known "magic" cluster,\textsuperscript{14} Importantly, the B≡B triple bond in the BO group is maintained in 16 and 28, as reflected in their bond distances: 1.21 Å in 16 and 1.21 Å in 28, which are compared to 1.203 and 1.234 Å in the gas-phase BO and BO\textsuperscript{−} clusters at the B3LYP/aug-cc-pVTZ level.\textsuperscript{27} In addition, the B−B single bond associated with the BO group is also typical: 1.65 Å in 16 and 1.64 Å in 28, as compared to those of 1.607 and 1.621 Å in B_{12}O\textsuperscript{2−} and B_{12}O\textsubscript{2} clusters at the B3LYP/aug-cc-pVTZ level.\textsuperscript{29} Note that the B−(B≡B) single σ bond is also highly covalent, with an overall net charge of Q(B≡B) = +0.09 |e| in 16 and Q(B≡B) = +0.16 |e| in 28.

7. Conclusions

In conclusion, we have studied the structural and electronic properties of the B_{12}Au\textsuperscript{+} and B_{13}O\textsubscript{16} clusters and their neutral species using anion photoelectron spectroscopy and quantum chemical calculations. The electron affinities of B_{12}Au and B_{13}O are determined to be 3.48 \pm 0.04 and 3.90 \pm 0.04 eV, respectively. Two isomeric species are observed for B_{13}Au\textsuperscript{+}, whereas only one isomer for B_{13}O\textsuperscript{−} is observed. The global-minimum structures are found to consist of an intact B_{12} motif with the Au or BO ligand bonded to the periphery of the highly stable aromatic B_{12} cluster. Structures and bonding of B_{12}Au\textsuperscript{+} and B_{13}O\textsuperscript{−} are also found to be similar to the B_{12}H\textsuperscript{+} monohydride cluster. Thus, all three clusters are isolobal to each other and represent the first chemical compounds formed by the highly stable aromatic planar B_{12} cluster.

Acknowledgements

S.D.L. would like to thank Professor A. I. Boldyrev for the Coalescence Kick (CK) global minimum search and the adaptive natural density partitioning (AdNDP) programs. This work was supported by the US National Science Foundation (DMR-0904034 to L.S.W) and the National Natural Science Foundation of China (No. 20873117 to S.D.L).

Notes and references

47 Zero-point energies (ZPEs) are not included in the B3LYP/B13O/6-311G(d,p)/Au/Stuttgart_rsc_1997_ecp+2fg data listed in Tables 1 and 2. With ZPE corrections, the ground-state ADEs are 3.15 eV for B12Au and 0.08 eV for B13O, which are within 0.01–0.02 eV of the original data.
48 Considering that the basis sets may be inadequate in dealing with anions because they do not include diffuse functions, we have run additional B3LYP calculations using the 6-311+G(d,p) basis sets for B and O. The calculated ground-state ADEs/VDEs are 3.19/3.37 eV for B12Au and 3.54 eV for B13O, which are in slightly better agreement with experiment. But the improvement is only 0.03 eV for B12Au and 0.08 eV for B13O.