ReB$_6$$^-$: A Metallaboron Analog of Metallabenzenes

Ling Fung Cheung, Joseph Czekner, G. Stephen Kocheril, and Lai-Sheng Wang$^*$

Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

$^*$ Supporting Information

ABSTRACT: Metallabenzenes are a class of molecules in which a CH unit in benzene is replaced by a functionalized transition-metal atom. While all-boron analogues of aromatic and antiaromatic hydrocarbons are well-known, there have not been any metallaboron analogs. We have produced and investigated two metal-doped boron clusters, ReB$_6$$^-$ and AlB$_6$$^-$, using high-resolution photoelectron imaging and quantum chemical calculations. Vibrationally resolved photoelectron spectra have been obtained and compared with the theoretical results. The ReB$_6$$^-$ cluster is found to be perfectly planar with a B-centered hexagonal structure (C$_{3v}$ 1A$_1$), while AlB$_6$$^-$ is known to have a similar structure, but with a slightly out-of-plane distortion (C$_{3v}$ 1A). Chemical bonding analyses show that the closed-shell ReB$_6$$^-$ is doubly $\sigma$- and $\pi$-aromatic, while AlB$_6$$^-$ is known to be $\sigma$-aromatic and $\pi$-antiaromatic. The out-of-plane distortion in AlB$_6$$^-$ is due to antiaromaticity, akin to the out-of-plane distortion of the prototypical antiaromatic cyclooctatetraene. The $\pi$-bonding in ReB$_6$$^-$ is compared with that in both benzene and rhenabenzene [(CO)$_4$ReC$_5$H$_5$], and remarkable similarities are found. Hence, ReB$_6$$^-$ can be viewed as the first metallaboron analog of metallabenzenes and it may be viable for syntheses with suitable ligands.

INTRODUCTION

Metallabenzenes consist of an interesting class of organometallic compounds, in which one CH unit in benzene is substituted by a metal atom. Various metallabenzenes have been synthesized, including several recently reported rhenabenzenes. Interesting aromatic and organometallic properties have been found for metallabenzenes. Both planar and nonplanar metallabenzenes have been observed. It was suggested that not only electronic but also steric factors can play a role in the planarity of metallabenzenes.

Boron is known to form delocalized bonds due to its electron deficiency. While borane cages (B$_n$H$_{2n-2}$), in particular, B$_9$H$_{12}$, have long been considered as three-dimensional aromatic systems, the aromaticity and planarity of size-selected bare boron clusters have been established fairly recently. via joint experimental and theoretical investigations. The study of size-selected boron clusters has given rise to the concepts of $\sigma$- and $\pi$-aromaticity, aromaticity, and even conflicting aromaticity, which can be described well by the adaptive natural density partitioning (AdNDP) method. Similar to metallabenzenes, both electronic and steric factors can play a role in the planarity of aromatic boron clusters. For example, the B$_{12}$ cluster is aromatic with six $\pi$-electrons, but it features an out-of-plane distortion (C$_{3v}$) because the B$_9$ ring is too small to host a B$_3$ unit. A subsequent study showed that substitution of a peripheral B atom by a larger, isoelectronic Al atom leads to a perfect planar and aromatic AlB$_{12}$ cluster. On the other hand, substitution of a B atom in the hexagonal C$_{3v}$ B$_7$ cluster led to a C$_3$ AlB$_6$$^-$ cluster, which has a planar B$_6$$^-$ moiety with the peripheral Al atom slightly out of plane because it has conflicting aromaticity: the AlB$_6$$^-$ cluster is $\sigma$-aromatic, but $\pi$-antiaromatic with four $\pi$-electrons. An interesting question arises: can the Al atom be replaced in AlB$_6$$^-$ by a transition-metal atom to produce a perfectly planar and aromatic hexagonal MB$_6$$^-$ cluster, which would be a metallaboron analog of metallabenzenes?

In addition to the Al-substituted B$_7$$^-$, a number of MB$_6$$^-$-type clusters have been studied, including main group, lanthanide, and transition-metal substituents. The early reports of the aromatic D$_{3h}$ CB$_6$$^2$- and the associated D$_{3h}$ CB$_6$$^-$ species were unfortunately higher-energy isomers, and their global minima were found by joint potential energy surface and theoretical studies to feature less symmetric structures in which the C atom is located on the periphery of the clusters. The gold atom in AuB$_6$$^-$ is found to bond to the B$_6$ moiety via a single covalent bond akin to a H atom. The SmB$_6$$^-$ and CeB$_6$$^-$ clusters have been reported recently, both exhibiting planar structures similar to that of AlB$_6$$^-$, but SmB$_6$$^-$ was found to be doubly antiaromatic.

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TaB$_6^-$ cluster was found to have a perfect planar structure and was considered to be doubly aromatic. However, it has a triplet ground state ($C_{3v}$, $B_1$) with five delocalized $\pi$-electrons and a single nonbonding 5$d$-electron. Hence, a planar MB$_6^-$ metallaboron cluster with similar electronic structure as benzene or metallabenzenes has not been reported.

In the current study, we investigate the ReB$_6^-$ cluster using high-resolution photoelectron (PE) imaging with complete vibrational resolution and quantum chemical calculations. The AlB$_6^-$ cluster is revisited using high-resolution PE imaging as a comparison. A more accurate electron affinity (EA) is measured for AlB$_6$ and the vibrationally resolved PE spectra confirm the previously reported bent structure for AlB$_6^-$.

The structure distortion in AlB$_6^-$ is consistent with its $\pi$-antiaromaticity, analogous to the out-of-plane distortion in the cyclooctatetraene (C$_8$H$_8$). The ReB$_6^-$ cluster is found to be closed-shell and perfectly planar. Chemical bonding analyses reveal that ReB$_6^-$ possesses six delocalized $\sigma$-electrons and six delocalized $\pi$-electrons, consistent with double aromaticity. The $\pi$-bonding in ReB$_6^-$ is found to display remarkable similarities to that in benzene and the recently synthesized rhenabenzenes.

## EXPERIMENTAL AND THEORETICAL METHODS

### High-Resolution Photoelectron Imaging

The experiments were conducted using a high-resolution PE imaging system coupled to a laser vaporization cluster source, which was described in detail previously. Briefly, the ReB$_6^-$ and AlB$_6^-$ clusters were produced by focusing the second harmonic of a Nd:YAG laser onto a disk target. The target was made of a mixture of enriched $^{10}$B, Re, and Ag powders for the production of ReB$_6^-$ or of enriched $^{11}$B, Al, and Ag powders for that of AlB$_6$. The Ag powder was added as a binder. The laser-induced plasma formed inside the nozzle was quenched by a helium carrier gas seeded with 10% argon, which initiated the nucleation. The nascent clusters were entrained in the carrier gas and underwent a supersonic expansion to produce a cold cluster beam.

Anionic clusters were extracted perpendicularly into a time-of-flight mass spectrometer. The $^{17}$Re$^{10}$B$_6^-$ or Al$^{11}$B$_6^-$ clusters of interest were mass-selected before entering the interaction zone of the velocity-map imaging (VMI) system.

A Deyang Tech dye laser pumped by a Nd:YAG laser was used to detach electrons from the size-selected clusters. Photoelectrons were focused onto a set of microchannel plates coupled with a phosphor screen and a charge-coupled device camera. Each experiment at a various photon energies (193, 266, and 355 nm), which revealed complicated vibrational structures are resolved, suggesting very little geometry change upon photodetachment. Discernable vibrational peaks are labeled as $a^g$ and their binding energies and assignments (vide infra) are summarized in Table 1.

### Theoretical Method

We carried out global minimum searches for ReB$_6^-$ using the simulated annealing algorithm coupled with density functional theory (DFT) for geometry optimizations. Around 300 different structures were generated and optimized at the PBE/LAN2DZ level of theory. The low-lying isomers within 1 eV of the global minima were further optimized using the B3LYP functional with the aug-cc-pV TZ basis set and the ECP for Re and the aug-cc-pVTZ basis set for B. Geometric optimization and vibrational analyses were carried out for ReB$_6^-$ and for AlB$_6$. Since the global minima of AlB$_6^-$ were already known, we redid the geometric optimization and performed vibrational analyses at the B3LYP/aug-cc-pVTZ level of theory. For comparison, we optimized the structures of benzene and a symmetric model of rhenabenzenes [(CO)$_2$Re$_3$C,H$_3$] at the B3LYP/aug-cc-pVTZ level of theory and performed chemical bonding analyses.

The adiabatic detachment energy (ADE) for the ground-state transition, which also represents the EA of the neutral, was calculated as the energy difference between the optimized anion and its corresponding neutral. Coupled cluster calculations [CCSD(T)] were done on the B3LYP geometry for ReB$_6^-$ using the same basis sets and ECP to calculate the ADE. Chemical bonding analyses were done using the AdNDP method. Nucleus-independent chemical shift (NICS) calculations were carried out to examine the aromaticity of ReB$_6^-$. Franck–Condon simulations were performed using PES-CAL. All calculations were done using Gaussian 09.

### RESULTS

#### Experimental Results

The PE images and spectra of ReB$_6^-$ at six different photon energies are shown in Figure 1. A sharp peak labeled as X denotes the 0–0 transition, which is from the anion ground state to that of the neutral. The X peak defines the EA of ReB$_6^-$ to be 2.3478 ± 0.0008 eV. Extremely weak intensities were observed for transitions to vibrationally excited states, indicating very little geometry change upon photodetachment. Discernable vibrational peaks are labeled as $a^g$ and their binding energies and assignments (vide infra) are summarized in Table 1.

The PE spectra of AlB$_6^-$ were reported previously at three photon energies (193, 266, and 355 nm), which revealed numerous detachment transitions. The 355 nm spectrum was partially vibrationally resolved for the ground-state transition, yielding an average vibrational spacing of 480 ± 40 cm$^{-1}$ and an EA of 2.49 ± 0.03 eV for AlB$_6^-$. Figure 2 shows the PE images and high-resolution PE spectra for the ground-state transition of AlB$_6^-$ at various photon energies. Much more complicated vibrational structures are resolved, suggesting significant structural changes between the ground states of the AlB$_6^-$ anion and its neutral. The sharp peak labeled X in Figure 2a denotes the 0–0 transition and yields a more accurate EA of 2.4958 ± 0.0004 eV for AlB$_6^-$. The resolved vibrational peaks
Comparison with the Computed Vibrational Frequencies of lence molecular orbital (MO) pictures are displayed in Figure S1a of the Supporting Information (SI). The $6a_1$ highest

level of theory is perfectly planar with peripheral Re atom, similar to that of AlB$_6$.


Table 1. Measured Binding Energies (BE), Energy Shifts Relative to the 0−0 Transition, and Assignments of the Observed Vibrational Peaks in the PE Spectra of ReB$_6^-$ and Comparison with the Computed Vibrational Frequencies of ReB$_6$ at the B3LYP/aug-cc-pVTZ/Re/aug-cc-pVTZ-pp Level of Theory

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<td>$b_1$</td>
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<td>$a_1$</td>
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*The calculated ADE for ReB$_6^-$ is 2.05 eV at the B3LYP/aug-cc-pVTZ Level of Theory.

Figure 2. Photoelectron images and spectra of AlB$_6^-$ at different photon energies. The double arrows below the images denote the laser polarization.

are labeled as $a$−$i$ and their binding energies and assignments are summarized in Table 2. Several peaks are assigned to fundamental vibrational excitations ($a$−$c$, $e$, and $h$), while the others are assigned to overtones ($f$ and $g$) or a combination vibrational level ($d$) (vide infra).

Computational Results. The global minimum of ReB$_6^-$ was found to be a B-centered six-membered ring with a peripheral Re atom, similar to that of AlB$_6^-$, except that ReB$_6^-$ is perfectly planar with $C_{2v}$ symmetry (Figure 3a). The anion has a closed-shell electron configuration ($^{1}A_1$): 1$a_1^21b_2^22a_1^22b_1^23a_1^24a_1^24b_2^25a_1^24b_2^21a_1^22b_1^26a_1^2$. The valence molecular orbital (MO) pictures are displayed in Figure S1a of the Supporting Information (SI). The $6a_1$ highest occupied MO (HOMO) is comprised of the nonbonding 5d$_{z^2}$ orbital. Removal of one electron from the HOMO of ReB$_6^-$ gives rise to the $^2A_1$ neutral ground state. Very little geometry change is observed between the anion and the neutral ground states due to the nonbonding nature of the HOMO, in agreement with the observed PE spectra (Figure 1). It has been shown previously that carbon avoided the central position of a B$_6$ ring in the CB$_6^-$ cluster because carbon is more electronnegative and prefers to form localized bonds on the periphery of the planar CB$_6^-$ cluster.

In the current case of ReB$_6^-$, the Re atom is too large to fit in the center of a B$_6$ ring. There are both geometric and electronic criteria to form M(OB)$_6^-$-type metal-centered aromatic borometallic clusters.

Recently, both ReB$_8^-$ and ReB$_9^-$ are found to be new members of the transition-metal-centered borometallic molecular wheel family. The optimized geometry of the AlB$_6^-$ anion and its corresponding neutral are shown in Figure 3b. As reported previously, AlB$_6^-$ is a B-centered six-membered ring with a slight out-of-plane distortion by the Al atom (Figure 3b). The planar C$_{2v}$ structure possesses an imaginary frequency and is 0.05 kcal/mol higher in energy than the distorted C$_{3v}$ structure. Further optimization following the imaginary frequency leads to the bent global minimum, which is closed-shell with C$_{3v}$ symmetry.
symmetry (1A'). The valence MO pictures of AlB$_6^-$ are shown in Figure S1b (SI) and its HOMO is a π-bonding orbital. Removal of an electron from the HOMO of AlB$_6^-$ yields the ground state of the neutral (2A") with the same symmetry but a much larger out-of-plane distortion by the Al atom. The large geometry change between the anion and neutral ground state is consistent with the complicated vibrational structures observed in the high-resolution PE spectra of AlB$_6^-$ (Figure 2).

**DISCUSSION**

Comparison of the High-Resolution Photoelectron Spectra of ReB$_6^-$ with the Theoretical Results. The calculated ADE of 2.42 eV for ReB$_6^-$ at the CCSD(T) level agrees well with the experimental value of 2.3478 eV (Table 1). To help assign the observed weak vibrational features, we computed the vibrational frequencies for both the ReB$_6^-$ anion and its neutral, as given in Table S1 (SI). We also did a Franck–Condon simulation as exhibited in Figure S2a (SI), which shows almost negligible Franck–Condon factors for any vibrational excitations accompanying the photodetachment process, because of the small geometry changes between the anion and neutral (Figure 3a). The only discernible Franck–Condon factor is for mode $\nu_4$, corresponding to peak c (Table 1). The other mode with visible Franck–Condon factor is the $\nu_4$ mode, corresponding to peak g. The displacement vectors of these modes are shown in Figure S3a (SI), which are consistent with the minor geometry changes between the anion and neutral (Figure 3a). Peaks b, e, and f can also be assigned to three totally symmetric fundamental vibrational modes, $\nu_6$, $\nu_3$, and $\nu_2$, respectively, as shown in Table 1. Peak a is assigned to a symmetry-forbidden mode, $\nu_{10}$, which corresponds to the lowest-frequency out-of-plane bending mode (Figure S3a, SI). We have previously observed symmetry-forbidden vibrational modes, also corresponding to low-frequency bending modes. Similarly, peak d can be tentatively assigned to a combinational mode of $\nu_{10}$ and $\nu_4$.

Overall, the observed vibrational features agree well with the computed frequencies and the Franck–Condon simulation,
confirming unequivocally the $C_2v$ planar global minimum structures for ReB$_6^-$ and neutral ReB$_6$ (Figure 3a).

Comparison of the High-Resolution Photoelectron Spectra of AlB$_6^-$ with the Theoretical Results. The more accurate ADE of 2.4958 eV measured for AlB$_6^-$ agrees well with the calculated value of 2.45 eV at the CCSD(T)/aug-cc-pVTZ level of theory (Table 2). Much more complicated vibrational structures are resolved in the high-resolution PE spectra of AlB$_6^-$ (Figure 2), because of the large geometry changes between the anion and the neutral (Figure 3b). The calculated vibrational frequencies (Table S2, SI) are used to guide the vibrational assignments. The large out-of-plane distortion of the Al atom in the neutral (Figure 3b) suggests that the most Franck–Condon-active vibrational mode should be the Al-bending mode during photodetachment. This is the $\nu_7$ mode with a computed frequency of 396 cm$^{-1}$ (Figure S3b, SI), corresponding to the strongest vibrational peak $c$ in the PE spectra (Figure 2), which gives an experimental frequency of 395 cm$^{-1}$. Peaks $f$ and $i$ also belong to the $\nu_7$ vibrational progression, as shown in Table 2. Peaks $a$, $b$, $e$, and $h$ can be assigned to four more fundamental vibrational frequencies, as given in Table 2. Finally, peak $d$ is assigned to a combinational mode of $\nu_4$ and $\nu_{21}$, and peak $g$ is assigned to the overtone of mode $\nu_{14}$ (Table 2). The displacement vectors for all the observed vibrational modes of AlB$_6$ are shown in Figure S3b (SI). Overall, the Franck–Condon simulation and the computed vibrational frequencies are in excellent agreement with the high-resolution photoelectron spectra, confirming the bent structure of AlB$_6^-$ and the large geometry changes in the neutral relative to the anion (Figure 3b).

Bonding Analyses for ReB$_6^-$ and AlB$_6^-$: We performed chemical bonding analyses for ReB$_6^-$ and AlB$_6^-$ using the AdNDP method. The AdNDP results for ReB$_6^-$ and AlB$_6^-$ are compared with those of benzene and rhenabenzenes in Figure 4. The AdNDP analyses for ReB$_6^-$ and AlB$_6^-$ reveal six two-center two-electron (2c–2e) peripheral B–B/Re bonds, a 5d$^1$ lone pair, and six delocalized bonds for ReB$_6^-$ (Figure 4a) and six 2c–2e peripheral B–B/Al bonds and five delocalized bonds for AlB$_6^-$ (Figure 4b). The ReB$_6^-$ cluster features three totally delocalized 7c–2e $\sigma$-bonds and three totally delocalized 7c–2e $\pi$-bonds (Figure 4a), both fulfilling the 4n + 2 Hückel rule for aromaticity, rendering ReB$_6^-$ doubly aromatic. The AdNDP analyses for AlB$_6^-$ have been reported previously and are presented here for comparison. As shown in Figure 4b, AlB$_6^-$ contains three totally delocalized 7c–2e $\sigma$-bonds and two totally delocalized 7c–2e $\pi$-bonds, which render AlB$_6^-$ $\sigma$-aromatic and $\pi$-antiaromatic. Hence, AlB$_6^-$ provides a rare case of conflicting aromaticity. The $\pi$-antiaromaticity in AlB$_6^-$ explains its out-of-plane distortion, analogous to the out-of-plane distortion of the prototypical antiaromatic cyclooctatetraene ($C_8H_8$).

Comparison of the Delocalized $\pi$-Bonds and Aromaticity in ReB$_6^-$ with Those in Benzene and Rhenabenzenes. We also conducted AdNDP analyses for benzene and [(CO)$_4$ReC$_5$H$_7$] for comparison, as shown in parts c and d of Figure 4, respectively. We see that the three delocalized $\pi$-bonds in ReB$_6^-$ are similar to those in benzene, with the 5d orbitals participating in the delocalized bonding. Curiously, the two 6c–2e delocalized $\pi$-bonds in rhenabenzenes exhibit very little participation from the Re 5d orbitals (Figure 4d). Hence, the $\pi$-bonding in ReB$_6^-$ is even more similar to that of benzene than that of rhenabenzenes, and ReB$_6^-$ can be considered as a true metallaromatic analog of metallabenzenes. It should be pointed out that planar metallacycles can exhibit both Hückel and Möbius aromaticity because of the possible participation of the $d_{xy}$ orbital in the $\pi$-bonding. Möbius aromaticity can occur for 4n $\pi$-metallacycles, such as the seven-membered ring metallacycloheptatriene [8$\pi$, FeH$_2$(CH)$_4$],. The ReB$_6^-$ cluster is clearly a Hückel aromatic system. It is conceivable that larger planar ReB$_6^-$ clusters may display Möbius aromaticity.

To further characterize the aromaticity in ReB$_6^-$, its NICS values were computed and compared with those of benzene and B$_{19}^-$ (ref 36) in Table S3 (SI). For ReB$_6^-$, since the central boron atom is very close to the geometric center of the molecule, we also computed the NICS values at different sites besides the geometric center (Table S3, SI). The large negative NICS values within the plane of the cluster in sites A, B, and C suggest strong $\sigma$-aromaticity. The NICS$_zz$ values for ReB$_6^-$ are all negative when the distance above the molecular plane is smaller than 0.6 Å, indicating strong $\pi$-aromaticity. The NICS$_zz$ value is very negative at site A, while less negative at site C. The values become more positive as the distance increases and the NICS$_zz$(1) at site X above the central B atom is +4.22. A positive NICS$_zz$ value was also found for the doubly aromatic B$_{19}^-$ cluster at 0.2 Å above the plane (Table S3, SI), which features a boron atom at the geometric center. Overall, the mainly negative NICS$_zz$ values are consistent with the AdNDP results that ReB$_6^-$ possesses both $\sigma$- and $\pi$-aromaticity and can be considered as a true metallaromatic analog of metallabenzenes.

CONCLUSIONS

We have produced the ReB$_6^-$ cluster and investigated its structure and bonding using high-resolution photoelectron imaging and computational chemistry. High-resolution photoelectron imaging for AlB$_6^-$ has also been done for comparison. Accurate electron affinities are measured for ReB$_6^-$ and AlB$_6^-$ as well as their vibrational frequencies. The ReB$_6^-$ cluster is found to have a planar B-centered hexagonal structure with $C_2$ symmetry and a closed-shell electronic structure. Chemical bonding analyses revealed that ReB$_6^-$ possess three delocalized $\sigma$-bonds and three delocalized $\pi$-bonds, rendering it doubly aromatic. In comparison, the AlB$_6^-$ cluster has three delocalized $\sigma$-bonds, but only two delocalized $\pi$-bonds. Thus, it is $\pi$-antiaromatic, consistent with its out-of-plane distortion, analogous to that in the prototypical antiaromatic cyclooctatetraene ($C_8H_8$). The delocalized $\pi$-bonding in ReB$_6^-$ is compared with that in both benzene and rhenabenzenes [(CO)$_4$ReC$_5$H$_7$]. The $\pi$-bonding in ReB$_6^-$ is found to be similar to that in benzene with the Re 5d orbitals participating in the delocalized bonding. Hence, ReB$_6^-$ can be considered as a metallaromatic analog of the metallabenzenes. The current study suggests that other metallaromatic analogs of metallabenzenes should exist and that these species may be viable for bulk syntheses with suitable ligation of the metal site.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b09110.

Computed vibrational frequencies, molecular orbitals, Franck–Condon simulations, displacement vectors of
The authors declare no competing financial interest.

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