Molecular Wheel $\text{B}_8^{2-}$ as a New Inorganic Ligand. Photoelectron Spectroscopy and ab Initio Characterization of $\text{LiB}_8^{-}$

Anastassia N. Alexandrova,† Hua-Jin Zhai,† Lai-Sheng Wang,*‡ and Alexander I. Boldyrev*‡

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300,
Department of Physics, Washington State University, 2710 University Drive, Richland,
Washington 99352, and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific
Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352

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The bare $\text{B}_8$ cluster was previously reported to be a $D_{3h}$ molecular wheel with a triplet group state. The $\text{B}_8^{2-}$ dianion was predicted to be a closed-shell singlet and double aromatic $D_{3h}$ molecular wheel. Here we report the experimental observation of $\text{B}_8^{2-}$ stabilized by a Li$^+$ cation in $\text{LiB}_8^{-}$ and its experimental characterization using photoelectron spectroscopy. Theoretical searches lead to a $C_7h$, $\text{LiB}_8^{-}$ global minimum structure, and its calculated photodetachment transitions are in good agreement with the experimental values. Except for a small out-of-plane distortion due to the asymmetric Li$^+$ capping, the $\text{B}_8^{2-}$ unit in $\text{LiB}_8^{-}$ is nearly identical to the bare $\text{B}_8^{2-}$, suggesting it is a robust and stable structural unit and may be used as a new ligand and building block in chemistry.

Three-dimensional borohydrides and their derivatives are known to be ligands in complex compounds.1–4 Exotic new complexes containing remarkable planar aromatic boranes have been synthesized by Fehlner and co-workers5,6 and predicted computationally by Alexandrova, Birch, and Boldyrev.7 A series of small carborane molecules containing multiple aromatic $\text{B}_3$ and $\text{B}_4$ units have also been reported by Berndt and co-workers.8–11 Pure boron clusters have been a subject of numerous previous studies.12–17 One of the most unexpected results of these studies was the prediction of planar or quasi-planar structures in bare boron clusters. In a series of recent articles18–23 we provided the first experimental and theoretical confirmation of planar boron clusters by combining photoelectron spectroscopy of size-selected anions and ab initio calculations. We analyzed the chemical bonding in planar $\text{B}_3^+–\text{B}_{15}$ neutral and anionic clusters and showed that their planarity could be understood on the basis of the multiple aromaticity ($\sigma$ and $\pi$) and antiaromaticity.

The elucidation of the chemical bonding in the bare boron clusters and the confirmation of their planar structures open opportunities to use them as new types of ligands or building blocks in chemistry. In order to do this, a boron cluster should first acquire a closed-shell electronic configuration, because open-shell systems are generally too reactive and susceptible to cluster–cluster agglomeration. The aromatic cyclopentadiene (C$_5$H$_5^-$) provides a good example. The neutral C$_5$H$_5^-$

moiety is open shell with one unpaired electron and needs to acquire one more electron to become a closed-shell anion. Indeed, the C₅H₅⁻ anion with six π electrons is very stable and is one of the most important and useful π-bonding ligands in chemistry. As discussed in our previous articles, the bare boron clusters possess multiple aromaticity and may be used as potential ligands, similar to the planar hydrocarbon aromatics such as C₅H₅⁻ or benzene. Among the boron clusters, B₃⁻, B₅²⁻, B₉⁻, B₁₀, B₁₁⁻, and B₁₂ are closed shell both σ- and π-aromatic systems and therefore represent the best candidates to be new inorganic ligands or building blocks of solids. In particular, Zhai, Kiran, Li, and Wang have demonstrated that B₁₁⁻ and B₁₂ can be viewed to be analogous to C₅H₅⁻ and benzenes, respectively. Kuznetsov and Boldyrev have predicted computationally the existence of MX₂ type salt molecules, where M = Li−Cs and X = B−Tl. Li and Jin predicted a series of MB₆ (M = Be−Ca) and MB₅ (M = Li−Cs) molecules.

However, there is no experimental evidence that such species can actually be made. In this Communication we present the first experimental observation of a Li⁺[B₅²⁻] charge-transfer salt in the gas phase and its theoretical and experimental characterization. We show that this complex indeed contains a planar aromatic B₈²⁻ anion stabilized by a Li⁺ in a C₇₁ molecule, providing the first experimental proof that planar pure boron clusters can be used as a new class of stable ligands and building blocks in chemistry.

Figure 1 shows the photoelectron spectrum of LiB₈⁻ at 193 nm (6.424 eV). Three prominent detachment bands (X, A, B) were observed. Band X represents the transition from the ground state of the LiB₈⁻ anion to the ground state of LiB₈. The VDE (vertical detachment energy), defined by the peak maximum, was measured to be 3.09 ± 0.05 eV. Since no vibrational structures were resolved, the ADE (adiabatic detachment energy) or the electron affinity of LiB₈ was evaluated from the onset of band X by drawing a straight line at the leading edge of the band and then adding the instrumental resolution to the intersection with the binding energy axis. The electron affinity thus evaluated was 2.85 ± 0.10 eV. Band A was measured to have a VDE of 4.40 eV, whereas the VDE of the relatively weak and broad band B was estimated to be ~5.7 eV. The observed VDEs are compared with ab initio calculations in Table 1.

We made a computational search for the global minimum structure of LiB₈⁻, which was found to have a Li⁺ cation coordinated to a B₉²⁻ heptagon with C₇₁ symmetry (Figure 2). Unlike the bare B₉²⁻ dianion, the central B atom was pushed slightly out of plane in LiB₈⁻ as a result of the asymmetric coordination by one Li⁺. The calculated geometries and harmonic frequencies for the C₇₁ LiB₈⁻ and low-lying alternative structures are summarized in the Supporting Information (Table S1 and Figure S1). The calculated natural atomic charges, molecular orbitals, geometrical parameters, and harmonic frequencies of the B₈²⁻ dianion are listed in Table S1. The calculated natural atomic charges, molecular orbitals, geometrical parameters, and harmonic frequencies of the B₈²⁻ dianion are listed in Table S1. The calculated natural atomic charges, molecular orbitals, geometrical parameters, and harmonic frequencies of the B₈²⁻ dianion are listed in Table S1.

![Figure 1](image1.png)

**Figure 1.** Photoelectron spectrum of LiB₈⁻ at 193 nm.

![Figure 2](image2.png)

**Figure 2.** Structure and selected molecular orbitals responsible for σ- and π-aromaticity of the C₇₁, 1A₁ global minimum structure of LiB₈⁻.

<table>
<thead>
<tr>
<th>Obsd features</th>
<th>Exptl VDE (eV)</th>
<th>Molecular orbital</th>
<th>ROVGF/6-311+G(2df)</th>
<th>TD B3LYP/6-311+G(2df)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>3.09 ± 0.05</td>
<td>3e₁</td>
<td>3.39 (0.90)</td>
<td>3.27</td>
</tr>
<tr>
<td>A</td>
<td>4.40 ± 0.04</td>
<td>2e₁</td>
<td>4.83 (0.90)</td>
<td>4.66</td>
</tr>
<tr>
<td>B</td>
<td>5.7 ± 0.1</td>
<td>2a₁</td>
<td>5.87 (0.87)</td>
<td>5.58</td>
</tr>
</tbody>
</table>

* Numbers in parentheses represent pole strengths.

The initial search for the global minima of LiB₈⁻ and vibrational frequency calculations were performed using analytical gradients with polarized split-valence basis sets (6-311+G*) and the hybrid method, known as B3LYP. Vertical electron detachment energies were calculated using the time-dependent density functional methods TD-B3LYP/6-311+G(2df) and the outer-valence Green-function method ROVGF/6-311+G(2df). Molecular orbitals were calculated at the RHF/6-311+G* level of theory. B3LYP, TD-B3LYP, and ROVGF calculations were performed using Gaussian 98 and Gaussian 03. Molecular orbitals were made using MOLDEN3.4 program.

The experiment was carried out using a magnetic-bottle time-of-flight photoelectron apparatus equipped with a laser vaporization supersonic cluster source. Various Bₙ⁻ and LiBₙ⁻ clusters were produced from the cluster source, and were analyzed using a time-of-flight mass spectrometer. The LiB₈⁻ anions with a mass/charge ratio of 87 were selected and decelerated before being photodetached. The use of ¹⁰B isotope-enriched boron greatly simplified the mass analysis and allowed a clean mass selection. An ArF excimer laser at 193 nm (6.424 eV) was used as the detachment photon source. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. Photoelectron spectra were calibrated using the known spectrum of Rh⁻, and the resolution of the apparatus was ΔEk/Ek ~ 2.5%, that is, ~25 meV for 1 eV electrons.

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Supporting Information Available: Calculated molecular properties of the LiB₈⁻ anion, alternative structures of LiB₈⁻, and the full set of molecular orbitals of LiB₈⁻. This material is available free of charge via the Internet at http://pubs.acs.org.

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