Bridging $\eta^2$-BO in $B_2(BO)_3^-$ and $B_3(BO)_3^-$ Clusters: Boronyl Analogs of Boranes

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Anion photoelectron spectroscopy and theoretical calculations are combined to probe the structures and chemical bonding of two boron-rich oxide clusters, $B_2O_3^-$ and $B_3O_3^-$, which are shown to be appropriately formulated as $B_2(BO)_2^-$ and $B_3(BO)_3^-$, respectively. The anion clusters are found to each possess a bridging $\eta^2$-BO group, as well as two terminal BO groups and are analogs of $B_2H_3^-$ and $B_3H_3^-$.

The structure and bonding of boranes and their derivatives are fascinating in chemistry due to the electron deficiency of boron that gives rise to multicenter chemical bonds.[1] The concept of three-center two-electron (3c–2e) bonds involving a bridging hydrogen represents a cornerstone in modern chemical bonding theory beyond the classical Lewis electron-pair description.[1,2] The $B_2H_3$ and $B_3H_3$ molecules and their anions are among the smallest boranes that possess a 3c–2e BHB bond.

Although a number of theoretical studies have been devoted to these species,[3–5] they have remained elusive experimentally.[6] Herein we report the observation and characterization of two boron boronyl clusters, $B_2O_3^-$ [i.e. $B_2(BO)_2^-$] and $B_3O_3^-$ [i.e. $B_3(BO)_3^-$]. Using anion photoelectron spectroscopy (PES) and ab initio calculations, we show that $B_2O_3^-$ and $B_3O_3^-$, each feature a bridging ($\eta^2$) and two terminal boronyl (BO) groups bonded to a $B_2$ and $B_3$ unit, which are exact analogs of $B_2H_3^-$ and $B_3H_3^-$, respectively. Boronyl as a monovalent ligand is known[7] and has been observed in a number of BO-containing clusters and compounds.[8,9] Bridging BO has been hinted to in recent theoretical calculations of some small boron oxide clusters,[10] but it has not been characterized experimentally. The current study provides further examples of the isolobal analogy between boronyl and H and between boron-rich oxide clusters and boranes.

The $B_2O_3^-$ and $B_3O_3^-$ clusters were produced in a laser vaporization supersonic cluster source and mass-selected for photodetachment PES experiment.[11] The photoelectron spectra are shown in Figure 1 at 193 and 157 nm. Both clusters are found to possess extremely high electron binding energies. The measured adiabatic (ADEs) and vertical (VDEs) detachment energies are given in Table 1, where they are also compared with theoretical data (vide infra). The ground-state band X of $B_2O_3^-$ (VDE: 4.34 eV) exhibits a well-resolved vibrational progression with a spacing of 1980 cm$^{-1}$, whose 0→0 transition defines the electron affinity of the $B_2O_3$ neutral cluster (4.34 ± 0.03 eV). The next detachment channel (band A) is located at 6.33 eV, separated from band X by ~2 eV. The photoelectron spectra of $B_3O_3^-$ (Figure 1, right column) are more congested. Four relatively broad bands (X, A, B, C) are observed between 4 and 6.5 eV binding energies. The VDE of the ground-state transition for $B_3O_3^-$ measured from the peak maximum of band X is 4.45 eV, whereas the electron affinity of the $B_3O_3$ neutral cluster is estimated from the reasonably well-defined onset of band X to be 4.22 ± 0.03 eV. Bands A and B are closely spaced and their relative intensities exhibit strong...

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Table 1. Experimental adiabatic (ADEs) and vertical (VDEs) detachment energies for \( \text{B}_5\text{O}_3^- \) and \( \text{B}_6\text{O}_3^- \), compared with theoretical values. All energies are given in eV.

<table>
<thead>
<tr>
<th>Species</th>
<th>Feature</th>
<th>ADE [expt](^{[a]})</th>
<th>VDE [expt](^{[a]})</th>
<th>Channel</th>
<th>ADE [theor]</th>
<th>VDE [theor](^{[c]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}_5\text{O}_3^- )</td>
<td>X</td>
<td>4.34 (3)(^{[b]})</td>
<td>4.34 (3)</td>
<td>( ^1\text{B}_v \rightarrow ^1\text{A}_1 )</td>
<td>4.27</td>
<td>4.35</td>
</tr>
<tr>
<td>A</td>
<td>6.33 (3)</td>
<td>( ^2\text{A}_1 \rightarrow ^1\text{A}_1 )</td>
<td>6.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{B}_6\text{O}_3^- )</td>
<td>X</td>
<td>4.22 (3)</td>
<td>4.45 (3)</td>
<td>( ^1\text{A}_v \rightarrow ^1\text{A}_1 )</td>
<td>4.05</td>
<td>4.32</td>
</tr>
<tr>
<td>A</td>
<td>5.16 (2)</td>
<td>( ^3\text{A}_v \rightarrow ^3\text{A}_1 )</td>
<td>5.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5.50 (3)</td>
<td>( ^1\text{A}_v \rightarrow ^1\text{A}_1 )</td>
<td>5.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-6.3</td>
<td>( ^1\text{A}_v \rightarrow ^1\text{A}_1 )</td>
<td>6.44</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^{[a]}\) Numbers in parentheses represent the experimental uncertainties in the last digit. \(^{[b]}\) Electron affinity of the neutral cluster. \(^{[c]}\) Detachment energies for the ground-state transition are calculated at B3LYP/aug-cc-pVTZ level.

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 photon-energy dependence. Band C around 6.3 eV is relatively weak, beyond which no PES transitions are observed. The observed PES features serve as electronic fingerprints of \( \text{B}_5\text{O}_3^- \) and \( \text{B}_6\text{O}_3^- \), facilitating structural assignments for these clusters via comparison with electronic structure calculations.

We performed initial searches for the global minima of \( \text{B}_5\text{O}_3^- \) and \( \text{B}_6\text{O}_3^- \), using the gradient embedded genetic algorithm (GEGA\(^{[12]}\)) at the B3LYP/3-21G level of theory. The low-lying structures of \( \text{B}_5\text{O}_3^- \) (1–4) and \( \text{B}_6\text{O}_3^- \) (9–13) and their neutrals (5–8 and 14–18), as shown in Figures S1 and S2 in the Supporting Information, were then re-optimized at the B3LYP level\(^{[13, 14]}\) using the augmented Dunning’s all-electron basis set (aug-cc-pVTZ).\(^{[15]}\) Their relative energies were further evaluated using the coupled-cluster CCSD(T)\(^{[16]}\) method at the B3LYP geometric

![Figure 2](image)

**Figure 2.** Optimized cluster structures for \( \text{B}_5(\text{BO})_3^- \) (1), \( \text{B}_6(\text{BO})_3^- \) (9), \( \text{B}_5\text{H}_3^- \) (19), and \( \text{B}_6\text{H}_3^- \) (20) at the B3LYP/aug-cc-pVTZ level. Bond distances are shown in \( \text{Å} \).
and 0.10 eV for 11 versus –0.7 eV for experiment; see Table S2, Supporting Information), despite the fact that they are predicted to be slightly lower in energy than 9 at both B3LYP and CCSD(T) levels. Overall, the calculated VDEs for structure 9 best fit the experimental data (Table 1). Hence, structure 9 with C_s (3A^2) symmetry is assigned to the true global minimum for B_2O_3, considering the energetic uncertainty of the computational methods.

Both B_2(BO)_3^+ (1) and B_3(BO)_3^+ (9) contain one \( \eta^2 \)-BO bridge bonded to the B_2 or B_3 core, respectively, reminiscent of the BHB 3c–2e bond (\( \tau \) bond) in boranes, or more specifically those in C_2s B_2H_3^- (19,4) and C_3s B_3H_3^- (20,5). The structures of 1 and 9 are dictated by the BO groups and they have little structural resemblance to the corresponding bare B_2^- and B_3^- clusters.(19,20) To understand the chemical bonding in these clusters, we performed adaptive natural density partitioning (AdNDP) analyses for B_2(BO)_3^+ (1) and B_3(BO)_3^+ (14).(20) As an extension of natural bond orbital (NBO) analysis, AdNDP represents the electronic structure in terms of \( n \)–center two-electron (\( n \text{c–} \text{2e} \)) bonds, where the values of \( n \) range from one to the total number of atoms in the cluster. AdNDP thus recovers the classical Lewis bonding elements (lone pairs and \( 2 \text{c–} \text{2e} \) bonds), and the delocalized \( n \text{c–} \text{2e} \) bonds as well. The AdNDP results for B_2(BO)_3^+ (1) are shown in Figure 3. Of the 34 valence electrons, 24 are localized in the three BO groups (three 1c–2e O 2s lone-pairs and three sets of B≡O triple bonds) and six are responsible for three 2c–2e B–B single bonds. The distances for the B≡O triple and B–B single bonds (1 and 9; Figure 2), –1.22 and –1.62 Å, respectively, are typical in boron oxide clusters,(18,19) and the structural and chemical integrity of the \( \eta^1 \)-BO and \( \eta^2 \)-BO groups is well maintained relative to the gas-phase BO radical.(17,21) The remaining four electrons in 1 are delocalized as one 3c–2e \( \pi \) bond and one bridging 3c–2e \( \eta^2 \)-bond, respectively, the latter of which is an analog of the 3c–2e BHB bond in boranes. According to the \((4n+2)\) Hückel rule the delocalized 3c–2e \( \pi \) and \( \alpha \) bonds render double (\( \pi \)) and \( \alpha \) aromaticity for B_2(BO)_3^+ (1), demonstrating the bonding capabilities of the \( \eta^2 \)-BO bridge as both a \( \alpha \) radical and a \( \pi \) radical. A similar \( \pi \) system does not exist in C_2s B_2H_3^- (19).

The structure of B_3(BO)_3^- (9) consists of a B_3 triangle with two terminal BO groups and a bridge BO group, which is analogous to that of B_3H_3^- (20), as shown in Figure 2. The structure of neutral B_3(BO)_3 (14) is similar to that of 9. Because the AdNDP method can currently only be applied to closed-shell systems, we focus on the neutral B_3(BO)_3 (14) cluster in our chemical bonding analysis. The bonding in the three B≡O groups in B_3(BO)_3 (14) is identical to that in B_2(BO)_3^+ (1), as can be readily recognized in Figure 4. Among the remaining six pairs of electrons, three are responsible for the 2c–2e B–B \( \alpha \) bond between the terminal B≡O and the B_3 core and a 2c–2e B–B \( \alpha \) bond within the B_3 core. The remaining three pairs of electrons are delocalized: one 3c–2e \( \alpha \) bond between the...
B≡O bridge and the B$_2$ core, one 3c–2e σ bond over the B$_3$
core, and one 4c–2e π bond over the B$_2$ core and the B atom
of the B≡O bridge. The 4c–2e π bond further shows the π
radical characteristics of the n$_p$-BO bridge beyond that of a σ
radical.

Boronol chemistry to date has been limited to BO terminal
bonding.[8,9] The observation of the n$_p$-BO bridge in B$_2$(BO)$_3$
(1) and B$_2$(BO)$_7$ (9) thus further establishes the isolobal analo-
gy between boron-rich oxide clusters and boranes.[9,10] Indeed,
1 and 9 represent the exact onset of a bridging n$_p$-BO group
in the B$_2$(BO)$_{10}$ and B$_2$(BO)$_{18}$ clusters with increasing BO con-
tent, where the competition between bridging and terminal
BO groups is intriguing and a single extra charge (anion versus
neutral) is capable of changing their global minimum struc-
tures. We found that the potential energy surfaces of B$_2$(BO)$_{10}$
and B$_2$(BO)$_{18}$ are similar to those of their borane analogs.[3–5]
Interestingly, the bonding and structures of 1 and 9 are rele-
vant to the recently synthesized boron compounds.[22] For example,
the double (π and σ) aromaticity in 1 imposes significant struc-
tural stabilization with B–B distance in its B$_2$ core reaching as
short as 1.453 Å despite the fact that the localized 2c–2e B–B
bond order is one, which is close to that of B≡B triple bond
(1.46 Å)[9b] and similar to the short B–B distances in aromatic
boron compounds.[22b] It is expected that the boron-rich oxide
clusters will be a fertile ground to discover new boronol spe-
cies with novel structures and bonding.

**Experimental Section**

The experiment was carried out using a magnetic-bottle PES ap-
ratus equipped with a laser vaporization cluster source.[11] Briefly,
B$_n$O$_{m-}$ clusters were produced by laser vaporization of a target
made of enriched $^{10}$B isotope (99.75 %) in the presence of a helium
assisted gas with novel structures and bonding.

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center bonds · photoelectron spectroscopy

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