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Bridging η^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, $B_5O_3^-$ and $B_6O_3^-$, which are shown to be appropriately formulated as $B_2(BO)_3^-$ and $B_3(BO)_3^-$, respectively. The anion clusters are found to each

possess a bridging η^2 -BO group, as well as two terminal BO groups and are analogs of $B_2H_3^-$ and $B_3H_3^-$. This finding advances the boronyl chemistry and helps establish the isolobal analogy between boron-rich oxide clusters and boranes.

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.^[3,6] The $B_2H_3^-$ anion was observed in the gas phase and its reactivities studied, but its structure was not characterized.^[3] A preliminary claim of B_3H_3 was later disputed to be more properly classed as “borohydrates”, which contain boron, hydrogen, and oxygen.^[6] Herein we report the observation and characterization of two boron boronyl clusters, $B_5O_3^-$ [i.e. $B_2(BO)_3^-$] and $B_6O_3^-$ [i.e. $B_3(BO)_3^-$]. Using anion photoelectron spectroscopy (PES) and ab initio calculations, we show that $B_5O_3^-$ and $B_6O_3^-$, each feature a bridging (η^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 σ 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 $B_5O_3^-$ and $B_6O_3^-$ 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

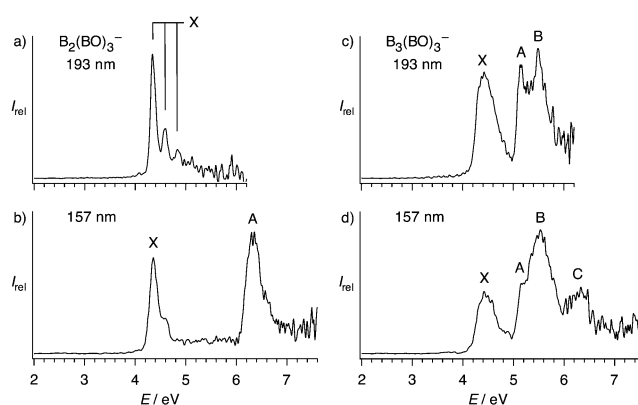


Figure 1. Photoelectron spectra of $B_5O_3^-$ (left column) and $B_6O_3^-$ (right column). The spectra are taken at 193 nm (6.424 eV) and 157 nm (7.866 eV).

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 $B_5O_3^-$ (VDE: 4.34 eV) exhibits a well-resolved vibrational progression with a spacing of $1980 \pm 50 \text{ cm}^{-1}$, whose $0 \leftarrow 0$ transition defines the electron affinity of the B_5O_3 neutral cluster ($4.34 \pm 0.03 \text{ eV}$). The next detachment channel (band A) is located at 6.33 eV, separated from band X by $\sim 2 \text{ eV}$. The photoelectron spectra of $B_6O_3^-$ (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 $B_6O_3^-$ measured from the peak maximum of band X is 4.45 eV, whereas the electron affinity of the B_6O_3 neutral cluster is estimated from the reasonably well-defined onset of band X to be $4.22 \pm 0.03 \text{ eV}$. 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 $B_5O_3^-$ and $B_6O_3^-$, compared with theoretical values. All energies are given in eV.						
Species	Feature	ADE [exptl] ^[a,b]	VDE [exptl] ^[a]	Channel	ADE [theor]	VDE [theor] ^[c]
$B_5O_3^-$	X	4.34 (3) ^[d]	4.34 (3)	${}^2B_1 \leftarrow {}^1A_1$	4.27	4.35
	A		6.33 (3)	${}^2A_1 \leftarrow {}^1A_1$		6.28
$B_6O_3^-$	X	4.22 (3)	4.45 (3)	${}^1A' \leftarrow {}^2A'$	4.05	4.32
	A		5.16 (2)	${}^3A'' \leftarrow {}^2A'$		5.23
	B		5.50 (3)	${}^3A' \leftarrow {}^2A'$		5.24
	C		~6.3	${}^1A'' \leftarrow {}^2A'$		5.69
				${}^1A' \leftarrow {}^2A'$		6.44

[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, whereas those for the excited states are at the time-dependent DFT level. [d] Ground-state vibrational frequency for the B_5O_3 neutral cluster is measured to be $1980 \pm 50 \text{ cm}^{-1}$ (Figure 1 a).

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 $B_5O_3^-$ and $B_6O_3^-$, facilitating structural assignments for these clusters via comparison with electronic structure calculations.

We performed initial searches for the global minima of $B_5O_3^-$ and $B_6O_3^-$, using the gradient embedded genetic algorithm (GEGA)^[12] at the B3LYP/3-21G level of theory. The low-lying structures of $B_5O_3^-$ (1–4) and $B_6O_3^-$ (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 geo-

metries. The $B_5O_3^-$ (1) and $B_6O_3^-$ (9) isomers (Figure 2) are among the lowest-lying anion structures at all levels of theory.

The global minimum (isomer 1) of $B_5O_3^-$ has C_{2v} (1A_1) symmetry,^[17] closely followed by isomers 2 and 3 (Figure S1, Supporting Information). Isomer 4, which consists of a B_3 triangle with two terminal BO units and a bridging O atom is 0.71 eV higher in energy. However, this structure becomes the global minimum in neutral B_5O_3 , in agreement with a previous study,^[10a] whereas the C_{2v} structure corresponding to the global minimum of the anion is 0.26 eV higher in energy (Figure S1, Supporting Information). The calculated VDEs for the top four anionic isomers are given in Table S1, Supporting Information. The ground-state VDE was calculated at B3LYP/aug-cc-pVTZ level as the energy difference between the anionic ground state and the neutral cluster at the anion geometry, whereas the higher VDEs were obtained using the time-dependent DFT procedure.^[18] Comparison of the computational data with the PES results rules out the low-lying isomers 3 and 4. Isomer 2 with C_s symmetry is only 0.01 eV higher in energy than the global minimum C_{2v} isomer at CCSD(T) level, and it has very similar structural parameters as the global minimum C_{2v} isomer and gives very similar computed VDEs as well. The structural distortion may be a computational artifact of the B3LYP functional.^[17] As shown in Table 1, the computational results for the global minimum structure 1 are in excellent agreement with the experimental data. The HOMO of $B_5O_3^-$ involves π bonding of the central B_3 unit with relatively strong antibonding interactions with the O atom on the bridging BO unit (Figure S3, Supporting Information). The calculated symmetric stretching frequencies for the corresponding neutral B_5O_3 cluster (isomer 5) are 1917 cm^{-1} (for the bridging $B=O$) and 2016 cm^{-1} (for the terminal $B=O$) at B3LYP/aug-cc-pVTZ level. The mode involving the bridging $B=O$ is expected to be active in photodetachment and the observed frequency ($1980 \pm 50 \text{ cm}^{-1}$) is in reasonable agreement with the calculated result. The excellent agreement between the theoretical results and the PES data provides considerable credence for the C_{2v} global minimum structure of $B_5O_3^-$ (1).

The low-lying structures for $B_6O_3^-$ (9–13) and B_6O_3 (14–18) are shown in Figure S2. Isomers 9–11 are nearly degenerate and are competing for the global minimum. In the neutral cluster, isomer 18 is the global minimum, while the corresponding anion (13) is 1.08 eV higher in energy than isomer 9. A recent computational study by Tai and Nguyen^[10b] located the majority of these anion and neutral structures (10–14 and 16–18). In addition, they also studied the D_{3h} $B_3(BO)_3^{2-}$ dianion and compared it to $B_3H_3^{2-}$. However, the $B_6O_3^-$ (9) isomer (Figure 2) was not reported by Tai and Nguyen.^[10b] As shown in Table S2, Supporting Information, isomers 12 and 13 can be ruled out on the bases of the energetics and the disagreement of the computed VDEs for these isomers with the experimental PES pattern. On the other hand, both isomers 10 and 11 seriously underestimate the observed X–A energy gap (0.24 eV for 10

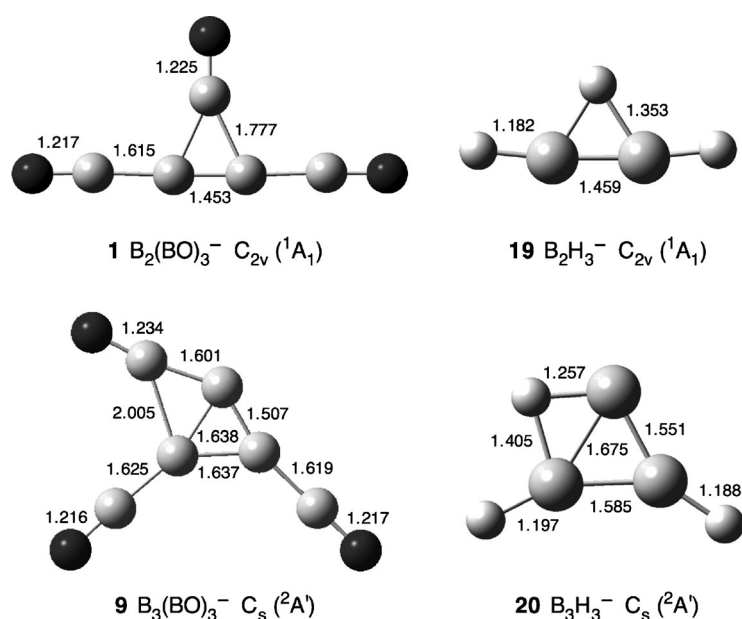


Figure 2. Optimized cluster structures for $B_2(BO)_3^-$ (1), $B_3(BO)_3^-$ (9), $B_2H_3^-$ (19), and $B_3H_3^-$ (20) at the B3LYP/aug-cc-pVTZ level. Bond distances are shown in Å.

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 ($^2A'$) symmetry is assigned to the true global minimum for $B_6O_3^-$, considering the energetic uncertainty of the computational methods.

Both $B_2(BO)_3^-$ (**1**) and $B_3(BO)_3^-$ (**9**) contain one η^2 -BO bridge bonded to the B_2 or B_3 core, respectively, reminiscent of the BHB $3c-2e$ bond (τ bond) in boranes, or more specifically those in C_{2v} $B_2H_3^-$ (**19**)^[3,4] and C_s $B_3H_3^-$ (**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_5^- and B_6^- clusters.^[19] 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 ($nc-2e$) 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 $2c-2e$ bonds), and the delocalized $nc-2e$ bonds as well. The AdNDP results for $B_2(BO)_3^-$ (**1**) are shown in Figure 3. Of the 34 valence

Figure 2), ~ 1.22 and ~ 1.62 Å, respectively, are typical in boron oxide clusters,^[8,9] and the structural and chemical integrity of the η^1 -BO and η^2 -BO groups is well maintained relative to the gas-phase BO radical.^[7,21] The remaining four electrons in **1** are delocalized as one $3c-2e$ π bond and one bridging $3c-2e$ η^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 $3c-2e$ π and σ bonds render double (π and σ) aromaticity for $B_2(BO)_3^-$ (**1**), demonstrating the bonding capabilities of the η^2 -BO bridge as both a σ radical and a π radical. A similar π system does not exist in C_{2v} $B_2H_3^-$ (**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 $B\equiv O$ 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 σ bond between the terminal $B\equiv O$ and the B_3 core and a $2c-2e$ B–B σ bond within the B_3 core. The remaining three pairs of electrons are delocalized: one $3c-2e$ σ bond between the

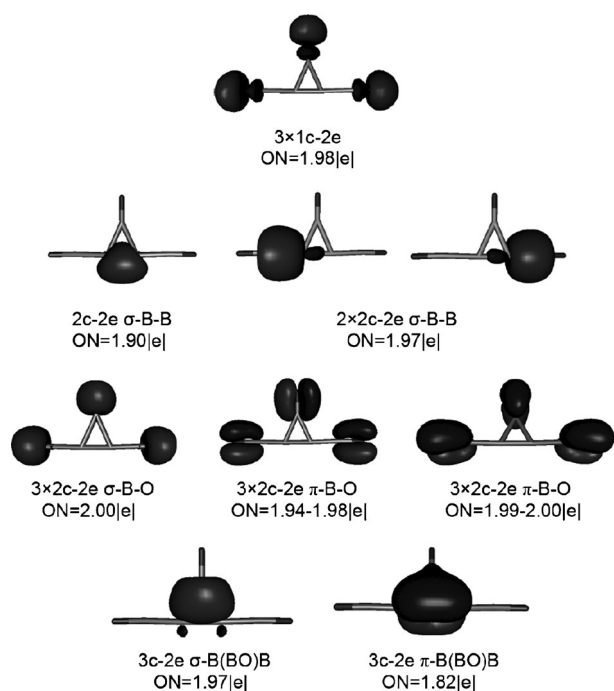


Figure 3. AdNDP bonding analysis of $B_2(BO)_3^-$ (**1**) at the B3LYP/6-31G(d) level. Occupation numbers (ONs) are indicated for all bonds, which are very close to the ideal value of $2.00 |e|$.

electrons, 24 are localized in the three BO groups (three $1c-2e$ O 2s lone-pairs and three sets of $B\equiv O$ triple bonds) and six are responsible for three $2c-2e$ B–B single bonds. The distances for the $B\equiv O$ triple and B–B single bonds (**1** and **9**;

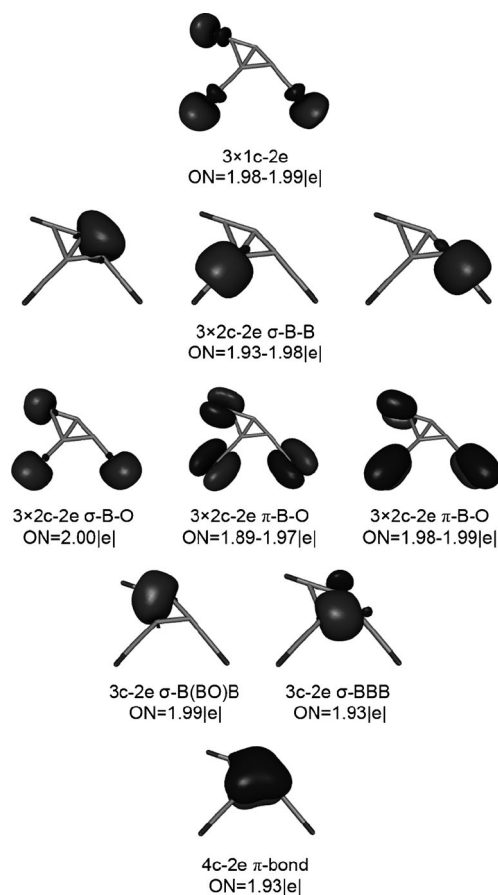


Figure 4. AdNDP bonding analysis of $B_3(BO)_3$ (**14**) at the B3LYP/6-31G(d) level. Occupation numbers (ONs) are indicated for all bonds, which are very close to the ideal value of $2.00 |e|$.

B≡O bridge and the B₃ core, one 3c–2e σ bond over the B₃ core, and one 4c–2e π bond over the B₃ core and the B atom of the B≡O bridge. The 4c–2e π bond further shows the π radical characteristics of the η²-BO bridge beyond that of a σ radical.

Boronyl chemistry to date has been limited to BO terminal bonding.^[8,9] The observation of the η²-BO bridge in B₂(BO)₃[−] (**1**) and B₃(BO)₃[−] (**9**) thus further establishes the isolobal analogy between boron-rich oxide clusters and boranes.^[7,9] Indeed, **1** and **9** represent the exact onset of a bridging η²-BO group in the B₂(BO)_n[−] and B₃(BO)_n[−] clusters with increasing BO content, 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 structures. We found that the potential energy surfaces of B₂(BO)₃[−] and B₃(BO)₃[−] are similar to those of their borane analogs.^[3–5] Interestingly, the bonding and structures of **1** and **9** are relevant to the recently synthesized boron compounds.^[22] For example, the double (π and σ) aromaticity in **1** imposes significant structural stabilization with B–B distance in its B₂ 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 boronyl species with novel structures and bonding.

Experimental Section

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source.^[11] Briefly, B_nO_m[−] clusters were produced by laser vaporization of a target made of enriched ¹⁰B isotope (99.75%) in the presence of a helium carrier gas seeded with 0.01% O₂ and analyzed using a time-of-flight mass spectrometer. The B₃O₃[−] and B₆O₃[−] species were each mass-selected and decelerated before being photodetached at two photon energies: 193 nm (6.424 eV) and 157 nm (7.866 eV). Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectrum of Au[−], and the energy resolution of the apparatus was ΔE_k/E_k ≈ 2.5%, that is, ~25 meV for 1 eV electrons.

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Keywords: aromaticity · boron · cluster compounds · multi-center bonds · photoelectron spectroscopy

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