BO\textsuperscript{−} is isoelectronic with CN\textsuperscript{−}.\textsuperscript{1} However, in comparison to CN\textsuperscript{−}, which is an important ligand in inorganic and biomolecules, the chemistry of BO\textsuperscript{−} is relatively unknown. The electron affinity (EA) of BO (2.51 eV)\textsuperscript{2,}\textsuperscript{3} is much smaller than that of CN (3.86 eV),\textsuperscript{4} which may explain the fact that CN\textsuperscript{−} is a stable anion in solution, but BO\textsuperscript{−} is not. However, the electronic structure and bond strength of BO\textsuperscript{−} are similar to those of CN\textsuperscript{−}, suggesting that it may be a robust chemical unit and can retain its structural integrity in chemical compounds. In a recent study, we indeed found that BO behaves like a monovalent structural unit in its bonding to Au in Au\textsubscript{n}BO\textsuperscript{−} (n = 1–3) clusters.\textsuperscript{5} Theoretical calculations also suggested that carbon boronyls (CBO\textsubscript{n}) (n = 3–7) are stable species on the potential-energy surfaces.\textsuperscript{6} Here we report a photoelectron spectroscopy (PES) and theoretical study on two boron oxide clusters, B\textsubscript{2}O\textsubscript{5}− and B\textsubscript{3}O\textsubscript{4}−, which are shown to possess a D\textsubscript{∞h} (\(\Sigma^\prime\)) linear and D\textsubscript{3h} (\(\Sigma^\prime\prime\)) triangular structure, respectively, and can be viewed as two and three boronyl groups bonded to a single B atom.

Bulk boron oxide (B\textsubscript{2}O\textsubscript{3}) is a highly stable glassy material, and the combustion of boron and boranes has received persistent interest over the past 50 years, primarily aimed at the development of energetic boron-based propellants.\textsuperscript{7} However, the electronic and structural properties of boron oxide clusters remain poorly understood.\textsuperscript{8} One of our research goals is to remedy this deficiency. Following our previous work on BO\textsuperscript{−} and BO\textsubscript{2}−,\textsuperscript{3} in this Communication we focus on B\textsubscript{3}O\textsubscript{2}− and B\textsubscript{4}O\textsubscript{3}−.

The experiment was done using a magnetic-potential-BES apparatus equipped with a laser vaporization cluster source (see Supporting Information). A \(^{10}\text{B}\)-enriched target was used with a He carrier gas seeded with 0.01% O\textsubscript{2}, producing B\textsubscript{2}O\textsubscript{5}− and B\textsubscript{3}O\textsubscript{4}− clusters with a variety of compositions. B\textsubscript{2}O\textsubscript{5}− and B\textsubscript{3}O\textsubscript{4}− were mass-selected for photodetachment. Figure 1 shows the PES spectra at several photon energies. The spectra for both species are similar and appear unusually simple, each showing only one vibrationally resolved band even at the highest detachment photon energy (6.424 eV).

We did calculations at the B3LYP level with the augmented Dunning’s all-electron basis set (aug-cc-pVTZ) (see Supporting Information). Our structural searches for B\textsubscript{2}O\textsubscript{5}− and B\textsubscript{3}O\textsubscript{4}− started from the well-characterized bare D\textsubscript{3h} B\textsubscript{3}− and D\textsubscript{3h} B\textsubscript{4}− \(\text{O}^\text{−3}\) O atoms were attached terminally to the bare clusters, but optimization led to a linear B(BO)\textsubscript{2}− (D\textsubscript{∞h}, \(\Sigma^\prime\)) and a triangular B(BO)\textsubscript{3}− (D\textsubscript{3h}, \(\Sigma^\prime\prime\)) structure (Figure 2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
species & transition & ADE & VDE \\
\hline
B(BO)\textsubscript{2}− & \(2\Sigma^\prime \rightarrow 2\Pi_u\) & 2.94 ± 0.02 & 2.94 ± 0.02 \\
& \(2 \Sigma^\prime \rightarrow 1 \Pi_u\) & 3.64 ± 0.03 & 3.64 ± 0.03 \\
B(BO)\textsubscript{3}− & \(2 \Sigma^\prime \rightarrow 1 \Lambda_u\) & 2.94 ± 0.02 & 2.94 ± 0.02 \\
& \(2 \Sigma^\prime \rightarrow 1 \Lambda_u\) & 3.64 ± 0.03 & 3.64 ± 0.03 \\
\hline
\end{tabular}
\caption{Experimental Electron Detachment Energies (ADE and VDE, in eV) of B\textsubscript{2}O\textsubscript{5}− and B\textsubscript{3}O\textsubscript{4}− and Vibrational Frequencies (in cm\textsuperscript{−1}), Compared with Theoretical Results (in Brackets)}
\end{table}

Figure 1. Photoelectron spectra of B\textsubscript{2}O\textsubscript{5}− at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV) and B\textsubscript{3}O\textsubscript{4}− at (c) 266 and (d) 193 nm. Inset in panel b shows the 355 nm (3.496 eV) spectrum of B\textsubscript{2}O\textsubscript{5}−. Vertical bars represent the resolved vibrational structures.

\textsuperscript{1} Washington State University.
\textsuperscript{2} Pacific Northwest National Laboratory.
\textsuperscript{3} Xinzhou Teachers’ University.
PES spectra. The calculated B changes, the B mode. Overall, the theoretical predictions are in excellent agreement with the experiment, lending considerable credence to the theoretical prediction of its high VDE.

The current finding of boron boronyl clusters may have several important implications. First, it may be generalized and used as a guide to predict the structures and bonding of a variety of boron-rich boron oxide clusters. Other metal and nonmetal boronyl clusters and compounds may also be viable targets to pursue. Second, certain highly stable boronyl-containing boron oxide clusters may be intermediates in the combustion of boron and boranes and are relevant to the mechanistic understanding of these critical combustion processes at the molecular level. Finally, the current finding suggests an interesting link between boron oxides and boranes, on the basis of which a rich boron oxide chemistry analogous to that of boranes may be developed.

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Supporting Information Available: Experimental and computational details, calculated ground state molecular properties, alternative optimized structures, and molecular orbital pictures of the ground state anions. This material is available free of charge via the Internet at http://pubs.acs.org.

References

10. Neutral B(BO) possesses a 3Πg electronic state (Table S1), which is expected to exhibit a Renner–Teller effect, preventing us from resolving a simple B progression.

Figure 2. Optimized structures for (a) B3O2+ (D∞h, 2Σ+) and B4O3 (D4h, 2Πg) and (b) B4O3+ (D∞h, 2Σ+) and B3O3 (D∞h, 2Πg). Bond lengths are in Å and those of the neutrals are given in parentheses.

Figure 3. Selected molecular orbitals primarily responsible for bonding between the BO groups and the central B atom in (a) B3O2 and (b) B4O3.