J|A|C|S
COMMUNICATIONS

Boronyls as Key Structural Units in Boron Oxide Clusters: $B(BO)_2^-$ and $B(BO)_3^-$

Hua-Jin Zhai,[†,‡] Si-Dian Li,[*,§] and Lai-Sheng Wang[*,†,‡]

Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354,
Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88,
P.O. Box 999, Richland, Washington 99352, and Xinzhou Teachers' University,
Xinzhou 034000, Shanxi, People's Republic of China

Received April 14, 2007; E-mail: lisidian@yahoo.com; ls.wang@pnl.gov

BO^- is isoelectronic with CN^-.[1] However, in comparison to CN^-, which is an important ligand in inorganic and biomolecules, the chemistry of BO^- is relatively unknown. The electron affinity (EA) of BO (2.51 eV)[2,3] is much smaller than that of CN (3.86 eV),[4] which may explain the fact that CN^- is a stable anion in solution, but BO^- is not. However, the electronic structure and bond strength of BO^- are similar to those of CN^-, 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_nBO^- (n = 1−3) clusters.[5] Theoretical calculations also suggested that carbon boronyls $(CBO)_n$ (n = 3−7) are stable species on the potential-energy surfaces.[6] Here we report a photoelectron spectroscopy (PES) and theoretical study on two boron oxide clusters, $B_3O_2^-$ and $B_4O_3^-$, which are shown to possess a $D_{\infty h}$ ($^3\Sigma_g$) linear and D_{3h} ($^2A_2''$) triangular structure, respectively, and can be viewed as two and three boronyl groups bonded to a single B atom.

Bulk boron oxide (B_2O_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.[7] However, the electronic and structural properties of boron oxide clusters remain poorly understood.[8] One of our research goals is to remedy this deficiency. Following our previous work on BO^- and BO_2^-,[3] in this Communication we focus on $B_3O_2^-$ and $B_4O_3^-$.

The experiment was done using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source (see Supporting Information). A ^{10}B-enriched target was used with a He carrier gas seeded with 0.01% O_2, producing $B_xO_y^-$ clusters with a variety of compositions. $B_3O_2^-$ and $B_4O_3^-$ 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). The 0−0 transition in each species defines an accurate adiabatic detachment energy (ADE): 2.94 eV for $B_3O_2^-$ and 3.64 eV for $B_4O_3^-$ (Table 1), which also represent the EA's of the neutral clusters. The resolved vibrational frequencies are also similar: 1950 cm^{-1} for B_3O_2 and 1980 cm^{-1} for B_4O_3. The 355 nm spectrum of $B_3O_2^-$ (insert of Figure 1a) reveals a partially resolved low-frequency vibration.

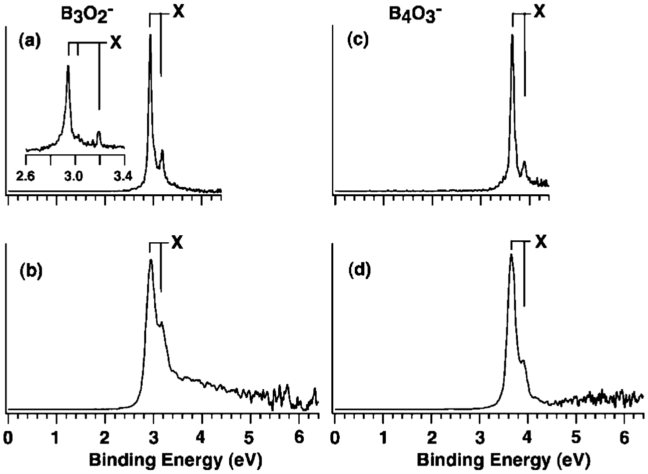

Figure 1. Photoelectron spectra of $B_3O_2^-$ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV) and $B_4O_3^-$ at (c) 266 and (d) 193 nm. Inset in panel a shows the 355 nm (3.496 eV) spectrum of $B_3O_2^-$. Vertical bars represent the resolved vibrational structures.

Table 1. Experimental Electron Detachment Energies (ADE and VDE, in eV) of $B_3O_2^-$ and $B_4O_3^-$ and Vibrational Frequencies (in cm^{-1}), Compared with Theoretical Results (in Brackets)

species	transition	ADE	VDE	vibrational frequency
$B(BO)_2^-$	$^3\Sigma_g \rightarrow {}^2\Pi_u$	2.94 ± 0.02	2.94 ± 0.02	1950 ± 40
		[3.012]	[3.074]	[1969]
$B(BO)_3^-$	$^2A_2'' \rightarrow {}^1A_1'$	3.64 ± 0.03	3.64 ± 0.03	1980 ± 60
		[3.749]	[3.815]	[1992]

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 $B_3O_2^-$ and $B_4O_3^-$ started from the well-characterized bare D_{3h} B_3^- and D_{2h} B_4^-.[9] O atoms were attached terminally to the bare clusters, but optimization led to a linear $B(BO)_2^-$ ($D_{\infty h}$, $^3\Sigma_g$) and a triangular $B(BO)_3^-$ (D_{3h}, $^2A_2''$) (Figure 2). Similar structures were obtained for the corresponding neutrals with very little structural change. The calculated total energies and vibrational frequencies for the two $B(BO)_n^-$ species and their neutrals are given in Table S1. A variety of alternative structures were also optimized and summarized in Figures S1−S4. However, all the other structures are substantially higher in energy, suggesting that the boronyl-containing $B(BO)_2^-$ ($D_{\infty h}$) and $B(BO)_3^-$ (D_{3h}) are extremely stable clusters.

To compare with the PES results, we further calculated the ground and excited-state electron detachment energies. The calculated ADE and VDE values from the $D_{\infty h}$ $B(BO)_2^-$ and D_{3h} $B(BO)_3^-$ are in excellent agreement with the experimental data (Table 1). The first excited-state is predicted to be beyond 6.4 eV for both species (Table S2), consistent with the simple PES pattern (Figure 1). The calculated BO stretching frequencies for the neutral $B(BO)_2$ and $B(BO)_3$ are also in excellent agreement with the experimental

---

[†] Washington State University.
[‡] Pacific Northwest National Laboratory.
[§] Xinzhou Teachers' University.

10.1021/ja072611y CCC: $37.00 © 2007 American Chemical Society

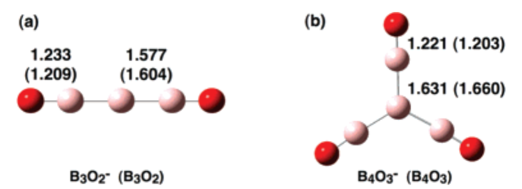

Figure 2. Optimized structures for (a) $B_3O_2^-$ ($D_{\infty h}$,$^3\Sigma_g$) and B_3O_2 ($D_{\infty h}$,$^2\Pi_u$) and (b) $B_4O_3^-$ (D_{3h}, $^2A_2''$) and B_4O_3 (D_{3h}, $^1A_1'$). Bond lengths are in Å and those of the neutrals are given in parentheses.

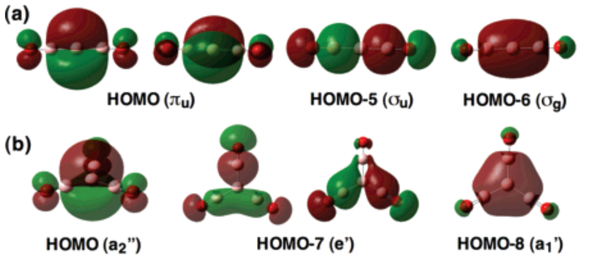

Figure 3. Selected molecular orbitals primarily responsible for bonding between the BO groups and the central B atom in (a) $B_3O_2^-$ and (b) $B_4O_3^-$.

data (Table 1). Figure 2 shows that in both species there is a slight contraction in the B−O bonds and a slight expansion in the B−B bonds from the anion to the neutral ground states, consistent with the observed B−O stretching mode. According to the structural changes, the B−B stretching mode should also be active in the PES spectra. The calculated B−B stretching frequency is 471 cm^{-1} for $B(BO)_2$ and 425 cm^{-1} for $B(BO)_3$ (Table S1). The resolution of the 266 nm spectrum of $B_4O_3^-$ (Figure 1c) was not sufficient to resolve the B−B mode. However, the 355 nm spectrum of $B_3O_2^-$ (inset of Figure 1a) did reveal a discernible feature for the B−B mode.[10] Overall, the theoretical predictions are in excellent agreement with the experiment, lending considerable credence to the identified ground-state structures for $B_3O_2^-$ and $B_4O_3^-$.

Molecular orbital (MO) analyses were performed to understand the chemical bonding of the two boron boronyl clusters (Figure S5). First, we note that the BO bond length and vibrational frequency in $B(BO)_2$ and $B(BO)_3$ are nearly identical to those in the bare BO (1.205 Å and 1935 cm^{-1}),[3,11] suggesting that indeed the BO unit can maintain its boronyl structural integrity. In Figure 3 we plot the anion MO's relevant to the BB bonding, that is, bonding of the BO unit to the central B atom. For $B_3O_2^-$ (Figure 3a), the HOMO-5 (σ_u) and HOMO-6 (σ_g) depict two B−B σ bonds, whereas the HOMO (π_u), which is half-filled ($^3\Sigma_g$), is responsible for B−B π bonding. Therefore, the BB bond order in $B(BO)_2^-$ may be considered as 1.5. Similarly, in $B(BO)_3^-$ we observe three B−B σ MO's (e′ and a_1' Figure 3b), responsible for a single B−B bond between each BO unit to the central B atom. The extra electron in the $B(BO)_3^-$ anion enters a π MO (a_2''), which is partially delocalized over all four B atoms, slightly enhancing the BB bonding in $B(BO)_3^-$ relative to $B(BO)_3$. Note that the delocalized nature of the a_2'' MO in $B(BO)_3^-$ is responsible for its extremely high electron binding energy (3.64 eV).

MO's other than those shown in Figure 3 are either O 2s lonepairs or primarily responsible for BO bonding (Figure S5), which can be clearly traced back to the corresponding MO's in BO and BO^-. Importantly, the triple bond nature of BO radical is perfectly maintained in $B(BO)_2^-$ and $B(BO)_3^-$, as also reflected from the BO bond distances (Table S1).

The highly symmetric $D_{\infty h}$ and D_{3h} structures for $B_3O_2^-$ and $B_4O_3^-$ (Figure 2) are surprising and demonstrate the role of BO as a robust structural unit. In fact, the structure and bonding in $B(BO)_n^-$ can be compared to those in BH_n^-.[12] By analogy, we anticipate that the T_d $B(BO)_4^-$ cluster would also be a highly stable species, similar to the well-known BH_4^- species. Indeed, our calculations predicted that the T_d $B(BO)_4^-$ species is a minimum on the potential-energy surface with an extremely high electron binding energy (ADE, 6.8 eV; VDE, 7.3 eV), which is unfortunately beyond our high photon energy at 193 nm (6.424 eV). We did observe the $B_5O_4^-$ species from the cluster source, but could not observe any photoelectron signals at 193 nm, consistent with 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.

Acknowledgment. This work was supported by NSF (Grant DMR-0503383) and performed at EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for DOE by Battelle. S.D.L. gratefully acknowledges financial support from the National Natural Science Foundation of China (No. 20573088).

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

(1) Pyykko, P. *Mol. Phys.* **1989**, *67*, 871.
(2) Wenthold, P. G.; Kim, J. B.; Jonas, K. L.; Lineberger, W. C. *J. Phys. Chem. A* **1997**, *101*, 4472.
(3) Zhai, H. J.; Wang, L. M.; Li, S. D.; Wang, L. S. *J. Phys. Chem. A* **2007**, *111*, 1030.
(4) Bradforth, S. E.; Kim, E. H.; Arnold, D. W.; Neumark, D. M. *J. Chem. Phys.* **1993**, *98*, 800.
(5) Zubarev, D. Yu.; Boldyrev, A. I.; Li, J.; Zhai, H. J.; Wang, L. S. *J. Phys. Chem. A* **2007**, *111*, 1648.
(6) Li, S. D.; Miao, C. Q.; Guo, J. C.; Ren, G. M. *J. Comput. Chem.* **2005**, *26*, 799.
(7) Bauer, S. H. *Chem. Rev.* **1996**, *96*, 1907.
(8) (a) Weltner, W., Jr.; Warn, J. R. W. *J. Chem. Phys.* **1962**, *37*, 292. (b) Sommer, A.; White, D.; Linevsky, M. J.; Mann, D. E. *J. Chem. Phys.* **1963**, *38*, 87. (c) Ruscic, B. M.; Curtiss, L. A.; Berkowitz, J. *J. Chem. Phys.* **1984**, *80*, 3962. (d) Doyle, R. J., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4120. (e) Hanley, L.; Anderson, S. L. *J. Chem. Phys.* **1988**, *89*, 2848. (f) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697. (g) Nemukhin, A. V.; Weinhold, F. *J. Chem. Phys.* **1993**, *98*, 1329. (h) Peiris, D.; Lapicki, A.; Anderson, S. L.; Napora, R.; Linder, D.; Page, M. *J. Phys. Chem. A* **1997**, *101*, 9935.
(9) Zhai, H. J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I.; Zakrzewski, V. G. *J. Phys. Chem. A* **2003**, *107*, 9319.
(10) Neutral $B(BO)_2$ possesses a $^2\Pi_u$ electronic state (Table S1), which is expected to exhibit a Renner−Teller effect, preventing us from resolving a simple B−B progression.
(11) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
(12) (a) Martin, J. M. L. *Chem. Phys. Lett.* **1997**, *273*, 98. (b) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053.

JA072611Y