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Inorganic Chemistry Communication

Molecular Wheel B_8^{2-} as a New Inorganic Ligand. Photoelectron Spectroscopy and ab Initio Characterization of LiB_8^-

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The bare B_8 cluster was previously reported to be a D_{7h} molecular wheel with a triplet group state. The B_8^{2-} dianion was predicted to be a closed-shell singlet and double aromatic D_{7h} molecular wheel. Here we report the experimental observation of B_8^{2-} stabilized by a Li^+ cation in LiB_8^- and its experimental characterization using photoelectron spectroscopy. Theoretical searches lead to a C_{7v} 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 B_8^{2-} unit in LiB_8^- is nearly identical to the bare 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-workers[5,6] and predicted computationally by Alexandrova, Birch, and Boldyrev.[7] A series of small carborane molecules containing multiple aromatic B_3 and 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 articles[18−23] 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 B_3−B_{15} neutral and anionic clusters and showed that their planarity could be understood on the basis of the multiple aromaticity (σ and π) 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 ($C_5H_5^-$) provides a good example. The neutral C_5H_5

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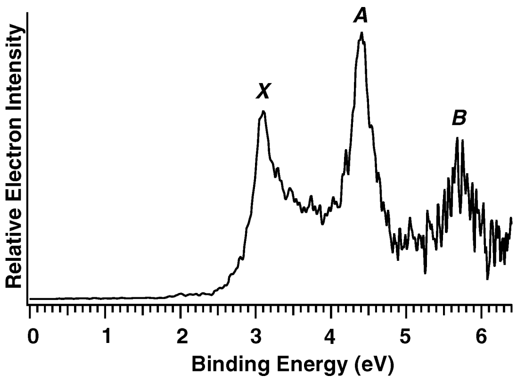

Figure 1. Photoelectron spectrum of LiB_8^- at 193 nm.

moiety is open shell with one unpaired electron and needs to acquire one more electron to become a closed-shell anion. Indeed, the $C_5H_5^-$ 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,[18−23] the bare boron clusters possess multiple aromaticity and may be used as potential ligands, similar to the planar hydrocarbon aromatics such as $C_5H_5^-$ or benzene. Among the boron clusters, B_3^-, B_8^{2-}, B_9^-, B_{10}, B_{11}^-, and B_{12} 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 B_{11}^- and B_{12} can be viewed to be analogous to $C_5H_5^-$ and benzenes, respectively.[22] Kuznetsov and Boldyrev have predicted computationally the existence of MX_3 type salt molecules, where M = Li−Cs and X = B−Tl.[24] Li and Jin predicted a series of MB_6 (M = Be−Ca)[25] and MB_5 (M = Li−Cs) molecules.[26]

However, there is no experimental evidence that such species can actually be made. In this Communication we present the first experimental observation of a $Li^+[B_8^{2-}]$ charge-transfer salt in the gas phase and its theoretical and experimental characterization. We show that this complex indeed contains a planar aromatic B_8^{2-} anion stabilized by a Li^+ in a C_{7v} 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 LiB_8^- 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 LiB_8^- anion to the ground state of LiB_8. 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 LiB_8 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.

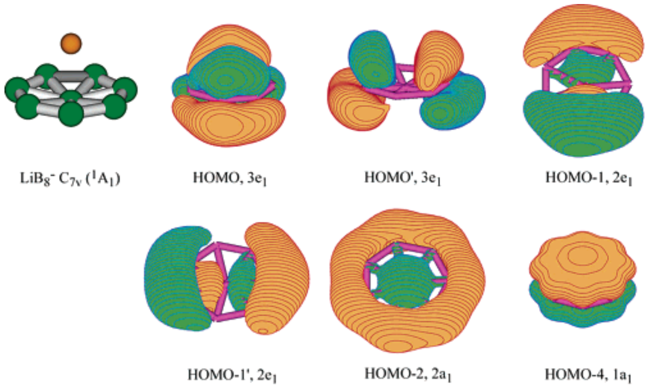

Figure 2. Structure and selected molecular orbitals responsible for σ- and π-aromaticity of the C_{7v}, $^1A_1$ global minimum structure of LiB_8^-.

Table 1. Experimental Vertical Detachment Energies (VDE) from the Photoelectron Spectrum of LiB_8^- and Comparison with Theoretical VDEs Calculated from the Global Minimum C_{7v} Structure of LiB_8^-

		theor VDE (eV)		
obsd features	exptl VDE (eV)	molecular orbital	ROVGF/ 6-311+G(2df)	TD B3LYP/ 6-311+G(2df)
X	3.09 ± 0.05	$3e_1$	3.39 (0.90)[a]	3.27
A	4.40 ± 0.04	$2e_1$	4.83 (0.90)[a]	4.66
B	5.7 ± 0.1	$2a_1$	5.87 (0.87)[a]	5.58

[a] Numbers in parentheses represent pole strengths.

We made a computational search for the global minimum structure of LiB_8^-, which was found to have a Li^+ cation coordinated to a B_8^{2-} heptagon with C_{7v} symmetry (Figure 2). Unlike the bare B_8^{2-} dianion, the central B atom was pushed slightly out of plane in LiB_8^- as a result of the asymmetric coordination by one Li^+. The calculated geometries and harmonic frequencies for the C_{7v} LiB_8^- and low-lying alternative structures are summarized in the Supporting Information (Table S1 and Figure S1). The calculated natural population of atomic charges are as follows: $Q(\mathrm{Li}) = +0.916|e|$, $Q(\mathrm{B_{central}}) = -0.008|e|$, and $Q(\mathrm{B_{peripheral}}) = -0.273|e|$, consistent with the primarily ionic bonding nature between Li^+ and the B_8^{2-} dianion. In order to verify further the identification of the global minimum structure of LiB_8^-, we compare ab initio photodetachment transitions, obtained using two theoretical methods, with the experimental observation in Table 1. The two theoretical methods give consistent VDEs, which are in good agreement with the experimental data, lending considerable credence to the C_{7v} global minimum structure for LiB_8^-.

Except for the slight out-of-plane distortion, the calculated natural atomic charges, molecular orbitals, geometrical parameters, and harmonic frequencies of the B_8^{2-} dianion in LiB_8^- show little perturbation from the Li^+ cation, indicating it is a rather robust and stable structural unit and possesses the potential to be a new ligand and building block in chemistry. Finally, it should be noted that the creation and characterization of the half-sandwich $Li^+[B_8^{2-}]$ in the current work provides an additional proof of the novel molecular wheel structure of the boron octamer and its extreme heptacoordination environment.[21]

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The initial search for the global minima of LiB_8^- and vibrational frequency calculations were performed using analytical gradients with polarized split-valence basis sets (6-311+G*)[27,28] and the hybrid method, known as B3LYP.[29-31] Vertical electron detachment energies were calculated using the time-dependent density functional methods TD-B3LYP/6-311+G(2df),[32,33] and the outer-valence Green-function method ROVGF/6-311+G(2df).[34-36] 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.[37] Molecular orbitals were made using MOLDEN3.4 program.[38]

The experiment was carried out using a magnetic-bottle time-of-flight photoelectron apparatus equipped with a laser vaporization supersonic cluster source.[39,40] Briefly, the LiB_8^- anions were produced by laser vaporization of a B/Li mixed target in the presence of a helium carrier gas. The target contained ∼30% Li in molar ratio and was 99.75% ^{10}B enriched. Various B_n^- and LiB_n^- clusters were produced from the cluster source, and were analyzed using a time-of-flight mass spectrometer. The LiB_8^- anions with a mass/charge ratio of 87 were selected and decelerated before being photodetached. The use of ^{10}B 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 $\Delta Ek/Ek \sim 2.5\%$, that is, ∼25 meV for 1 eV electrons.

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Supporting Information Available: Calculated molecular properties of the LiB_8^- anion, alternative structures of LiB_8^-, and the full set of molecular orbitals of LiB_8^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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