Manganese-centered tubular boron cluster – MnB$_{16}^-$: A new class of transition-metal molecules


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We report the observation of a manganese-centered tubular boron cluster (MnB$_{16}^-$), which is characterized by photoelectron spectroscopy and \textit{ab initio} calculations. The relatively simple pattern of the photoelectron spectrum indicates the cluster to be highly symmetric. \textit{Ab initio} calculations show that MnB$_{16}^-$ has a Mn-centered tubular structure with C$_{4v}$ symmetry due to first-order Jahn-Teller effect, while neutral MnB$_{16}$ reduces to C$_{2v}$ symmetry due to second-order Jahn-Teller effect. In MnB$_{16}^-$, two unpaired electrons are observed, one on the Mn 3d$_{z^2}$ orbital and another on the B$_{16}$ tube, making it an unusual biradical. Strong covalent bonding is found between the Mn 3d orbitals and the B$_{16}$ tube, which helps to stabilize the tubular structure. The current result suggests that there may exist a whole class of metal-stabilized tubular boron clusters. These metal-doped boron clusters provide a new bonding modality for transition metals, as well as a new avenue to design boron-based nanomaterials. \textit{Published by AIP Publishing}. [\texttt{http://dx.doi.org/10.1063/1.4946796}]

I. INTRODUCTION

Despite its electron deficiency, boron can form strong covalent bonds with almost all elements in the periodic table. In the bulk, boron forms polyhedral units to accommodate its electron deficiency with a remarkable set of allotropes, which are all superhard materials.\textsuperscript{1,2} In finite systems, boron seems to deal with its electron deficiency by forming planar or quasiplanar (2D) structures. Indeed, size-selected boron clusters (B$_n$) have been found to be 2D up to at least 25 atoms as anions\textsuperscript{3–5} or up to 15 atoms as cations.\textsuperscript{6} In the case of neutral boron clusters, direct experimental studies of their structures are challenging and the 2D–3D transition has not been experimentally established yet. Even though neutral B$_{20}$ and B$_{14}$ were suggested to have 3D structures computationally,\textsuperscript{7,8} an infrared/ultraviolet double ionization experiment failed to detect these structures.\textsuperscript{9} Recent works show that negatively charged boron clusters continued to be planar at B$_{27}^-$, B$_{30}^-$, B$_{35}^-$, and B$_{36}^-$\textsuperscript{10–13} All the 2D boron clusters consist of a peripheral boron ring featuring 2-center-2-electron (2c-2e) $\sigma$ bonds and delocalized $\sigma$ and $\pi$ bonds over the cluster plane.\textsuperscript{9–14} Very recently, 3D isomers for anionic boron clusters were observed to occur at B$_{25}^-$, B$_{39}^-$, and B$_{40}^-$\textsuperscript{15–17} which form extraordinary borospherene cage structures.

Boron-based nanotubes were proposed,\textsuperscript{18,19} following the discovery of carbon nanotubes. Tubular boron clusters have been of interest, because they could be viewed as potential embryos for boron nanotubes.\textsuperscript{7} Although a double-ring tubular structure was computationally shown to be the global minimum for neutral B$_{30}$,\textsuperscript{20} it was not experimentally confirmed.\textsuperscript{9} On the other hand, a double-ring tubular B$_{16}$ cation has been shown to compete for the global minimum,\textsuperscript{8} even though the neutral and anionic B$_{16}$ clusters were found to be planar.\textsuperscript{21}

The structures and properties of boron clusters can be tuned by doping with transition metal atoms. Following the elucidation of the bonding in the B$_9^-$ cluster, which has a D$_{5h}$ molecular wheel structure with a central boron atom,\textsuperscript{22} a design principle was advanced to replace the central boron atom to make transition metal centered boron rings (M$_n$B$_n^-$).\textsuperscript{23} A series of such aromatic borometallic molecular wheels have been produced experimentally and characterized for $n = 8–10$. Furthermore, the CoB$_{12}^-$ and RhB$_{12}^-$ clusters have been found to adopt half-sandwich-type structures in which the quasi-planar and aromatic B$_{12}$ moiety simply coordinates to the metal center.\textsuperscript{24}

Metal-doped boron clusters have been investigated computationally.\textsuperscript{25–27} Very recently, a cobalt-doped boron cluster CoB$_{16}^-$ was observed experimentally and characterized using photoelectron spectroscopy (PES) and \textit{ab initio} calculations.\textsuperscript{28} It was found to possess a Co-centered drum or tubular structure with two B$_8$ rings sandwiching the Co atom. This study has stimulated a number of questions. First, are there other metal atoms that can form similar drum structures? What is the minimum or maximum ring size that can sustain such drum structures? Are there electronic or geometric requirements or design principles for such structures?

In this article, we report a combined PES and \textit{ab initio} investigation of a Mn-doped B$_{16}$ cluster. Photoelec-
The photoelectron spectrum of MnB\textsubscript{16}– displayed well-resolved features that can be used to compare with theoretical data. \textit{Ab initio} calculations revealed a Mn-centered double-ring tubular structure distorted from D\textsubscript{4d} to C\textsubscript{4v} symmetry due to Jahn-Teller effect. The C\textsubscript{4v}, MnB\textsubscript{16}– contains two unpaired electrons, one localized on the Mn 3d\textsubscript{ff} orbitals and another de-localized on the tubular B\textsubscript{16} frame. The neutral MnB\textsubscript{16} is found to be distorted to C\textsubscript{2v}, symmetry, because of the second-order Jahn-Teller effect\textsuperscript{28} with only one unpaired Mn 3d\textsubscript{z2} electron. The Mn atom in both MnB\textsubscript{16}– and MnB\textsubscript{16} is found to engage in covalent interactions with the B\textsubscript{16} frame to stabilize the drum structure.

II. EXPERIMENTAL METHOD

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic cluster source, details of which has been described elsewhere.\textsuperscript{29} Briefly, the MnB\textsubscript{16}– cluster was produced by laser vaporization of a Bi\textsubscript{10}/Mn mixed target with a helium carrier gas seeded with 5% argon. The Bi component acted as a binder and provided Bi\textsuperscript{−} as a calibrant for the PES. Clusters formed in the nozzle were entrained in the carrier gas and underwent a supersonic expansion. Anions from the cluster beam were extracted and analyzed by a time-of-flight mass spectrometer. The MnB\textsubscript{16}– anion of interest was mass-selected and decelerated before being photodetached. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. For the current study, the 193 nm (6.424 eV) radiation from an ArF excimer laser was used. The energy resolution of the apparatus was ΔEk/Ek = 2.5%, that is, ~25 meV for 1 eV electrons.

III. THEORETICAL METHODS

The global minimum searches for MnB\textsubscript{16}– were performed using a constrained Basin-Hopping (BH) method\textsuperscript{30} in the TGMin code\textsuperscript{13} and the Coalescence Kick (CK) program,\textsuperscript{31} as well as manual structural constructions. In TGMin, scalar relativistic\textsuperscript{32–34} density functional theory (DFT) formalism with the PBE exchange-correlation functional\textsuperscript{15} was applied with double-\zeta\textsubscript{valence basis set\textsuperscript{36} via the ADF2013.01 program.\textsuperscript{37,38} In CK, the program generated a number of different trial structures in singlet, triplet, and quintet states, which followed geometry optimizations at the PBE0/3-21G\textsuperscript{39,40} level of theory in Gaussian 09.\textsuperscript{41} Low-lying isomers were further optimized at PBE and PBE0 levels of theory with triple-\zeta\textsubscript{valence plus polarization functions (TZP)}\textsuperscript{42,43} basis set via the ADF2013.01 program. Frequency calculations were performed to verify the identified structures were true minima on the potential energy curve. To achieve a more accurate relative energy assessment, single point calculations for the three lowest lying isomers were carried out using ROHF-UCSD(T) method through Molpro 2012.\textsuperscript{44} The valence triple-\zeta\textsubscript{basis set (cc-pVTZ)}\textsuperscript{36} was applied for B and the Stuttgart energy-consistent relativistic pseudopotentials ECP10MDF (Mn) with the corresponding ECP10MDF basis set were used for Mn.\textsuperscript{55,46}

To compare with the experimental PES data, the vertical detachment energies (VDEs) and adiabatic detachment energy (ADE) of the global minimum structure of anion were calculated. The first VDE and ADE were performed at three levels (PBE/TZP, PBE0/TZP, and ROHF-UCSD(T)/B/cc-pVTZ/Mn/ECP10MDF). The first VDE was calculated as the energy difference between the anion ground state and the neutral at the optimized anion geometry. The ADE was calculated as the energy difference of the anion and neutral MnB\textsubscript{16} at their respective optimized geometries. The higher VDEs were approximated via \textit{ΔSCE}-Time-Dependent Density Functional Theory (TDDFT)\textsuperscript{47–49} by adding TDDFT vertical excitation energies to the first VDE. In TDDFT calculation, we used the statistically averaged orbital potential (SAOP) functional with TZP basis set, which showed the correct asymptotic 1/r behavior.\textsuperscript{50} The chemical bonding pattern was illustrated by adaptive natural density partitioning (AdNDP)\textsuperscript{51–53} method at PBE0/TZVP\textsuperscript{54} level of theory and visualized by GaussView.\textsuperscript{55} Structural and molecular orbital (MO) visualizations were also performed using GaussView. In order to illustrate the interaction between Mn and B\textsubscript{16}–, we also calculated the binding energy using both ROCCSD(T) and UCSCD(T) with 6-311+G* basis sets for B\textsuperscript{56,57} and TZP for Mn for the less time-consuming. The geometry of each part was fully optimized at the level of PBE0/TZP.

IV. EXPERIMENTAL RESULTS

The photoelectron spectrum of MnB\textsubscript{16}– is shown in Fig. 1(a), compared with simulated spectrum in Fig. 1(b).

![Fig. 1](image-url) FIG. 1. (a) The photoelectron spectrum of MnB\textsubscript{16}– at 193 nm (6.424 eV), (b) The simulated spectrum at the TD-SAOP/TZP level. The vertical bars in the simulated spectra represent the calculated VDEs (Table I). The simulations were done by fitting the calculated VDEs with unit-area Gaussian functions of 0.1 eV half-width.
V. THEORETICAL RESULTS AND COMPARISON WITH EXPERIMENT

Unbiased global minimum searches for MnB\textsubscript{16}\textsuperscript{−} at different spin multiplicities were performed by the TGMin program\textsuperscript{15} using the minimum-hopping algorithms\textsuperscript{50} and the CK program,\textsuperscript{31} as well as manual structural constructions. More than 2500 structures were generated by the TGMin code and about 10 000 structures from the CK algorithm independently. Low-lying isomers within 3.03 eV of the global minimum (see Fig. S1 in the supplementary material\textsuperscript{58}) were further optimized at PBE and PBE0 levels of theory with TZP as basis set. The single point energies of the three lowest lying isomers at ROHF-UCCSD(T)/B/cc-pVTZ/Mn/ECP10MDF\textsuperscript{7} were also calculated to better establish the order of the relative energies. Spin contamination of the ROHF-UCCSD(T) method was found to be negligible here. The T\textsubscript{1} diagnostic values were found to be negligible (<0.03) in the UCCSD(T) calculations, implying that the relative energies of the isomers were credible from the single-determinant methods. The global minimum of MnB\textsubscript{16}\textsuperscript{−} (Fig. 2) was found to be I (C\textsubscript{4v}, \textsuperscript{3}B\textsubscript{2}) with two unpaired electrons at all levels of theory (Fig. S1),\textsuperscript{58} being slightly distorted from the perfect D\textsubscript{8h} structure. The nearest two competing isomer II (C\textsubscript{2v}, \textsuperscript{1}A\textsubscript{1}) and III (D\textsubscript{8h}, \textsuperscript{5}B\textsubscript{1}) are 0.58 eV and 0.54 eV higher, respectively, at the PBE0 level (see Fig. S1).\textsuperscript{58} At the higher ROHF-UCCSD(T) level of theory, isomers II and III were found to be even higher in energy, being 0.84 and 0.81 eV above the C\textsubscript{4v} global minimum, respectively (Fig. S1).\textsuperscript{58} Thus, the drum MnB\textsubscript{16}\textsuperscript{−} (\textsuperscript{3}B\textsubscript{2}) with C\textsubscript{4v} symmetry is considerably more stable than any other isomers. We note that all the low-lying isomers can be viewed as derived from the global minimum C\textsubscript{4v} structure, providing further evidence for the stability of the Mn-centered tubular structure. The B–B bond lengths in each B\textsubscript{8} ring of the global minimum are around 1.58–1.62 Å (see Fig. 2), quite similar to the corresponding values in CoB\textsubscript{16} (1.55–1.63 Å).\textsuperscript{28} The optimized structures and coordinates for the global minima of MnB\textsubscript{16}\textsuperscript{−} and MnB\textsubscript{16} can be found in Fig. S2.\textsuperscript{58}

The relative energies of isomers II and III were too high, compared with the global minimum structure I. Since our cluster beam was expected to be relatively cold, isomers II and III were unlikely to be significantly populated or contribute to the observed spectrum. The VDE and ADE calculations were only performed for the global minimum

### Table I. Comparison of experimental VDEs for MnB\textsubscript{16}− with the calculated values at TD-SAOP/TZP. All energies are in eV.

<table>
<thead>
<tr>
<th>VDE (expt.)</th>
<th>Final state and electron configuration</th>
<th>VDE \textsuperscript{a} (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>28.4(8)</td>
<td>2.90</td>
</tr>
<tr>
<td>A</td>
<td>3.61(6)</td>
<td>3.43</td>
</tr>
<tr>
<td>B</td>
<td>4.28(6)</td>
<td>4.24</td>
</tr>
<tr>
<td>C</td>
<td>~5.3</td>
<td>5.19</td>
</tr>
<tr>
<td>D</td>
<td>~5.5</td>
<td>5.43</td>
</tr>
<tr>
<td>E</td>
<td>~5.7</td>
<td>5.94</td>
</tr>
<tr>
<td>F</td>
<td>~6.0</td>
<td>6.20</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The first VDE is calibrated via the experimental data with other peaks shifted accordingly.

\textsuperscript{b}The orbitals shown in bold face indicate the major electron detachment channels.

(\textit{vide infra}). The photodetachment features are labeled with X, A, B, \ldots and the measured VDEs are given in Table I, where they are compared with the theoretical data. The lowest binding energy band X corresponds to the detachment transition from the ground state of MnB\textsubscript{16}− to that of MnB\textsubscript{16}; while bands A, B, \ldots denote detachment transitions to excited states of MnB\textsubscript{16}. The X band was observed at a VDE of 2.89 eV from the band maximum, whereas the ADE was estimated from the leading edge of the X band as 2.71 eV, which also represents the electron affinity (EA) of MnB\textsubscript{16}. The difference between the ADE and VDE suggests some geometry changes between the anion ground state and that of the neutral. Two well-separated and broad bands (A and B) were observed at VDEs of 3.61 and 4.28 eV, respectively. Above 5 eV, the spectrum became rather congested and four bands were labeled tentatively for the sake of discussion. The broad higher binding energy bands could indicate large geometry changes or more likely multiple detachment channels, as borne out in the comparison with theory in Fig. 1(b) and Table I. The spectrum of MnB\textsubscript{16}− was also taken at 266 nm (not shown), but no more new features were resolved than the 193 nm spectrum.

![Optimized structures of MnB\textsubscript{16}− and MnB\textsubscript{16} at PBE0/TZP, as well as their point group symmetries and spectroscopic states. All distances are in Å.](image-url)
Theoretical first VDE and ADE values of MnB$_{16}^-$ (C$_{4v}$, $^2\Sigma_g^-$) from various theoretical methods (PBE/TZP, PBE0/TZP, and ROHF-UCSSD(T)/B/cc-pVTZ/Mn/ECP10MDF).

<table>
<thead>
<tr>
<th>Method</th>
<th>First VDE</th>
<th>ADE$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>2.80</td>
<td>PBE</td>
</tr>
<tr>
<td>PBE0</td>
<td>2.72</td>
<td>CCSD(T)</td>
</tr>
<tr>
<td></td>
<td>2.61</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Energies are zero-point energy corrected. Experimental ADE: 2.71(8) eV.

Single point energy at the geometry of the optimized structure gained from PBE0 density functional.

structure I. The first VDE was calculated as the energy difference between the anion triplet ground state and the neutral doublet state at the anionic geometry. The ADE was calculated as the energy difference of the anion and neutral MnB$_{16}$ at their respective optimized geometries. The first VDE and ADE calculated at three levels (PBE/TZP, PBE0/TZP, and ROHF-UCSSD(T)/B/cc-pVTZ/Mn/ECP10MDF) are in excellent agreement with the experimental data as shown in Table II. The higher VDEs from the C$_{4v}$ MnB$_{16}^-$ were computed using $\Delta$SCF-TDDFT with the SAOP functional. Higher VDEs with quartet final states were approximated by using the spin-flip TDDFT method. For the computed VDEs given in Table I, the first VDE was shifted to align with the experimental value, and the higher VDEs were shifted accordingly for better comparison with the experimental data.

We found that band A corresponded to three detachment channels while band B corresponded to two detachment channels. Very congested VDEs were computed with ten detachment channels in the energy range between 5 and 6.4 eV. The computed VDEs were fitted with unit-area Gaussian functions of 0.1 eV width to produce a simulated PES spectrum as shown in Fig. 1(b). Overall, the computed VDEs and simulated spectrum are in good agreement with the experiment, providing considerable credence to the C$_{4v}$ global minimum for MnB$_{16}^-$.

VI. DISCUSSION

A. Electronic structure and chemical bonding analyses

To understand the structures and chemical bonding of this unique coordination geometry to the Mn atom in the MB$_{16}^-$ cluster, we examined the valence MOs for the C$_{4v}$ MnB$_{16}^-$ in a local coordinate system as shown in Fig. 3. The orbital energy levels are shown in Fig. S3. MnB$_{16}^-$ was found to have two unpaired electrons in the singly occupied molecular orbital (SOMO) 4b$_2$ orbital and the SOMO-1 9a$_1$ orbital. The SOMO 4b$_2$ is a delocalized orbital on the B$_8$ tubular frame, while the SOMO-1 9a$_1$ is mainly from the Mn 3d$_{z^2}$ orbital. This metal–ligand biradical bonding is noteworthy as it has only been seen previously in lanthanide or actinide complexes.59–61 The C$_{4v}$ symmetry of MnB$_{16}^-$ is due to the Jahn-Teller effect because of the unpaired electrons. The first VDE of MnB$_{16}^-$ corresponds to one electron detachment from the SOMO, producing the neutral $^2\Sigma_g^-$ ground state. In neutral MnB$_{16}$, it turned out that the SOMO 9a$_1$ and the doubly-occupied HOMO 8a$_1$ are nearly degenerate in the C$_{4v}$ symmetry, so that the second-order Jahn-Teller effect distorted MnB$_{16}$ to C$_{2v}$ symmetry.62

We further performed bonding analyses using the unrestricted Adaptive Natural Density Partitioning (UAdNDP) method at the PBE0/TZP level of theory.51 As an extension of the popular Natural Bond Orbital method,63 the UAdNDP analyses can display both localized and delocalized bonding in molecules simultaneously, providing relatively simple bonding pictures for complicated molecular structures. The UAdNDP analyses revealed that the 56 valence electrons in MnB$_{16}$ can be divided into four bonding types as shown in the four rows in Fig. 4. The first row displays localized bonds, consisting of a single electron localized in the 3d$_{z^2}$ orbital on Mn and sixteen 2c-2e $\sigma$ bonds in the two B$_8$ rings. The occupation number (ON) on the 3d$_{z^2}$ orbital is 0.99, suggesting a nearly perfectly localized electron in the Mn 3d$_{z^2}$ orbital. The ON of the sixteen 2c-2e $\sigma$ bonds is 1.78, compared to the ideal case of 2.00. In fact, the sixteen 2c-2e $\sigma$ bonds can also be represented by sixteen 3c-2e $\sigma$ bonds on the sixteen B$_3$ triangles on the drum surface with ON close to 2. Three-center bonding is characteristic of all boron compounds and clusters.3,4,14–46

The remaining three rows describe totally delocalized bonding between the two B$_8$ rings and between the central Mn atom and the B$_{16}$ tubular frame. The “+” sign means that the delocalized bonds between the two B$_8$ rings overlap positively, while the “−” sign means they overlap negatively. The second row consists of three 16c-2e $\sigma + \sigma$ bonds and two 17c-2e $\sigma + \sigma$ bonds, the ONs of which are 1.85–1.90 and 2.00, respectively. The third 16c-2e bonds represent delocalized $\sigma$ bonding in the B$_{16}$ frame, and the two 17c-2e $\sigma + \sigma$ bonds represent covalent bonding between Mn (3d$_{xy}$ and 3d$_{z^2}$) and the B$_{16}$ tubular frame. The third row consists of one 16c-2e $\sigma – \sigma$ bond and two 17c-2e $\sigma – \sigma$ bonds, the ONs of which are...
1.91 \text{e} and 2.00 \text{e}, respectively. The one 16c-2e $\sigma - \sigma$ bond stands for the delocalized $\sigma$ bonding in each B$_8$ ring with anti-bonding character between the two B$_8$ rings. The two 17c-2e $\sigma - \sigma$ bonds are interesting and they describe mainly covalent bonding between Mn (3d$_{xz}$ and 3d$_{yz}$) and B$_{16}$. The last row consists of three 16c-2e and one 16c-1e $\pi - \pi$ bonds. These four bonds all represent $\pi$ bonding interactions between the two B$_8$ rings. The 16c-1e one-electron bond corresponds to the SOMO of MnB$_{16}^-$ (Fig. 3). The neutral MnB$_{16}$ has a very similar bonding pattern, but without the 16c-1e bond.

Both the AdNDP and MO analyses indicate that the main bonding interactions between Mn and the B$_{16}$ frame come from the radial (p$_r$) or tangential (p$_t$) 2p orbitals of B and the Mn 3d orbitals. These bonding interactions represent a new bonding mode for the 3d orbitals imposed by the unique B$_{16}$ tubular frame. The bond order indices of each Mn–B bond obtained from Mayer, G-J, and N-M(3)\cite{67,68,69,70} approaches are 0.28, 0.25, and 0.26, respectively. The bond lengths between Mn and B are around 2.22-2.26 Å at the PBE0 level, which is slightly longer than a single Mn–B bond (2.04 Å) based on the latest recommended covalent radii for Mn and B by Pyykkö.\cite{71,72} Since there are sixteen Mn–B bonds, the host-guest interaction is expected to be substantial in MnB$_{16}^-$. The calculated spin populations and effective charges based on Mulliken,\cite{73} Voronoi,\cite{74} and Hirshfeld\cite{75} methods revealed that the Mn atom in both MnB$_{16}^-$ and MnB$_{16}$ has a zero-valent oxidation state, which reinforces the covalent interactions between Mn and the B$_{16}$ frame and enrich the low-oxidation-state chemistry of transition metals.\cite{76,77}

B. Binding energy between Mn and B$_{16}^-$

For a quantitative understanding of the bonding between the Mn guest and the B$_{16}^-$ tubular host, we computed the binding energy between Mn and the double ring structure of B$_{16}^-$ ($^2A_1$): MnB$_{16}^-$ ($^3B_2$) $\rightarrow$ Mn ($^2A_{1g}$) + B$_{16}^-$ ($^2A_1$). The binding energy was calculated to be 650 kJ/mol at the UCCSD(T)/6-311+G*/PBE0/TZP level of theory. The magnitude of this binding energy is significant, suggesting strong covalent interactions between the Mn 3d and B 2p orbitals. Note that the global minimum of B$_{16}^-$ is a 2D structure with the tubular isomer $\sim$150 kJ/mol higher in energy at the B3LYP/6-311-G* level of theory.\cite{21} Clearly, the strong 3d-2p interactions stabilize the tubular structure in both MnB$_{16}^-$ and CoB$_{16}^-$. It is conceivable that other transition metals may also form similar MB$_{16}^-$ type tubular structures. Nevertheless, because of the delicate balance between the overlap of the d orbitals and the B 2p orbitals on the tube frame, it would require both careful experimental and theoretical efforts to find out if smaller or larger M-centered double-ring tubular boron structures would be feasible.\cite{78}

VII. CONCLUSIONS

In summary, the current work has uncovered a second member of a metal-centered boron drum cluster in MnB$_{16}^-$. The covalent interactions between the 3d orbitals of Mn and the B$_{16}$ framework stabilize the double-ring tubular structure, relative to the planar structure for the bare B$_{16}^-$ cluster. The Jahn-Teller effects are found to distort the anionic MnB$_{16}^-$.\cite{21,78}
to $C_3v$ symmetry and the neutral MnB$_{16}$ to $C_{2v}$ symmetry from the ideal $D_{4d}$ symmetry. The B$_{16}$ tubular frame provides an interesting host for the transition metal atoms and a new bonding modality. It would be interesting to discover if other transition metal atoms can be doped into the B$_{16}$ tube or if larger tubes or novel structures would be possible to host transition metal atoms.  

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40See supplementary material at http://dx.doi.org/10.1063/1.4946796 for a full set of the optimized low-lying structures of MnB$_{16}$, the detailed structures of its neutral and anion ground state, and a molecular orbital correlation diagram.