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Manganese-centered tubular boron cluster – MnB₁₆⁻: A new class of transition-metal molecules

Tian Jian,^{1,a)} Wan-Lu Li,^{2,a)} Ivan A. Popov,³ Gary V. Lopez,¹ Xin Chen,² Alexander I. Boldyrev,^{3,b)} Jun Li,^{2,c)} and Lai-Sheng Wang^{1,d)}

¹Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

²Department of Chemistry & Key Laboratory of Organic Optoelectronics and Molecular Engineering

of Ministry of Education, Tsinghua University, Beijing 100084, China

³Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, USA

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We report the observation of a manganese-centered tubular boron cluster (MnB₁₆⁻), which is characterized by photoelectron spectroscopy and *ab initio* calculations. The relatively simple pattern of the photoelectron spectrum indicates the cluster to be highly symmetric. *Ab initio* calculations show that MnB₁₆⁻ has a Mn-centered tubular structure with C_{4v} symmetry due to first-order Jahn-Teller effect, while neutral MnB₁₆ reduces to C_{2v} symmetry due to second-order Jahn-Teller effect. In MnB₁₆⁻, two unpaired electrons are observed, one on the Mn 3d_z² orbital and another on the B₁₆ tube, making it an unusual biradical. Strong covalent bonding is found between the Mn 3d orbitals and the B₁₆ 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. *Published by AIP Publishing*. [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.^{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 anions³⁻⁵ or up to 15 atoms as cations.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 B₂₀ and B₁₄ were suggested to have 3D structures computationally,^{7,8} an infrared/ultraviolet double ionization experiment failed to detect these structures.⁹ Recent works show that negatively charged boron clusters continued to be planar at B_{27} , B_{30} , B_{35} , and B_{36} .¹⁰⁻¹³ All the 2D boron clusters consist of a peripheral boron ring featuring 2-center 2-electron (2c-2e) σ bonds and delocalized σ and π bonds over the cluster plane.⁹⁻¹⁴ Very recently, 3D isomers for anionic boron clusters were observed to occur at B28⁻, B39⁻, and $B_{40}^{-,15-17}$ which form extraordinary borospherene cage structures.

Boron-based nanotubes were proposed,^{18,19} following the discovery of carbon nanotubes. Tubular boron clusters have been of interest, because they could be viewed as

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potential embryos for boron nanotubes.⁷ Although a doublering tubular structure was computationally shown to be the global minimum for neutral B_{20} ,^{7,20} it was not experimentally confirmed.⁹ On the other hand, a double-ring tubular B_{16}^+ cation has been shown to compete for the global minimum,⁶ even though the neutral and anionic B_{16} clusters were found to be planar.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 B₉⁻ cluster, which has a D_{8h} molecular wheel structure with a central boron atom,²² a design principle was advanced to replace the central boron atom to make transition metal centered boron rings (M OB_n^-).²³ A series of such aromatic borometallic molecular wheels have been produced experimentally and characterized for n = 8-10. Furthermore, the CoB₁₂⁻ and RhB₁₂⁻ clusters have been found to adopt half-sandwich-type structures in which the quasi-planar and aromatic B₁₂ moiety simply coordinates to the metal center.²⁴

Metal-doped boron clusters have been investigated computationally.^{25–27} Very recently, a cobalt-doped boron cluster CoB_{16}^- was observed experimentally and characterized using photoelectron spectroscopy (PES) and *ab initio* calculations.²⁸ It was found to possess a Co-centered drum or tubular structure with two B₈ 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 *ab initio* investigation of a Mn-doped B_{16} cluster. Photoelec-

^{a)}These authors contributed equally to this work.

^{b)}Electronic mail: a.i.boldyrev@usu.edu

^{c)}Electronic mail: junli@tsinghua.edu.cn

^{d)}Electronic mail: Lai-Sheng_Wang@brown.edu

tron spectrum of MnB_{16}^- displayed well-resolved features that can be used to compare with theoretical data. *Ab initio* calculations revealed a Mn-centered double-ring tubular structure distorted from D_{8d} to C_{4v} symmetry due to Jahn-Teller effect. The C_{4v} MnB_{16}^- contains two unpaired electrons, one localized on the Mn $3d_{z^2}$ orbital and another delocalized on the tubular B_{16} frame. The neutral MnB_{16} is found to be distorted to C_{2v} symmetry, because of the second-order Jahn-Teller effect²⁸ with only one unpaired Mn $3d_{z^2}$ electron. The Mn atom in both MnB_{16}^- and MnB_{16} is found to engage in covalent interactions with the B_{16} frame to stabilize the drum structure.

II. EXPERIMENTAL METHOD

The experiment was carried out using a magneticbottle PES apparatus equipped with a laser vaporization supersonic cluster source, details of which has been described elsewhere.²⁹ Briefly, the MnB₁₆⁻ cluster was produced by laser vaporization of a Bi/10B/Mn mixed target with a helium carrier gas seeded with 5% argon. The Bi component acted as a binder and provided Bi⁻ 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 MnB₁₆⁻ 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 $\Delta Ek/Ek \approx 2.5\%$, that is, ~25 meV for 1 eV electrons.

III. THEORETICAL METHODS

The global minimum searches for MnB₁₆⁻ were performed using a constrained Basin-Hopping (BH) method³⁰ in the TGMin code¹³ and the Coalescence Kick (CK) program,³¹ as well as manual structural constructions. In TGMin, scalar relativistic^{32–34} density functional theory (DFT) formalism with the PBE exchange-correlation functional³⁵ was applied with double- ζ valence basis set³⁶ via the ADF2013.01 program.^{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^{39,40} level of theory in Gaussian 09.⁴¹ Low-lying isomers were further optimized at PBE and PBE0 levels of theory with triple- ζ valence plus polarization functions (TZP)^{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-UCCSD(T) method through Molpro 2012.⁴⁴ The valence triple- ζ basis set (cc-pVTZ)³⁶ was applied for B and the Stuttgart energy-consistent relativistic pseudopotentials ECP10MDF (Mn) with the corresponding ECP10MDF basis set were used for Mn.45,46

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-UCCSD(T)/B/ccpVTZ/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 MnB₁₆ at their respective optimized geometries. The higher VDEs were approximated via Δ SCF-Time-Dependent Density Functional Theory (TDDFT)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.⁵⁰ The chemical bonding pattern was illustrated by adaptive natural density partitioning (AdNDP)⁵¹⁻⁵³ method at PBE0/TZVP⁵⁴ level of theory and visualized by GaussView.⁵⁵ Structural and molecular orbital (MO) visualizations were also performed using GaussView. In order to illustrate the interaction between Mn and B_{16}^{-} , we also calculated the binding energy using both ROCCSD(T) and UCCSD(T) with 6-311+G* basis sets for B^{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_{16}^{-} is shown in Fig. 1(a), compared with simulated spectrum in Fig. 1(b)



FIG. 1. (a) The photoelectron spectrum of MnB_{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.

TABLE I. Comparison of experimental VDEs for MnB_{16}^- with the calculated values at TD-SAOP/TZP. All energies are in eV.

	VDE (expt.)	Final state and electron configuration ^b	VDE ^a (theoretical)
X	2.89(8)	${}^{2}A_{1}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{0}$	2.90
A	3.61(6)	${}^{2}B_{2}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}8e^{4}8a_{1}{}^{2}9a_{1}{}^{0}4b_{2}{}^{1}$ ${}^{4}B_{2}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}8e^{4}8a_{1}{}^{1}9a_{1}{}^{1}4b_{2}{}^{1}$	3.43 3.45
		${}^{2}B_{2}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}8e^{4}8a_{1}{}^{1}9a_{1}{}^{1}4b_{2}{}^{1}$	3.57
В	4.28(6)	${}^{4}\text{E}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}\textbf{8}e^{3}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$ ${}^{2}\text{B}_{2}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}8e^{4}\textbf{8}a_{1}{}^{1}9a_{1}{}^{1}4b_{2}{}^{1}$	4.24 4.40
С	~5.3	${}^{2}\text{E}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{4}\textbf{8}e^{3}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$ ${}^{4}\text{A}_{2}, \dots 6e^{4}\textbf{3}b_{1}{}^{1}3b_{2}{}^{2}7e^{4}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$	5.19 5.37
D	~5.5	${}^{4}A_{1}, \dots 6e^{4}3b_{1}{}^{2}\textbf{3b}_{2}{}^{1}7e^{4}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$ ${}^{2}E, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}\textbf{7}e^{3}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$ ${}^{4}E, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}\textbf{7}e^{3}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$	5.43 5.46 5.50
E	~5.7	${}^{2}\text{E}, \dots 6e^{4}3b_{1}{}^{2}3b_{2}{}^{2}7e^{3}8e^{4}8a_{1}{}^{2}9a_{1}{}^{1}4b_{2}{}^{1}$	5.94
F	~6.0	$\label{eq:alpha} \begin{array}{l} {}^2A_2,\ldots 6e^4 3b_1{}^13b_2{}^27e^48e^48a_1{}^29a_1{}^14b_2{}^1\\ {}^2A_1,\ldots 6e^43b_1{}^23b_2{}^17e^48e^48a_1{}^29a_1{}^14b_2{}^1\\ {}^2E,\ldots 6e^33b_1{}^23b_2{}^27e^48e^48a_1{}^29a_1{}^14b_2{}^1\\ {}^4E,\ldots 6e^33b_1{}^23b_2{}^27e^48e^48a_1{}^29a_1{}^14b_2{}^1 \end{array}$	6.20 6.28 6.34 6.38

^aThe first VDE is calibrated via the experimental data with other peaks shifted accordingly.

^bThe orbitals shown in bold face indicate the major electron detachment channels.

(vide infra). The photodetachment features are labeled with X, A, B, ... 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_{16}^{-} to that of MnB_{16} ; while bands A, B, ... denote detachment transitions to excited states of MnB₁₆. 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_{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_{16}^{-} was also taken at 266 nm (not shown), but no more new features were resolved than the 193 nm spectrum.

V. THEORETICAL RESULTS AND COMPARISON WITH EXPERIMENT

Unbiased global minimum searches for MnB₁₆⁻ at different spin multiplicities were performed by the TGmin program¹³ using the minimum-hoping algorithm³⁰ and the CK program,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 material⁵⁸) 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 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_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_{16}^{-} (Fig. 2) was found to be I (C_{4v} , ${}^{3}B_{2}$) with two unpaired electrons at all levels of theory (Fig. S1),⁵⁸ being slightly distorted from the perfect D_{8d} structure. The nearest two competing isomer II (C_{2v} , ¹ A_1) and III (D_{8d} , ⁵ B_1) are 0.58 eV and 0.54 eV higher, respectively, at the PBE0 level (see Fig. S1⁵⁸). 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_{4v} global minimum, respectively (Fig. S1⁵⁸). Thus, the drum MnB_{16}^{-} (³B₂) with C_{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 C4v structure, providing further evidence for the stability of the Mn-centered tubular structure. The B-B bond lengths in each B₈ ring of the global minimum are around 1.58-1.62 Å (see Fig. 2), quite similar to the corresponding values in CoB_{16}^- (1.55-1.63 Å).²⁸ The optimized structures and coordinates for the global minima of MnB_{16}^{-} and MnB_{16} can be found in Fig. S2.⁵⁸

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



FIG. 2. Optimized structures of MnB_{16}^- and MnB_{16} at PBE0/TZP, as well as their point group symmetries and spectroscopic states. All distances are in Å.

TABLE II. Theoretical first VDE and ADE values of MnB_{16}^- (C_{4v} , ${}^{3}B_2$) from various theoretical methods (PBE/TZP, PBE0/TZP, and ROHF-UCCSD(T)/B/cc-pVTZ/Mn/ECP10MDF).

First VDE			ADE ^a		
PBE	PBE0	CCSD(T) ^b	PBE	PBE0	CCSD(T) ^b
2.80	2.90	2.72	2.60	2.61	2.66

^aEnergies are zero-point energy corrected. Experimental ADE: 2.71(8) eV. ^bSingle 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 MnB₁₆ at their respective optimized geometries. The first VDE and ADE calculated at three levels (PBE/TZP, PBE0/TZP, and ROHF-UCCSD(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} MnB₁₆⁻ were computed using Δ 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 MnB₁₆⁻.

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 MB₁₆⁻ cluster, we examined the valence MOs for the C_{4v} MnB₁₆⁻ in a local coordinate system as shown in Fig. 3. The orbital energy levels are shown in Fig. S3.⁵⁸ MnB₁₆⁻ was found to have two unpaired electrons in the singly occupied molecular orbital (SOMO) 4b₂ orbital and the SOMO-1 9a₁ orbital. The SOMO $4b_2$ is a delocalized orbital on the B_{16} tubular frame, while the SOMO-1 $9a_1$ is mainly from the Mn $3d_{z^2}$ orbital. This metal-ligand biradical bonding is noteworthy and 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 MnB₁₆⁻ corresponds to one electron detachment from the SOMO, producing the neutral ${}^{2}A_{1}$ ground state. In neutral MnB₁₆, it turned out that the SOMO 9a1 and the doubly-occupied HOMO $8a_1$ are nearly degenerate in the C_{4v} symmetry, so that



FIG. 3. Valence canonical molecular orbitals (CMOs) of MnB_{16}^{-} at the PBE0/TZP level. All the orbitals plotted here are just generated from the interactions between the 3*d* orbitals of Mn and the 2s/2p orbitals of B. The gray block corresponds to the energy levels mainly from the B 2s/2p orbitals (isovalue = 0.03 a.u.). Herein, r, t, and v represent radial, tangential, and vertical *p*-orbitals of each B atom in a local coordinate system (LCS), respectively, where the z-axis is across the two centers of the double ring and x-axis points to the center.

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/TZVP level of theory.⁵¹ As an extension of the popular Natural Bond Orbital method,⁶³ the AdNDP 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 MnB₁₆⁻ 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 B₈ rings. The occupation number (ON) on the $3d_{z^2}$ orbital is 0.99 |e|, suggesting a nearly perfectly localized electron in the Mn $3d_{r^2}$ orbital. The ON of the sixteen 2c-2e σ bonds is 1.78 |e|, compared to the ideal case of 2.00 |e|. In fact, the sixteen 2c-2e σ bonds can also be represented by sixteen 3c-2e σ bonds on the sixteen B₃ triangles on the drum surface with ON close to 2. Three-center bonding is characteristic of all boron compounds and clusters.^{3,4,64–66}

The remaining three rows describe totally delocalized bonding between the two B₈ rings and between the central Mn atom and the B₁₆ tubular frame. The "+" sign means that the delocalized bonds between the two B₈ 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 |e| and 2.00 |e|, respectively. The three 16c-2e bonds represent delocalized σ bonding in the B₁₆ frame, and the two 17c-2e $\sigma + \sigma$ bonds represent covalent bonding between Mn (3d_{xy} and 3d_{x²-y²}) and the B₁₆ 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 |e| and 2.00 |e|, respectively. The one 16c-2e $\sigma - \sigma$ bond stands for the delocalized σ bonding in each B₈ ring with anti-bonding character between the two B₈ rings. The two 17c-2e $\sigma - \sigma$ bonds are interesting and they describe mainly covalent bonding between Mn (3d_{xz} and 3d_{yz}) and B₁₆. The last row consists of three 16c-2e and one 16c-1e $\pi - \pi$ bonds. These four bonds all represent π bonding interactions between the two B₈ rings. The 16c-1e one-electron bond corresponds to the SOMO of MnB₁₆⁻ (Fig. 3). The neutral MnB₁₆ 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 B₁₆ 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 B₁₆ tubular frame. The bond order indices of each Mn–B bond obtained from Mayer,⁶⁷ G-J,⁶⁸ and N-M(3)^{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.^{71,72} Since there are sixteen Mn–B bonds, the host-guest interaction is expected to be substantial in MnB₁₆⁻. The calculated spin populations and effective charges based on Mulliken,73 Voronoi,74 and Hirshfeld75 methods revealed that the Mn atom in both MnB_{16}^{-} and MnB₁₆ has a zero-valent oxidation state, which reinforces the covalent interactions between Mn and the B₁₆ frame and enrich the low-oxidation-state chemistry of transition metals.76,77

B. Binding energy between Mn and B₁₆⁻

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}^- (²A₁): MnB_{16}^- (³B₂) $\rightarrow Mn$ (⁶A_{1g}) + B_{16}^- (²A₁). 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 ~150 kJ/mol higher in energy at the B3LYP/6-311-G* level of theory.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 MB₁₆⁻ 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.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}^-

to C_{4v} symmetry and the neutral MnB_{16} to C_{2v} symmetry from the ideal D_{8d} 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.⁷⁸

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- ¹B. Albert and H. Hillebrecht, Angew. Chem., Int. Ed. 48, 8640 (2009).
- ²A. R. Oganov and V. L. Solozhenko, J. Superhard Mater. **31**, 285 (2009).
- ³A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, Coord. Chem. Rev. **250**, 2811 (2006).
- ⁴A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W. L. Li, C. Romanescu, L. S. Wang, and A. I. Boldyrev, Acc. Chem. Res. **47**, 1349 (2014).
- ⁵Z. A. Piazza, I. A. Popov, W. L. Li, R. Pal, X. C. Zeng, A. I. Boldyrev, and L. S. Wang, J. Chem. Phys. **141**, 034303 (2014).
- ⁶E. Oger, N. R. M. Crawford, R. Kelting, P. Weis, M. M. Kappes, and R. Ahlrichs, Angew. Chem., Int. Ed. **46**, 8503 (2007).
- ⁷B. Kiran, S. Bulusu, H. J. Zhai, S. Yoo, X. C. Zeng, and L. S. Wang, Proc. Natl. Acad. Sci. U. S. A. **102**, 961 (2005).
- ⁸L. J. Cheng, J. Chem. Phys. **136**, 104301 (2012).
- ⁹C. Romanescu, D. J. Harding, A. Fielicke, and L. S. Wang, J. Chem. Phys. 137, 014317 (2012).
- ¹⁰W. L. Li, R. Pal, Z. A. Piazza, X. C. Zeng, and L. S. Wang, J. Chem. Phys. 142, 204305 (2015).
- ¹¹W. L. Li, Y. F. Zhao, H. S. Hu, J. Li, and L. S. Wang, Angew. Chem., Int. Ed. **53**, 5540 (2014).
- ¹²W. L. Li, Q. Chen, W. J. Tian, H. Bai, Y. F. Zhao, H. S. Hu, J. Li, H. J. Zhai, S. D. Li, and L. S. Wang, J. Am. Chem. Soc. **136**, 12257 (2014).
- ¹³Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li, and L. S. Wang, Nat. Commun. 5, 3113 (2014).
- ¹⁴D. Y. Zubarev and A. I. Boldyrev, J. Comput. Chem. 28, 251 (2007).
- ¹⁵Y. J. Wang, Y. F. Zhao, W. L. Li, T. Jian, Q. Chen, X. R. You, T. Ou, X. Y. Zhao, H. J. Zhai, S. D. Li, J. Li, and L. S. Wang, J. Chem. Phys. **144**, 064307 (2016).
- ¹⁶Q. Chen, W. L. Li, Y. F. Zhao, S. Y. Zhang, H. S. Hu, H. Bai, H. R. Li, W. J. Tian, H. G. Lu, H. J. Zhai, S. D. Li, J. Li, and L. S. Wang, ACS Nano 9, 754 (2015).
- ¹⁷H. J. Zhai, Y. F. Zhao, W. L. Li, Q. Chen, H. Bai, H. S. Hu, Z. A. Piazza, W. J. Tian, H. G. Lu, Y. B. Wu, Y. W. Mu, G. F. Wei, Z. P. Liu, J. Li, S. D. Li, and L. S. Wang, Nat. Chem. **6**, 727 (2014).
- ¹⁸I. Boustani and A. Quandt, Eur. Phys. Lett. **39**, 527 (1997).
- ¹⁹A. Gindulyte, W. N. Lipscomb, and N. L. Massa, Inorg. Chem. **37**, 6544 (1998).
- ²⁰W. An, S. Bulusu, Y. Gao, and X. C. Zeng, J. Chem. Phys. **124**, 154310 (2006).
- ²¹A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, J. Am. Chem. Soc. **130**, 7244 (2008).

- ²²H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, and L. S. Wang, Angew. Chem., Int. Ed. **42**, 6004 (2003).
- ²³C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev, and L. S. Wang, Acc. Chem. Res. 46, 350 (2013).
- ²⁴I. A. Popov, W. L. Li, Z. A. Piazza, A. I. Boldyrev, and L. S. Wang, J. Phys. Chem. A **118**, 8098 (2014).
- ²⁵Y. Liao, C. L. Cruz, P. v. R. Schleyer, and Z. Chen, Phys. Chem. Chem. Phys. 14, 14898 (2012).
- ²⁶C. Xu, L. J. Cheng, and J. L. Yang, J. Chem. Phys. 141, 124301 (2014).
- ²⁷N. M. Tam, H. T. Pham, L. V. Duong, M. P. Pham-Ho, and M. T. Nguyen, Phys. Chem. Chem. Phys. **17**, 3000 (2015).
- ²⁸I. A. Popov, T. Jian, G. V. Lopez, A. I. Boldyrev, and L. S. Wang, Nat. Commun. 6, 8654 (2015).
- ²⁹L. S. Wang, H. S. Cheng, and J. Fan, J. Chem. Phys. **102**, 9480 (1995).
- ³⁰S. Goedecker, J. Chem. Phys. **120**, 9911 (2004).
- ³¹A. P. Sergeeva, B. B. Averkiev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, J. Chem. Phys. **134**, 224304 (2011).
- ³²E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
- ³³E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).
- ³⁴E. van Lenthe, A. Ehlers, and E. J. Baerends, J. Chem. Phys. **110**, 8943 (1999).
- ³⁵J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- ³⁶T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
- ³⁷G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. van Gisbergen, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).
- ³⁸ADF 2010.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.
- ³⁹C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
- ⁴⁰J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. **102**, 939 (1980).
- ⁴¹M. J. Frisch *et al.*, GAUSSIAN 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- ⁴²P. L. Barbieri, P. A. Fantin, and F. E. Jorge, Mol. Phys. 104, 2945 (2006).
- ⁴³S. F. Machado, G. G. Camiletti, A. C. Neto, F. E. Jorge, and R. S. Jorge, Mol. Phys. **107**, 1713 (2009).
- ⁴⁴H. J. Werner *et al.*, MOLPRO, version 2012.1, a package of *ab initio* programs, 2012, see http://www.molpro.net.
- ⁴⁵M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. 86, 866 (1987).
- ⁴⁶J. M. L. Martin and A. Sundermann, J. Chem. Phys. 114, 3408 (2001).
- ⁴⁷J. Li, X. Li, H. J. Zhai, and L. S. Wang, Science **299**, 864 (2003).
- ⁴⁸H. J. Zhai, B. Kiran, B. Dai, J. Li, and L. S. Wang, J. Am. Chem. Soc. **127**, 12098 (2005).
- ⁴⁹S. Van Gisbergen, J. Snijders, and E. Baerends, Comput. Phys. Commun. 118, 119 (1999).
- ⁵⁰P. Schipper, O. Gritsenko, S. van Gisbergen, and E. Baerends, J. Chem. Phys. 112, 1344 (2000).
- ⁵¹D. Y. Zubarev and A. I. Boldyrev, Phys. Chem. Chem. Phys. **10**, 5207 (2008).
- ⁵²D. Y. Zubarev and A. I. Boldyrev, J. Org. Chem. **73**, 9251 (2008).
- ⁵³D. Y. Zubarev and A. I. Boldyrev, J. Phys. Chem. A **113**, 866 (2008).
- ⁵⁴A. Schäfer, C. Huber, and R. Ahlrichs, J. Chem. Phys. 100, 5829 (1994).
- ⁵⁵R. Dennington, T. Keith, and J. Millam, GaussView, version 4.1, Semichem, Inc., Shawnee Mission, KS, 2007.
- ⁵⁶R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. 72, 650 (1980).
- ⁵⁷P. v. R. Schleyer, J. Comput. Chem. 4, 294 (1983).
- ⁵⁸See 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.
- ⁵⁹K. Zhao and R. M. Pitzer, J. Phys. Chem. **100**, 4798 (1996).
- ⁶⁰X. F. Wang, H. G. Cho, L. Andrews, M. Y. Chen, D. A. Dixon, H. S. Hu, and J. Li, J. Phys. Chem. A **115**, 1913 (2011).
- ⁶¹H. S. Hu, F. Wei, X. Wang, L. Andrews, and J. Li, J. Am. Chem. Soc. 136, 1427 (2014).
- ⁶²R. G. Pearson, J. Mol. Struct.: THEOCHEM 12, 25 (1983).
- ⁶³J. P. Foster and F. Weinhold, J. Am. Chem. Soc. 102, 7211 (1980).
- ⁶⁴W. N. Lipscomb, Science **196**, 1047 (1977).
- ⁶⁵O. El Bakouri, M. Sola, and J. Poater, Phys. Chem. Chem. Phys. (published online 2016).

- ⁶⁶L. S. Wang, Int. Rev. Phys. Chem. 35, 69 (2016).
- ⁶⁷I. Mayer, Chem. Phys. Lett. **97**, 270 (1983).
- ⁶⁸M. Gopinathan and K. Jug, Theor. Chim. Acta **63**, 497 (1983).
- ⁶⁹A. Michalak, R. L. DeKock, and T. Ziegler, J. Phys. Chem. A **112**, 7256 (2008).
- ⁷⁰R. F. Nalewajski, J. Mrozek, and A. Michalak, Int. J. Quantum Chem. 61, 589 (1997).
- ⁷¹P. Pyykkö and M. Atsumi, Chem. Eur. J. **15**, 12770 (2009).
- ⁷²P. Pyykkö, J. Phys. Chem. A **119**, 2326 (2015).
 ⁷³K. B. Wiberg, Tetrahedron **24**, 1083 (1968).

- ⁷⁴F. M. Bickelhaupt, N. J. van Eikema Hommes, C. Fonseca Guerra, and E. J. Baerends, Organometallics 15, 2923 (1996).
- ⁷⁵F. Hirshfeld, Theor. Chim. Acta **44**, 129 (1977).
- ⁷⁶H. C. Hu, H. S. Hu, B. Zhao, P. Cui, P. Cheng, and J. Li, Angew. Chem., Int. Ed. 54, 11681 (2015).
- ⁷⁷P. Cui, H. S. Hu, B. Zhao, J. T. Miller, P. Cheng, and J. Li, Nat. Commun. 6, 6331 (2015).
- ⁷⁸W. L. Li, T. Jian, X. Chen, T. T. Chen, G. V. Lopez, J. Li, and L. S. Wang, "The Planar CoB₁₈⁻ Cluster as a Motif for Metallo-Borophenes," Angew. Chem., Int. Ed. (in press, 2016).