TM₄B₁₈⁰⁻ (TM = Hf, Ta, W, Re, Os): new structure construction with TM doped B wheel units†

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We report the global search for the lowest energy structures of the transition metal (TM) doped B clusters, TM₄B₁₈⁰⁻ (TM = Hf, Ta, W, Re, Os) and their electronic properties. A combination of the comprehensive genetic algorithm (CGA) method with density functional theory (DFT) calculations shows that they are composed of four planar TM@B₉ wheel units by sharing B atoms, except for Os₄B₁₈⁰⁻, which consists of two types of planar molecular wheels of Os@B₇ and Os@B₉. Among these nanoclusters, it is found that the Ta₄B₁₈ cluster has a closed-shell with a large HOMO–LUMO gap of 2.61 eV. Adaptive natural density partitioning analysis (AdNDP) reveals that the Ta₄B₁₈ cluster has σ antiaromaticity and π aromaticity, i.e., a conflicting aromaticity. The simulated photoelectron spectra (PES) of all anionic clusters are also provided for future experimental investigations.

1. Introduction

As an adjacent element of carbon (C), boron (B) has three valence electrons (2s²2p¹), and possesses a diverse and complex range of chemistry. Due to the characteristic of electron deficiency, B aggregates into various structures by sharing electrons and easily forms multilayer-two electron (mc–2e) bonds, which lead to various cluster structures.¹–³ In the past decade, combining experimental and theoretical calculations, it was found that small and medium-sized pure B clusters could have the planar,⁴–⁶ quasi-planar,⁷–⁹ double ring,¹⁰,¹¹ cage-like,¹²–¹⁵ bilayer,¹⁶,¹⁷ and core–shell¹⁸ structures. The Bₙ⁻ clusters possess the planar or quasi-planar structures form up to the size of n ~ 38, whereas the neutral counterparts from n = 20 exhibit a transition from the planar to the double-ring tubular shape.¹⁹

The discoveries of planar B₁₆⁰⁻,⁹ fullerene-like B₄₀⁰⁻ (ref. 15) and bilayer B₁₈⁰⁻ (ref. 17) represent three major breakthroughs in the study of boron clusters. The planar B₁₆ proves the viability of monolayer boron sheets with hexagonal vacancies, which leads to the concept of borophene. The cage-like B₄₀ can be regarded as a boron analogue of C₆₀ (ref. 20) and the bilayer B₁₈ can be extended to a two-dimensional bilayer phase.²⁶

Doping transition-metal (TM) atoms is known as an effective approach to stabilize pure B clusters and to change their geometries and electronic properties. Up to now, the doping of B clusters with different numbers of metal atoms has led to many novel structures, e.g. (i) planar molecular wheel,²¹–²³ (ii) half-sandwich,²⁴ inverse sandwich²⁵,²⁶ and inverse triple-decker²⁷ clusters, (iii) drum-like structures,²⁸–³⁰ (iv) the endohedral boron cages,³¹–³⁴ and (v) metallo-borospherenes.³⁵–³⁸

Doping single TM atom into small-sized B clusters produces perfect TM-centered monocyclic B wheel clusters such as Co@B₁₈⁻,³¹ Rh@B₁₈⁻,³² and Ta@B₁₈⁻.³³ The 10 coordination number (CN) of Ta@B₁₈⁻ is known as the highest number among the planar species. With the increase of the number of B atoms, the structure growth pattern changes into the half-sandwich structures and the metal-centered B drum structures, such as Rh@B₁₂⁻,³⁴ Co@B₁₆⁻,³⁵ Rh@B₁₈⁻,³⁶ and Ta@B₂₀⁻.³⁷ Some highly stable endohedral B cages are also predicted by theoretical calculations, for example, Mo@B₂₆⁻,³² W@B₃₄⁻,³³ and Co@B₄₀⁻.³⁴

A new class of di-metal-doped inverse sandwich complexes, including La₄B₁₈⁻,²⁵ Pr₂Bₗ⁻,²⁶ and La₄B₁₈⁻,²⁶ have been observed by photoelectron spectra (PES) and density functional theory (DFT) calculations. Because of the unique (d–p) bond between metallic 5d orbitals and Bₙ rings, these lowest energy structures exhibit a higher level of stability than the other isomers. The first icosahedral clusters of M₄B₁₈⁻ (M = Rh, Ir)²⁹ were found in the theoretical investigations. Moreover, the PES results combined with DFT calculations has confirmed that the La₄B₁₈⁻ cluster has a La–Bₙ–La–Bₙ–La inverse triple-decker structure, which is used to assemble 1D lanthanide B nanowires.²⁷ More recently, the first metallo-borospherenes La₄B₁₈⁻ and Tb₃B₁₈⁻ (D₃h)²⁵ were observed in the experiment, and the calculations confirmed that their structures are composed of two Bₙ rings linked together at their three corners with three B₂ units. The core–shell spheroidal triderahedral metallo-borospherene La₄[B₄@B₁₈⁻] (ref. 36) and the smallest metallo-borospherene Ta₃B₁₈⁻ (ref. 37) were subsequently predicted. Among them, the D₃h Ta₃B₁₈⁻ compound is first metallo-borospherene with σ + π + δ triple aromaticity. The

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perfect core–shell La$_4$[B@B$_4$@B$_{24}$]$^{0/−}$ clusters have been theoretically proposed to possess four equivalent inter-connected B$_6$ triangles on the cage surface.\(^{38}\)

In this work, we report the schematic study of the four TM atoms doped B$_n$ clusters, TM$_4$B$_{18}$$^{0/−}$ (TM = Hf, Ta, W, Re, Os). These clusters can be thought of as being built up with four TM doped B wheel units by sharing B atoms on their peripheral ring. Among them, the bonding pattern shows this Ta$_4$B$_{18}$ has 50 skeleton electrons on the cage surface suggesting a spherical aromatic system with filled 1s + 1p + 1d + 2s + 1f + 2p + 2d molecular orbitals. It is also found that the ground-state structure of Ta$_4$B$_{18}$ shows a conflicting aromaticity.

2. Computational methods

The optimization of the lowest energy structures of TM$_4$B$_{18}$$^{0/−}$ (TM = Hf, Ta, W, Re, Os) were conducted using our developed comprehensive genetic algorithm (CGA) code\(^{40}\) incorporated with DFT calculations (CGA-DFT). The all-electron method with double-$\zeta$ numerical plus polarization d-function (DND) basis sets and the Perdew–Burke–Enzerhof (PBE) functional within the generalized gradient approximation (GGA)\(^{41}\) were used during each step of CGA using DMol$^3$ package.\(^{42}\) Each structure was optimized without any symmetry constraint. The CGA code randomly generated sixteen initial parent configurations for each cluster system. The new structures were created by mating, perturbation, and exchange of the atom type of a pair of different types of atoms.\(^{43}\) In order to achieve the global minimum of potential energy surface (PES), all cluster systems had at least 3000 iterations.

After the global search of CGA-DFT, the low-energy isomers were more accurately optimized by Gaussian16 program\(^{44}\) for TM$_4$B$_{18}$$^{0/−}$ (TM = Hf, Ta, W, Re, Os). The previous studies proved the feasibility of the PBE0 functional\(^{45}\) to describe the energy differences between different isomers of TM doped B clusters.\(^{35,37,39,46–48}\) Moreover, our previous study of the single TM atom doped B$_n$ ($n = 7$–10) clusters\(^{49}\) also confirmed that PBE0 functional can precisely describe the interactions between TM atom and B atom by comparing with the high-level CCSD(T)$^{39}$ results. For basis set, the 6-311G* was proved enough to describe B atom in our study of pure boron clusters.\(^{51}\) We further calculated the equilibrium bond lengths and vibrational frequencies of TM (TM = Hf, Ta, W, Re, Os) dimer under the different basis sets and found that the def2-TZVP basis set is more suitable for TM atom (see Table S1†). Therefore, PBE0 functional combined with 6-311G* basis set for B and def2-TZVP basis set for TM atoms were chosen for our systems. Furthermore, chemical bonding analyses were performed utilizing the adaptive natural density partitioning (AdNDP 2.0) program.\(^{52}\)

3. Results and discussion

3.1. Lowest energy structures of TM$_4$B$_{18}$$^{0/−}$ (TM = Hf, Ta, W, Re, Os)

The optimized lowest energy structures of neutral TM$_4$B$_{18}$ (TM = Hf, Ta, W, Re, Os) clusters and corresponding anionic species, along with their point group symmetries with 0.1 Å tolerance, are presented in Fig. 1. More information about the low-lying isomer structures is given in Fig. S1 of the ESI.† The summary of the structural and electronic properties of the ground state in both neutral and anionic series is listed in Table 1. All ground states are found to be singlet or doublet with exception of the Re$_4$B$_{18}$ cluster, which has the triplet states of spin multiplicity.

As shown in the upper panel of Fig. 1, the lowest energy configuration of the neutral Hf$_4$B$_{18}$ has $D_2$ symmetry and it is composed of four twisted umbrella-like Hf@B$_4$ units by sharing the B atoms on their rings. The distances between the Hf atoms are in the range of 3.132 to 3.560 Å, and the average bond length between metal atoms ($R_{\text{TM–TM}}$) is 3.346 Å. The bonding lengths between each Hf atom and its neighboring B atoms are in

Fig. 1 The lowest energy structures of TM$_4$B$_{18}$ (TM = Hf, Ta, W, Re, Os) clusters (upper panel) and corresponding anionic clusters (lower panel). The point group symmetry of each cluster is presented in parentheses. The blue and pink spheres are TM and B, respectively.
The inorganic chemistry of metal boron clusters (MxBy, TM = Hf, Ta, W, Re, Os) is presented. The structural and electronic properties of these clusters are discussed, focusing on the bonding and electronic structures.

Between 2.378 and 2.458 Å, and the average bond length between metal atom and B (R_{TM-B}) is 2.419 Å. The distances between B atoms are in the range of 1.533 and 1.783 Å, which is smaller than that of the B=B double bond (1.56 Å) and the largest value is longer than that of the B-B single bond (1.70 Å). Moreover, the bonding length between B atoms are in the range of 1.564 to 1.766 Å and the average is 1.629 Å. For Re_{4B18}, compared with the previously reported planar molecular wheel Re@B_{9}^{2+}, we find that the bonding length of Re_{4B18} (1.568–1.694 Å) between adjacent B atoms is longer than the Re@B_{9} (1.543–1.571 Å) at the PBE0 levels.

The optimized structure of Os_{4B18} is a hollow cage-like structure with C_{2v} symmetry, which is different from the other TM_{4B18} (TM = Hf, Ta, W, Re, Os) clusters. The Os_{4B18} is insufficient to support the large spherical B skeleton due to the further reduction of metal atomic radius. Therefore, the lowest energy structure of cage-like Os_{4B18} is assembled by two types of planar molecular wheels of Os@B_{7} and Os@B_{8}, and the Os atoms on cage surface with the coordination numbers (CN) are 7 and 8. Moreover, the bonding length between B atoms is in the range of 1.564 to 1.766 Å, and the average (R_{B-B}) is 1.681 Å, which is very close to the single bond value. The bonding lengths between each Os atom and its neighboring B atom are in the range of 2.104–2.250 Å, and the R_{B-B} is 2.170 Å. It can be seen from Table 1 that the average distance between Os and B atoms (R_{TM-B}) becomes shorter rapidly when the size of metal atom decreases, which leads to a tighter bond between the TM and B atom. The coordinates of the lowest energy structures of TM_{4B18} (TM = Hf, Ta, W, Re, Os) are listed in Table S2 of the ESI.

All corresponding global minima of anionic clusters are exhibited in the lower panel of Fig. 1. The geometric structures of TM_{4B18}^{-} (TM = Hf, Ta, W, Re, Os) are very similar to their corresponding neutral clusters. However, owing to the Jahn–Teller effect, the capture of one additional electron results in the low point group symmetries for Hf and Ta. The lowest energy structure of Hf_{4B18}^{-} has C_{2} symmetry, and each Hf atom transfers fewer electrons (1.007 [e]) to the B_{18} skeleton than the neutral. The structures of TM_{4B18}^{-} (TM = Ta, W, Re) are very similar like the neutral ones and consist of planar molecular wheels of the TM@B_{9} unit. However, compared with the
corresponding neutral clusters, their $R_{TM-TM}$ is shorter and $R_{B-B}$ is slightly longer. NPA shows each TM atom donates electrons to the B$_{18}$ skeleton in the range of $-0.189$ [e] to $0.383$ [e], which forms the typical covalent bonds. The structure of Os$_5$B$_{18}$ (C$_{2h}$) is also a hollow cage-like structure, its $R_{TM-B}$ and $R_{B-B}$ are little changed. The coordinates of all anionic clusters are listed in Table S3 of the ESI.† The TM$_4$B$_{18}$ (TM = Hf, Ta, W, Re, Os) clusters can be thought that they are constructed with four TM doped B wheel units by sharing B atoms. This approach could be a new pathway to produce various TM doped B cluster structures.

To gain a better understanding of the stability of these nanoclusters, we further examined the electronic properties. The binding energies per atom ($E_b$) is regarded as an effective parameter to evaluate the thermodynamic stability of a cluster, which is calculated by

$$E_b = (4E_{TM} + 18E_B - E_{TM,B_{18}^-})/22$$

(1)

In the eqn (1), $E_{TM,B_{18}^-}$, $E_{TM}$ and $E_B$ represent the total energy of TM$_4$B$_{18}$ (TM = Hf, Ta, W, Re, Os) clusters, a TM atom, and a B atom, respectively. Here, the larger $E_b$ value implies the more favorable thermodynamic stability of a cluster. In neutral clusters, the W$_4$B$_{18}$ has a maximum $E_b$ value of 6.16 eV, while the Hf$_4$B$_{18}$ has a minimum $E_b$ value (5.80 eV). The $E_b$ values of TM$_4$B$_{18}$ (Ta, W, Re) are larger than those of others, so these clusters have a higher thermodynamic stability. The same trend is observed for the corresponding anions. As a reflection of the energy cost for an electron jumping from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the HOMO–LUMO energy gap ($E_{HL}$) can reveal the chemical stability of a cluster. In comparison with cage-like Ta$_3$B$_{12}$ which possess a $E_{HL}$ of 2.50 eV with three equivalent Ta@B$_8$ octagons sharing two eclipsed B$_3$ triangles at the top and bottom interconnected by three B$_2$ units on the waist, the lowest energy structures of Hf$_4$B$_{18}$ and Ta$_4$B$_{18}$ possess a large $E_{HL}$ of 2.60 and 2.61 eV, respectively, being less chemically reactive than others. For all anionic clusters, due to the trapping of an electron, the $E_{HL}$ of these species is decreased and significantly less than the neutral clusters. Among them, the W$_4$B$_{18}^-$ cluster has the largest $E_{HL}$ value of 1.87 eV, while the $E_{HL}$ of the Re$_4$B$_{18}^-$ cluster is the smallest, only 1.37 eV. Moreover, vibrational frequency calculations confirm that there are no imaginary frequencies for all these ground-state structures, and the corresponding lowest frequencies are listed in Table 1.

### 3.2. Bonding analysis

The structural and electronic properties of TM$_4$B$_{18}$ (TM = Hf, Ta, W, Re, Os) nanoclusters show that the neutral Ta$_4$B$_{18}$ and Hf$_4$B$_{18}$ clusters are chemically more inert than the others (larger $E_{HL}$) but relatively the Ta$_4$B$_{18}$ has larger $E_b$ (thermodynamically more stable) than Hf$_4$B$_{18}$. Based on this analysis, we further investigate the bonding properties of the Ta$_4$B$_{18}$ cluster. The molecular orbital (MO) energy-level diagram and the relevant MOs of Ta$_4$B$_{18}$ derived from the Ta$_4$ moiety and B$_{18}$ skeleton, which is presented in Fig. 2. It shows the interactions between the orbitals of the four Ta atoms and the group orbitals of the B$_{18}$ skeleton.

![Fig. 2. The Kohn–Sham molecular orbital correlation diagram for Ta$_4$B$_{18}$. It shows the interactions between the orbitals of the Ta$_4$ atoms and the group orbitals of the B$_{18}$ skeleton.](Image)

Fig. 2. The Kohn–Sham molecular orbital correlation diagram for Ta$_4$B$_{18}$. It shows the interactions between the orbitals of the Ta$_4$ atoms and the group orbitals of the B$_{18}$ skeleton.
(σ) bonds, 4 equivalent Ta (dxy)–B9 (σ) bonds, and 4 equivalent Ta (dz2)–B9 (π) bonds. As shown in the bottom row of Fig. 3, there are 9 totally delocalized 22c–2e bonds distributed on the entire spherical skeleton with ON = 2.00 |e|. Among them, 6 are σ and the other 3 are π bonds. Therefore, the Ta4B18 cluster has 10 delocalized σ bonds in total (4 equivalent 3c–2e σ bonds plus 6 equivalent 22c–2e bonds), leading to the σ antiaromaticity according to 4n (n = 5) Hückel’s rule. Meanwhile, the 3 totally delocalized π-bonds (22c–2e bonds) satisfies the Hückel rules of 4n + 2 (n = 1) of π aromaticity. Thus, Ta4B18 is a conflicting aromatic system with 20 σ and 6 π totally delocalized electrons. Note that 50 skeletal electrons are distributed on the cage surface is a magic number for a closed-shell three-dimensional spherical structure in which the 25 delocalized orbitals are completely filled with electron pairs leading to a closed-shell 1S21P61D102S21F142P62D10 configuration.

Fig. 3 AdNDP bonding patterns of Ta4B18, with the occupation numbers (ON).

Fig. 4 The simulated photoelectron spectra of TM4B18− (TM = Hf, Ta, W, Re, Os) clusters.
3.3. Simulated photoelectron spectra of TM$_4$B$_{18}^-$ (TM = Hf, Ta, W, Re, Os)

Photoelectron spectra (PES) can be used as the fingerprints about the electronic structures of nanoclusters. Therefore, we simulated the PES of TM$_4$B$_{18}^-$ (TM = Hf, Ta, W, Re, Os) anionic clusters, hoping to help experimentally determine these lowest energy structures.

First, we consider the simulated PES of Ta$_4$B$_{18}^-$ and Re$_4$B$_{18}^-$ by comparing with the experimentally reported of Ta@B$_9$ and Re@B$_9$. As displayed in Fig. 4, the spectral features are labeled X, A, B, etc. In each spectrum, the X peak represents the vertical detachment energy (VDE) which denotes the transition from the anionic ground-state to the neutral ground-state, and the other (A, B, etc.) peaks indicate transitions to the excited state of the neutral complexes. The VDE of Ta$_4$B$_{18}^-$ is approximately 2.77 eV. After this first peak, there are five peaks between 3.5 eV and 5.5 eV. In the experimental spectrum of Ta@B$_9$, the first X peak is located at around 3.64 eV, indicating the structure of Ta$_4$B$_{18}^-$ assembled by Ta@B$_9$ has the lower electron binding energy. For the simulated spectrum of Re$_4$B$_{18}^-$, the first two peaks are somewhat weak and close each other. The experimental PES of Re@B$_9$ also shows two close peaks at 4.02 eV and 4.34 eV, respectively. These lower binding energies of Re$_4$B$_{18}^-$ are similar to those of Ta$_4$B$_{18}^-$ by comparison with the experimental results. Presumably, this is caused by the interaction between planar molecular unit wheels (Ta@B$_9$ and Re@B$_9$).

The PES of Hf$_4$B$_{18}^-$ is simulated and shows a compact spectral pattern, and the first peak is approximately 2.16 eV, following by four consecutive peaks of the same intensity. There are four major peaks (X, A, B, C) of the simulated spectrum of W$_4$B$_{18}^-$, and the VDE is approximately 3.19 eV. The simulated spectrum of Os$_4$B$_{18}^-$ also presents a compact spectral pattern with a VDE of 3.02 eV. To provide detailed data for the future experiment, we further calculated the vertical ionization potentials (VIP) and vertical electron affinities of neutral clusters, and adiabatic detachment energy (ADE) of anionic clusters, which are shown in Table 2. The W$_4$B$_{18}^-$ shows a larger VIP value (7.52 eV) and VEA value (2.82 eV) than others. The Re$_4$B$_{18}^-$ shows a larger ADE value of 3.07 eV than others. However, the spherical Ta$_4$B$_{18}^-$ has a large VIP value (7.37 eV) and a moderate VEA value (2.46 eV).

4. Conclusion

We carried out an unbiased search for the lowest energy structures of TM$_4$B$_{18}^{0/-}$ clusters (TM = Hf, Ta, W, Re, Os). The structural analysis shows that they are composed of the four planar molecular TM@B$_9$ wheel units sharing the B atoms except for Os$_4$B$_{18}^{0/-}$, which has a hollow cage-like structure assembled by two types of planar molecular wheels of Os@B$_7$ and Os@B$_8$ due to the reduction of the atomic radius. According to the electronic properties, spherical Ta$_4$B$_{18}^-$ has a large $E_S$ and $E_{HL}$. The chemical bonding analyses showed that it has the π antiaromaticity with 4n ($n = 5$) and π aromaticity with 4n + 2 ($n = 1$) from Hückel’s rule, resulting in a conflicting aromatic system. Finally, the PES of all anionic clusters was simulated which provides predictive information for future experimental investigations.

Conflicts of interest

There are no conflicts to declare.

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