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Geometrical requirements for transition-metal-centered aromatic boron wheels: the case of VB_{10}^{-} [†]

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A class of transition-metal-centered aromatic boron wheels $(D_{nh}-M \odot B_n^{q-})$ have been recently produced and characterized according to an electronic design principle. Here we investigate the interplay between electronic and geometric requirements for the molecular wheels using the case of VB₁₀⁻, which is isoelectronic to the decacoordinated molecular wheels, Ta $\odot B_{10}^{-}$ and Nb $\odot B_{10}^{-}$. Photoelectron spectra of VB₁₀⁻ are observed to be broad and complicated with relatively low electron binding energies, in contrast to the simple and high electron binding energies observed for the molecular wheels of its heavier congeners. An unbiased global minimum search found the most stable isomer of VB₁₀⁻ to be a singlet "boat"-like structure (C₂), in which the V atom is coordinated to a quasi-planar B₁₀ unit. A similar triplet C_{2v} boat-like isomer is found to be almost degenerate to the C₂ structure, whereas the beautiful molecular wheel structure, D_{10h}-V \odot B₁₀⁻, is significantly higher in energy on the potential energy surface. Therefore, even though the VB₁₀⁻ system fulfills the electronic requirement to form a D_{10h}-M \bigcirc B₁₀⁻ aromatic molecular wheel, the V atom is too small to stabilize the ten-membered boron ring.

1. Introduction

Boron is known to form planar or quasi-planar two-dimensional (2D) clusters (B_n) for an extended size range due to its ability to participate in both localized and delocalized bonding.¹⁻¹⁰ Photoelectron spectroscopy (PES) studies combined with high level ab initio calculations have shown that anionic boron clusters remain planar with up to at least 21 atoms (\mathbf{B}_{21}) , the largest boron cluster characterized both experimentally and theoretically.¹¹ All planar boron clusters are shown to consist of a peripheral ring and one or more inner atoms, where the peripheral ring features classical two-center-two-electron (2c-2e) localized σ bonds, while the inner atoms bond to the outer ring almost exclusively via delocalized multi-center-two-electron (nc-2e) σ and π bonds. The same chemical bonding principles can be applied to rationalize the structures of the planar neutral $(n \le 19)^{7,12}$ and cationic $(n \le 15)^{13}$ boron clusters. Amongst the planar boron clusters, $B_8^{2-}(D_{7h})$ and $B_9^{-}(D_{8h})$ exhibit highly symmetric wheel structures with one central boron atom.3,14 Chemical bonding analyses of the B_8^{2-} and B_9^{-} clusters, using both molecular orbitals (MO) and the Adaptive Natural Density Partitioning (AdNDP) technique,¹⁵ showed that the two systems each have 12 electrons participating in the delocalized

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bonding: equal to one electron from each peripheral boron atom plus all three valence electrons from the central boron atom and the excess electrons from the negative charge. More interestingly, it was found that the delocalized electrons participate equally in delocalized σ and π bonds, rendering these clusters doubly aromatic (σ + π) with enhanced stability.¹⁶

Based on the bonding model established for B_8^{2-} and B_9^{-} , where the key feature is the double ($\sigma + \pi$) aromatic characters with 6σ and 6π delocalized bonding electrons, we advanced an electronic design principle for transition-metal-centered aromatic boron ring clusters of the form D_{nb} -M^(x) $\bigcirc B_n^{q-17}$ Briefly, 2n electrons are required for the 2c–2e σ bonds on the peripheral *n*-membered boron ring, $4N_1 + 2$ and $4N_2 + 2$ electrons are required for delocalized σ and π bonds, respectively, to fulfill the Hückel rule for aromaticity $(N_1, N_2 = 0, 1, 2, ...)$. The design principle simply states that the total number of electrons, needed for the B_n ring (2n) and the 12 electrons for the double aromaticity $(N_1 = N_2 = 1)$, must be equal to the total number of valence electrons, 3n + x + q (3n is the number of valence electrons of the boron atoms, x is the valence of the central metal atom M, and q is the charge of the molecular wheel), *i.e.*, n + x + q = 12. A series of wheel-type metal-doped boron clusters have been theoretically investigated previously.¹⁸⁻²³ According to the design principle, we recently observed experimentally the first metal-centered aromatic boron wheels, D_{9h} -Ru \bigcirc B₉⁻ and D_{8h} -Co \bigcirc B₈⁻ in a combined photoelectron spectroscopy and *ab initio* study.¹⁷ For these systems, $N_1 = N_2 = 1$ and therefore Ru has a formal valence of II and Co has a

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formal valence of III. Two nine-membered molecular wheels, D_{9h} -Rh \bigcirc B₉ and D_{9h} -Ir \bigcirc B₉, were reported subsequently as the first examples of neutral molecular wheels.²⁴ The largest molecular wheels that have been found to date are the decacoordinated Ta \bigcirc B₁₀⁻ and Nb \bigcirc B₁₀⁻ clusters, in which $N_1 = 2$ and $N_2 = 1$ for a total of 16 delocalized electrons to fulfill double aromaticity.^{25,26} In the photoelectron spectrum of NbB₁₀⁻, we observed minor contributions from a low-lying C_{2v} "boat"-like structure, suggesting it is energetically close to the global minimum D_{10h} -Nb \bigcirc B₁₀⁻ molecular wheel, whereas for TaB₁₀⁻, the Ta \bigcirc B₁₀⁻ molecular wheel is overwhelmingly favored.²⁵

The change in the relative stability of the low-lying isomers of TaB_{10}^{-} and NbB_{10}^{-} prompted us to further investigate the effects of the atomic size of the transition metal on the stability of the molecular wheels using the valence isoelectronic substitution of Ta and Nb by V. The VB₁₀⁻ cluster fulfills the electronic design principle to form a doubly aromatic $V \otimes B_{10}^{-1}$ molecular wheel. Indeed, a previous theoretical report showed that $V \otimes B_{10}^{-}$ was a minimum on the potential energy surface of $VB_{10}^{-.23}$ In the present study, we show that $V \odot B_{10}^{-}$ is a local minimum, which is significantly higher in energy above a "boat"-like three-dimensional structure, which was identified as the second low-lying isomer for NbB_{10}^{-} and TaB_{10}^{-25} We find that the molecular wheel D_{10h} -M \odot B₁₀⁻ becomes less favored going up the periodic table from Ta to V, as a result of decreasing atomic size. The current experimental and computational results demonstrate that the V atom is too small to stabilize the 10-membered boron ring.

2. Experimental methods

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic cluster source, details of which have been described previously.²⁷ Briefly, vanadium-doped boron clusters were produced by laser vaporization of a cold-pressed disk target containing $\sim 15\%$ (by mass) isotopically-enriched boron ¹¹B (96%) and $\sim 10\%$ V balanced by Bi, which acted as a binder and at the same time provided the Bi⁻ atomic anion calibrant for the PES apparatus. The clusters, entrained in a He carrier gas containing 5% Ar, underwent a supersonic expansion to form a collimated and vibrationally cold cluster beam. The negatively charged clusters were subsequently analyzed using a time-of-flight mass spectrometer. The VB10⁻ cluster of interest was mass-selected and decelerated before being photodetached by a probe laser, operated at either 193 nm (6.424 eV) from an ArF excimer laser, or 266 nm (4.661 eV) and 355 nm (3.496 eV) from a Nd:YAG laser. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Bi⁻, and the kinetic energy resolution of the apparatus was $\Delta E_k/E_k \sim 2.5\%$, *i.e.*, ~25 meV for 1 eV electrons.

3. Theoretical methods

The potential energy surface of the VB_{10}^{-} cluster was scanned for the global minimum and low lying isomers using the Cartesian Walking (CW) method,¹¹ modified to allow for multiple atom types. Briefly, the CW method uses a constrained random walking procedure on a grid of Cartesian points, placing one atom down at each step to generate trial structures that are then optimized using density functional theory (DFT) calculations with a gradient-based local optimization procedure. For the current work, grids with dimensions, $12 \times 12 \times 12$ and $16 \times 16 \times 16$, using a mesh of 0.32 Å (about 1/5 the length of the B–B diatomic bond), were created. Walks were constrained by allowing a maximum distance of about 2.3 Å per step and by rejecting all moves which placed an atom within 1.3 Å or less than any previously placed atoms. Optimization of roughly 600 trial structures was carried out at the PBEPBE²⁸/3-21G^{29,30} level of theory using a singlet spin multiplicity for each structure.

All isomers below 50 kcal mol⁻¹ relative to the global minimum at PBEPBE/3-21G were further optimized using the PBEPBE functional and the 6-311+G* basis set^{31,32} for boron and the Stuttgart'97 small core energy-consistent pseudopotential and basis set combination³³ for vanadium (PBEPBE/B/ 6-311+G*/V/Stuttgart'97). Vibrational frequencies were calculated to ensure that each structure was a minimum on the potential energy surface. All isomers within 50 kcal mol⁻¹ of the global minimum at PBEPBE/B/6-311+G*/V/Stuttgart'97 were then re-optimized at the same level of theory with triplet spin multiplicities. The lowest-lying isomers were also optimized with quintet spin multiplicities, but all were found to rise in energy.

Single point energy calculations at the CCSD(T)/B/6-311+G*/V/Stuttgart'97//PBEPBE/B/6-311+G*/V/Stuttgart'97 level of theory were carried out, including a T1 diagnostic test, to estimate possible multireference characters of the VB_{10} isomers. For the two lowest-lying isomers, we found T1 diagnostic values of 0.085 and 0.102, respectively, higher than the threshold value of 0.02,³⁴ suggesting that the VB₁₀⁻ system cannot be accurately described by single reference post-Hartree-Fock methods. Consequently, a number of density functional methods employing the hyper and pure generalized gradient approximations (GGA) and hybrid-GGA functionals were tested for the VB_{10}^{-} system. For each functional, the two lowest energy structures (isomers I and II) were geometrically relaxed at the DFT/B/6-311+G(d)/V/Stuttgart'97 level of theory starting from their optimized PBEPBE/B/6-311+G(d)/V/ Stuttgart'97 coordinates. Following the relaxation, the first vertical detachment energy (VDE) was calculated. Based on the accuracy of the first VDE as compared with the experimental data and minimal spin-contamination of the neutral species, we decided to further study the VB_{10}^{-} system using the PBEPBE and BP86^{35,36} functionals.

For VB₁₀⁻, the two lowest energy isomers are of similar geometry, but differing spin states (singlet and triplet). For both isomers, the first VDE value was calculated as the energy difference between the doublet neutral cluster and the anionic cluster at the relaxed anion geometry at the DTF/B/ $6-311+G^*/V/$ Stuttgart'97 level of theory. For the triplet isomers, the first quartet VDE was calculated as the energy difference between the lowest triplet anionic state and the lowest quartet neutral state at the anionic geometry. To approximate the higher VDEs of the final doublet states, the difference in energy of the highest occupied Kohn–Sham (KS) molecular orbital and the KS eigenenergies of the deeper alpha orbitals was added to the first doublet VDE value. Similarly, to approximate the VDEs of the higher quartet state, the difference in energy of the highest occupied beta KS molecular orbital and the deeper beta orbitals was added to the first quartet VDE. The calculated VDEs for the two lowest energy isomers at BP86 and PBEPBE levels of theory are given in Tables 1 and 2, where they are compared with the experimental results. All DFT and coupled cluster calculations were performed with the Gaussian09 software package.³⁷ The Molekel program³⁸ was used for molecular visualization.

4. Experimental results

The photoelectron spectra of VB_{10}^{-} are shown in Fig. 1 at three photon energies. The observed spectral features are labeled with letters (X, A, B, C, ...). The measured VDEs

Table 1 Observed vertical detachment energies (VDEs) from the photoelectron spectra of VB_{10}^{-} and comparison with theoretical calculations of the global minium isomer I (C_2 , ¹A)

Observed	VDE ^a	Final state electronic	VDE	(theo.)
feature	(exp.)	configuration	BP86	PBEPBE
\mathbf{X}^{b}	2.47 (5)	^{2}A 5 $h^{2}6a^{2}6h^{2}7a^{2}7h^{2}8h^{2}8a^{2}0a^{2}10a^{1}$	2.37	2.28
А	2.91 (4)	${}^{2}A$ ${}^{5}h^{2}6a^{2}6h^{2}7a^{2}7h^{2}9h^{2}9a^{2}0a^{1}10a^{2}$	2.90	2.80
В	3.27 (5)	^{2}A $^{5}h^{2}c^{2}ch^{2}7^{2}7h^{2}0h^{2}0h^{2}h^{2}10h^{2}10h^{2}$	3.24	3.15
С	4.16 (3)	^{2}B	4.06	3.94
D	4.96 (6)	^{2}B	4.74	4.64
		² A	4.80	4.70
Е	5.62 (6)	² B	5.24	5.14
		² A	5.33	5.21
		$ \sum_{a=1}^{a=1} \sum_{b=1}^{a=2} \sum_{a=1}^{a=2} \sum_{b=1}^{a=2} \sum_{b=1}^{a=2}$	5.41	5.33

^{*a*} The numbers in the parentheses represent the uncertainty in the last digit. ^{*b*} The adiabatic detachment energy of the ground state transition is measured to be 2.24 ± 0.08 eV.

are summarized in Table 1, where they are compared with theoretical calculations. The 355 nm spectrum (Fig. 1a) of VB_{10}^{-} displays three detachment bands: X, A, and B. Band X has a VDE of 2.47 eV without any fine features resolved. The adiabatic detachment energy (ADE) or the electron affinity of the neutral VB₁₀ is measured to be 2.24 ± 0.08 eV. Band A has a VDE of 2.91 eV, closely followed by band B with a VDE of 3.27 eV. All these features are broad even at 355 nm, indicating that there is either more than one detachment transition in each band or a large geometry change between the anionic and neutral cluster. The 266 nm spectrum (Fig. 1b) contains one sharp feature ("*") at a VDE of 3.77 eV and a broad band C at a VDE of 4.16 eV. Closely following band C, a shoulder labeled with "**" was observed at a VDE of 4.4 eV. Two additional bands are observed in the 193 nm spectrum (Fig. 1c), a broad band D at a VDE of 4.96 eV and band E at a VDE of 5.62 eV. Due to the low signal-to-noise ratios, no other detachment bands can be definitively identified in the higher binding energy side. The features labeled with * and ** are relatively weak and, as will be shown below, they do not belong to the global minimum, which gives rise to the main bands labeled with the letters.

Fig. S1 (ESI[†]) compares the 193 nm spectrum of VB_{10}^- with those of NbB_{10}^- and $TaB_{10}^{-.25}$ We note that the lower binding energy bands (X, A, B) of the VB_{10}^- spectrum are similar to the weak features (X', A', B') in the NbB_{10}^- spectrum, which came from the 3D boat-like low-lying isomer (C_{2v} , ${}^{1}A_{1}$).

5. Theoretical results and comparison with experiment

5.1. The structures and low-lying isomers of VB₁₀⁻

Fig. 2 presents all the calculated isomers of VB_{10}^- within 20 kcal mol⁻¹ of the global minimum at the BP86 and PBEPBE levels of theory. The singlet boat-like structure, isomer I, is found to be the global minimum of VB_{10}^- according to the BP86 functional. Isomer II, a C_{2v} triplet boat-like structure,

Table 2 Calculated vertical detachment energies (VDEs) for the low-lying isomer II of $VB_{10}^{-}(C_{2v}, {}^{3}A_{2})$ and possible contributions of this isomer to the observed photoelectron features

Observed feature	VDE (exp.)	Final state electronic configuration	VDE (theo.)	
			BP86	PBEPBE
		${}^{2}A_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{0}$	2.27	2.19
		${}^{2}A_{1} \dots 2b_{1} {}^{2}3b_{1} {}^{2}3b_{2} {}^{2}2a_{2} {}^{2}5a_{1} {}^{2}4b_{2} {}^{2}4b_{1} {}^{2}6a_{1} {}^{2}3a_{2} {}^{2}7a_{1} {}^{0}4a_{2} {}^{1}$	2.80	2.71
		${}^{4}A_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{1}7a_{1}^{1}4a_{2}^{1}$	2.93	2.75
		${}^{2}A_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{1}7a_{1}^{1}4a_{2}^{1}$	3.02	2.95
		${}^{4}A_{1} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	3.08	2.91
		${}^{2}A_{1} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{1}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	3.22	3.14
*	3.77 (3)	${}^{4}B_{1} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{1}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	4.15	3.97
**	~4.4	${}^{2}B_{1} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{1}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	4.29	4.23
		${}^{4}B_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{1}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	4.81	4.65
		${}^{2}B_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{2}4b_{2}^{1}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	4.91	4.76
		${}^{2}A_{1} \dots 2b_{1} {}^{2}3b_{1} {}^{2}3b_{2} {}^{2}2a_{2} {}^{2}5a_{1} {}^{1}4b_{2} {}^{2}4b_{1} {}^{2}6a_{1} {}^{2}3a_{2} {}^{2}7a_{1} {}^{1}4a_{2} {}^{1}$	4.94	4.76
		${}^{4}A_{1} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{2}5a_{1}^{1}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	5.05	4.90
		${}^{2}A_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{1}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	5.18	4.98
		${}^{4}A_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{2}2a_{2}^{1}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	5.29	5.09
		${}^{2}B_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{1}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	5.33	5.34
		${}^{4}B_{2} \dots 2b_{1}^{2}3b_{1}^{2}3b_{2}^{1}2a_{2}^{2}5a_{1}^{2}4b_{2}^{2}4b_{1}^{2}6a_{1}^{2}3a_{2}^{2}7a_{1}^{1}4a_{2}^{1}$	5.36	5.15
		${}^{4}B_{1} \dots 2b_{1}^{2}3b_{1}^{-1}3b_{2}^{-2}2a_{2}^{-2}5a_{1}^{-2}4b_{2}^{-2}4b_{1}^{-2}6a_{1}^{-2}3a_{2}^{-2}7a_{1}^{-1}4a_{2}^{-1}$	5.48	5.17



Fig. 1 Photoelectron spectra of VB_{10}^{-} at (a) 355 nm (3.496 eV), (b) 266 nm (4.661 eV), and (c) 193 nm (6.424 eV).

is only 0.45 kcal mol^{-1} higher than isomer I. The PBEPBE functional suggests the opposite ordering, with isomer II being slightly more stable than isomer I by 0.50 kcal mol^{-1} . Thus, these two isomers can be viewed as degenerate within the

accuracy of the theoretical methods and are both expected to contribute to the observed photoelectron spectra. The next higher-lying isomer is 7 kcal mol⁻¹ higher than the global minimum at the BP86 level and 15 kcal mol⁻¹ higher at the PBEPBE level, which is unlikely to be present in the supersonic cluster beam. The anticipated $V \odot B_{10}^{-1}$ wheel structure is found to be a much higher energy isomer, more than 13 kcal mol⁻¹ higher in energy than the global minimum at the BP86 level and 27 kcal mol⁻¹ at the PBEPBE level.

5.2. Isomer I (C_2 , ¹A)

The calculated VDEs at BP86 and PBEPBE levels of theory for isomer I are compared with the experimental VDEs in Table 1. Isomer I has a closed-shell electronic configuration $(^{1}A, C_{2})$ and only doublet final states are expected upon one electron detachment. The first electronic band corresponds to electron detachment from the highest occupied molecular orbital (HOMO) (10a, Table 1) of the ground state of the anion to produce the neutral ²A ground state. The calculated first VDE, 2.37 eV at the BP86 level and 2.28 eV at the PBEPBE level, is in good agreement with the experimental value of 2.47 eV. Optimization of the corresponding neutral cluster gives a structure with C_{2v} symmetry (Fig. 3c). The energy difference between the optimized neutral and anion vielded a calculated ADE value of ~ 2.2 eV at different levels of theory, in good agreement with the experimental ADE of 2.24 eV. The large difference between the ADE and VDE is a result of the geometry change between the anion and neutral ground states, consistent with the broad ground state PES band (X) (Fig. 1).

The second and third detachment channels correspond to electron removal from the HOMO-1 (9a) and HOMO-2 (8a), respectively. The VDEs calculated for these two detachment



Fig. 2 The low-lying structures of VB_{10}^- , their electronic states, point group symmetries, and relative energies at BP86 and PBEPBE DFT/B/ 6-311+G(d)/V/Stuttgart'97 levels of theory. All relative energies, given in kcal mol⁻¹, have been corrected for zero-point energies. The relative ordering, electronic states, and geometries are based on the BP86 calculations.



Fig. 3 Comparison of the detailed structures of (a) the global minimum isomer I (¹A, C_2) and (b) the low-lying isomer II (³A₂, C_{2v}) with that of their optimized neutral (²A₁, C_{2v}) (c). Selected V–B distances are given in Å. Only distances below 2.24 Å are shown. All structures are from the BP86/6-311+G(d)/V/Stuttgart'97 level of theory.

channels are 2.90 and 3.24 eV at the BP86 level, in excellent agreement with features A (2.91 eV) and B (3.27 eV). Electron detachment from HOMO-3 (8b) results in a calculated VDE of 4.06 eV, agreeing well with band C at 4.16 eV. The next two detachment channels were calculated to have very close VDEs at 4.74 and 4.80 eV (BP86), comparing well to the broad band D at 4.96 eV. The VDEs of the next three detachment channels are calculated also to be close, at 5.24, 5.33, and 5.41 eV (BP86), consistent with band E or possible features not definitively identified beyond band E in the higher binding energy region (Fig. 1).

The calculated VDEs at the BP86 level are fitted with Gaussians to produce a simulated spectrum, as shown in Fig. 4a, displaying pictorially the good agreement with the experimental spectrum (Fig. 4c). This good agreement lends considerable credence that the closed-shell C_2 boat-like 3D structure I is the global minimum of VB₁₀⁻.

5.3. Isomer II $(C_{2v}, {}^{3}A_{2})$

Isomer II has an open-shell electronic configuration $({}^{3}A_{2}, C_{2y})$ and both doublet and quartet neutral states are expected to be produced upon one electron detachment. The calculated VDEs are given in Table 2 at BP86 and PBEPBE levels of theory. The first VDE is calculated to be 2.27 eV (BP86) and 2.19 eV (PBEPBE), which are lower than the first VDE of isomer I and are not in good agreement with the experiment. However, this isomer may contribute to the lower binding energy tail in the PES spectra (Fig. 1). Geometry optimization of the doublet neutral ground state led to the structure as that derived from isomer I. There is little structure change between isomer II (Fig. 3b) and its corresponding neutral state (Fig. 3c). Thus, relatively sharp detachment transitions are expected from isomer II. The sharp peak labeled as "*" does not correspond to any detachment channel from isomer I and may come from isomer II. Our calculation shows that detachment from HOMO-4 produces a ${}^{4}B_{2}$ final state with a VDE of 4.15 eV (BP86), which is the closest to the "*" feature. Detachment from the same orbital also produces a low-spin ${}^{2}B_{2}$ state with a VDE of 4.29 eV, which may account for the feature labeled as "**" at 4.4 eV (Fig. 1). The calculated VDEs



Fig. 4 Simulated spectra of (a) isomer I and (b) isomer II at the BP86/B/6-311+G(2df)/V/Stuttgart'97 level of theory, compared with (c) experimental spectrum at 193 nm. The simulated spectra were generated by fitting the calculated VDEs given in Tables 1 and 2 with Gaussian functions of 0.08 eV width.

in Table 2 for isomer II are fitted with Gaussians to produce a simulated spectrum, as shown in Fig. 4b. Clearly, most of the features from isomer II would be buried in the more dominating spectral features of isomer I and we cannot rule out minor contributions of this isomer to the observed PES spectra. The weak features "*" and "**" are likely evidence of the presence of isomer II. These observations suggest that the BP86 energies are in better agreement with the experiment, *i.e.*, the closed-shell C_2 boat structure should be the global minimum of VB₁₀⁻ and the triplet C_{2v} structure is a low-lying isomer.

6. Chemical bonding in VB_{10}^{-}

The global minimum of VB_{10}^{-} (¹A, C_2) can be viewed as a V atom coordinated by a B_{10} unit. The B_{10} moiety has the same atomic connectivity of the quasi-planar bare B_{10}^{-} cluster,⁵ but is bent and distorted due to the interaction with the V atom. Fig. 3 compares the structures of isomers I and II with that of the neutral. In the global minimum isomer I, the V atom is bonded with six boron atoms with V–B distances less than 2.2 Å, whereas isomer II only features four such V–B bonds. The stronger interaction between V and the B_{10} moiety in isomer I is the origin of its higher stability. The neutral VB₁₀ cluster has nearly identical structures as isomer II with very slight changes of the four V–B bond lengths. On the other hand,



HOMO-12 (4a) HOMO-13 (3a) HOMO-14 (2a) HOMO-15 (2b) HOMO-16 (1b) HOMO-17 (1a)

Fig. 5 Valence canonical molecular orbitals for the global minimum isomer I (C_2 , ¹A) of VB₁₀⁻ at the BP86/B/6-311+G(d)/V/Stuttgart'97 level. Three different views are presented for each orbital for better visualization.

there are substantial structural changes between the global minimum isomer I and the neutral cluster, consistent with the broad PES transitions.

Fig. 5 depicts the MO pictures of the VB_{10}^{-} (¹A, C_2) global minimum. The 3D structure makes it difficult to visualize the MOs and, thus, three different views of each MO are shown in Fig. 5. Orbital composition analyses show that the HOMO has a large electron density between V and the two closest B atoms (B4 and B8, Fig. 3a). Detaching one electron from this orbital weakens the interaction between V and the two boron atoms, leading to the C_{2v} neutral structure, in which the V–B4 and V–B8 distances are significantly increased. The HOMO–1 and HOMO–2 also have large contributions from vanadium with contributions of 45.8% and 40.3%, respectively. The contributions of V to the other MOs are minor and therefore the remaining MOs in VB₁₀⁻ are quite similar to their counterparts in the pure B₁₀ cluster.⁵

7. Geometrical requirements for metal-doped aromatic boron wheels

The global minimum 3D structure of VB_{10}^{-} is similar to the lowest-lying second isomer of TaB_{10}^{-} and NbB_{10}^{-} .²⁵ For TaB_{10}^{-} , this boat-like 3D isomer is 8.6 kcal mol⁻¹ higher in energy than the global minimum $Ta \odot B_{10}^{-}$ molecular wheel, whereas in NbB_{10}^{-} the boat-like 3D isomer is only 5.4 kcal mol⁻¹ higher and became accessible experimentally (Fig. S1b, ESI†). In VB_{10}^{-} , however, the boat-like 3D structure becomes the global minimum and the $V \odot B_{10}^{-}$ molecular wheel becomes significantly unstable, even though it fits with our electronic design principle for forming the doubly aromatic molecular wheel. We see a systematic destabilization of the $M \odot B_{10}^{-}$ molecular wheel going up the periodic table from Ta to V due to the decreasing atomic size. The smaller atomic size and its more contracted 3d orbitals make V energetically unfavorable to fit inside a B_{10} ring. Thus, both the electronic design principle and the atomic sizes must both be taken into account when designing metal-centered boron wheels. The larger early 5d elements should be more favorable to stabilize larger boron rings, whereas the late 3d transition metals are expected to be better suited to form smaller metal-doped boron wheels. Hence, the $Ta \odot B_{10}^{-}$ and $Nb \odot B_{10}^{-}$ systems may be the largest metal-doped boron wheels to be expected for transition metals.²⁶ Even larger metal-doped boron wheels may require consideration of lanthanide or actinide elements.

8. Conclusions

We have carried out an experimental and theoretical study on the VB₁₀⁻ cluster to investigate the geometric requirement for the design of transition-metal-centered aromatic molecular wheels. Photoelectron spectra were obtained for VB₁₀⁻ and compared with theoretical calculations. A 3D boat-like structure featuring V interacting with a B₁₀ unit is found to be the global minimum for VB₁₀⁻. The V \odot B₁₀⁻ molecular wheel is a much higher energy isomer, even though it fits with the electronic design principle to form the doubly aromatic wheel structure. Combining the current study with recent works on other M \odot B_n^{k-} wheel-type clusters,^{17,24,25} we conclude that 3d transition metals are suitable for eight- and nine-membered boron ring wheel structures, but they are too small for tenmembered boron ring species.

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