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Geometric and electronic factors in the rational design of transition-metal-centered boron molecular wheels

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The effects of the electronic and geometric factors on the global minimum structures of MB₉⁻ (M = V, Nb, Ta) are investigated using photoelectron spectroscopy and *ab initio* calculations. Photoelectron spectra are obtained for MB₉⁻ at two photon energies, and similar spectral features are observed for all three species. The structures for all clusters are established by global minima searches and confirmed by comparison of calculated and experimental vertical electron detachment energies. The VB₉⁻ cluster is shown to have a planar C_{2v} V \odot B₉⁻ structure, whereas both NbB₉⁻ and TaB₉⁻ are shown to have C_s M \odot B₉⁻ type structures with the central metal atom slightly out of plane. Theoretical calculations suggest that the V atom fits perfectly inside the B₉ ring forming a planar D_{9h} V \odot B₉²⁻ structure, while the lower symmetry of V \odot B₉⁻ is due to the Jahn-Teller effect. The Nb and Ta atoms are too large to fit in the B₉ ring, and they are squeezed out of the plane slightly even in the M \odot B₉²⁻ dianions. Thus, even though all three M \odot B₉²⁻ dianions fulfill the electronic design principle for the doubly aromatic molecular wheels, the geometric effect lowers the symmetry of the Nb and Ta clusters. *Q* 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4798935]

I. INTRODUCTION

Atomic clusters not only exhibit size and shape dependent properties, but also provide a rich source to discover novel structures and chemical bonding, which allow rational design of molecules and nanostructures with tailored physical and chemical properties. A major goal of our research in the past decade has been the elucidation of the structure and chemical bonding of negatively charged boron clusters, B_n^- , using photoelectron spectroscopy (PES) and *ab* initio studies.¹⁻¹⁰ The prevalence of planar or quasi-planar (2D) structures for an extended range of cluster sizes (n \leq 23 for anions,¹⁰ n < 20 for neutrals,⁴ and n < 16 for cations¹¹) can be traced to the electron deficient character of the boron atom and its propensity for delocalized multicenter chemical bonds.¹² As a result, all planar boron clusters consist of a peripheral ring formed of 2c-2e (two-center two-electron) σ bonds and one or more inner atoms bonded to the outer ring by delocalized σ and π bonds, giving rise to aromatic or antiaromatic boron clusters and all-boron hydrocarbon analogues.^{2,6,7} More recent computational studies reaffirmed the planarity and the aromaticity of the small boron clusters.^{13–17} More interestingly, planar B₆ rings have been observed to be major structural features in recently synthesized transition metal boride compounds,^{18,19} suggesting that planar boron clusters can indeed become potential ligands or material building blocks, as proposed previously.⁵

Two of the boron cluster anions, B_9^- and B_8^{2-} , have highly symmetric (D_{nh}) wheel-type structures.^{1,3} Chemical bonding analyses using the Adaptive Natural Density Partitioning (AdNDP) algorithm²⁰ revealed that both clusters are doubly aromatic with 6 π and 6 σ electrons, thus, fulfilling the Hückel rule for σ and π aromaticity ($4N_{\pi} + 2$ and $4N_{\sigma}$ + 2 electrons, $N_{\pi}, N_{\sigma} \ge 0$). Based on the bonding model developed for B_8^{2-} (or $B \odot B_7^{2-}$) and B_9^- (or $B \odot B_8^{-}$),²¹ we advanced an electronic design principle for transition metal centered monocyclic boron clusters.^{22,23} In essence, the design principle can be reduced to a simple electron counting rule, where the total number of valence electrons in $M \odot B_n^{q-}$ needs to satisfy the relationship

$$3n + q + x = 2n + 12$$
 or $n + q + x = 12$, (1)

where *x* is the formal valence of the transition metal, *q* is the charge, and *n* is the size of the boron ring. The sum on the right hand side of the first form of Eq. (1) represents the number of electrons required for *n* peripheral B–B bonds (2*n* electrons) and two (σ and π) aromatic systems (2×6 electrons). The design principle was successfully applied to two boron ring sizes, *n* = 8, 9: Co©B₈⁻ (*x* = 3) and Ru©B₉⁻ (*x* = 2),²² Rh©B₉ (*x* = 3) and Ir©B₉ (*x* = 3),²⁴ and Fe©B₉⁻, were previously calculated as the global minima on their potential energy surfaces.^{26,27} Several other main-group element and transition-metal-centered boron rings were investigated theoretically before, but none was shown to be the global minimum.^{28–35}

According to the design principle, a valence-I transition metal (x = 1) is required to stabilize a 10-membered boron ring. However, previous studies showed that the valence-I Au atom binds covalently to the periphery of a planar B₁₀ motif in AuB₁₀⁻ and that Au $(\mathbb{B}B_{10})$ ⁻ is only a high energy isomer.³⁶ The existence of M $(\mathbb{C}B_{10})$ ⁻ wheel-type clusters was

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discovered in Ta \bigcirc B₁₀⁻ and Nb \bigcirc B₁₀^{-.37} The bonding situation for these doubly (σ and π) aromatic clusters is slightly different from that encountered previously, as they both have 10 σ -delocalized electrons ($N_{\sigma} = 2$ in the $4N_{\sigma} + 2$ Hückel rule), even though they have the same six π delocalized electrons. Hence, all valence electrons of the metals participate in delocalized bonding, with no lone pairs.³⁷ A modified electronic requirement for this type of molecular wheels is

$$3n + q + x = 2n + 16$$
 or $n + q + x = 16$. (2)

However, we have found that the fulfillment of the electronic requirement is not sufficient for achieving a perfectly planar molecular wheel: the geometric or steric constraints need also to be considered. In our previous work with 8and 9-membered boron rings, we found that valence isoelectronic substitution of the central atom by larger atoms leads to clusters where the metal atoms lie above the ring $(C_{nv}$ symmetry).^{22,24} More significant structural changes were observed upon valence isoelectronic substitution by smaller atoms in the B_{10} ring systems $M \odot B_{10}^{-}$. Two isomers were found to compete for the global minimum of the MB10⁻ (M = V, Nb, Ta) series: the M©B₁₀⁻ and a "boat"-like isomer.^{37,38} The energy difference between the isomers decreased with the decrease of atomic size and, as a consequence, $V(c)B_{10}^{-}$ became an extremely high energy isomer relative to the "boat"-like global minimum isomer, even though it fulfills the modified electronic design principle given by Eq. (2).^{23,38}

In order to better understand the relationship between the electronic and the geometric constraints on the stability of metal-centered wheel-type boron clusters, here we investigate a new group of clusters, MB9⁻, MB9, and MB9²⁻ (M = V, Nb, Ta). Photoelectron spectra of the MB_9^- species are obtained and theoretical calculations are carried out for species of all three charge states. Global minimum searches were performed for the MB₉⁻ species. The structures of the neutral and doubly charged clusters were obtained by following imaginary mode(s) revealed in the respective D_{9h} geometry optimizations and frequency calculations. We find that the MB_9^{2-} species are all closed shell and fulfill the electronic design principle, but only V(\hat{c})B₉²⁻ possesses the perfect D_{9h} molecular wheel structure, whereas $Nb(c)B_9^{2-}$ and $Ta(c)B_9^{2-}$ both have C_{9v} structures because of the slightly larger atomic sizes of Nb and Ta. All the neutral MCB9 clusters are found to be in a triplet state with C_{9v} symmetry, whereas all the $M(\hat{c})B_9^-$ species have lower symmetries due to the Jahn-Teller effect. These clusters provide the opportunity for understanding the electronic and geometric requirements for designing metal-centered aromatic boron wheel clusters and the relationship between spectroscopy, bonding, and structures of the new class of borometallic complexes.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Photoelectron spectroscopy

The experiment was performed using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, as described in detail previously.^{39,40} Briefly, the

metal-doped boron clusters were produced by laser vaporization of a disk target made of isotopically enriched ¹¹B and V or Nb or Ta. The clusters were entrained by a He carrier gas seeded with 5% Ar and underwent a supersonic expansion to form a collimated molecular beam. The composition and cooling of the clusters were controlled by the time delay between the carrier gas pulse and the ablation laser pulse.^{41,42} Negatively charged clusters were extracted and analyzed with a time-of-flight mass spectrometer. The species of interest were mass-selected and decelerated before being photodetached by a pulsed laser beam at 193 nm (6.424 eV) from an ArF excimer laser or 266 nm (4.661 eV) from a Nd: YAG laser. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. The spectra were calibrated with the known spectra of Bi⁻. The kinetic energy resolution of the apparatus, $\Delta Ek/Ek$, was better than 2.5%, i.e., \sim 25 meV for 1 eV electrons.

B. Computational methods

The search for the global minimum structures of VB9⁻, NbB9⁻, and TaB9⁻ was performed using the Coalescence Kick (CK) method.⁸ The initial CK search was performed using the PBE0 hybrid density functional^{43–45} and the LANL2DZ basis set.⁴⁶ Low energy isomers $(\Delta E < 50 \text{ kcal mol}^{-1})$ found at the PBE0/LANL2DZ level were reoptimized with subsequent frequency calculations at the PBE0/M/Stuttgart⁴⁷/B/aug-cc-pVTZ^{48,49} level for NbB₉⁻ and TaB₉⁻ and the ROPBE0/V/Stuttgart/B/augcc-pVTZ level for VB₉⁻. Figures S1–S3 in the supplementary material⁵⁰ display all the optimized structures. Single-point energy calculations for all the MB₉⁻ species were performed using the restricted openshell coupled cluster method ROCCSD(T),⁵¹⁻⁵⁴ at the ROCCSD(T)/M/Stuttgart/B/aug-cc-pVTZ level. Vertical detachment energies (VDEs) were calculated for the global minimum structures at ROPBE0/M/Stuttgart/B/aug-cc-ROCCSD(T)/M/Stuttgart/B/aug-cc-pVTZ, pVTZ, and EOM-CCSD^{55–58}/M/Stuttgart/B/6-311+G(d) levels for comparison with the experimental data. The calculations were performed using GAUSSIAN 09.59 Molekel 5.4.0.8 was used for visualization.⁶⁰

III. EXPERIMENTAL RESULTS

The photoelectron spectra of VB_9^- , NbB_9^- , and $TaB_9^$ are presented in Figs. 1–3, respectively, at two photodetachment energies. The 266 nm spectra give better spectral resolutions for the low binding energy features. All observed PES features are labeled with letters and the measured VDEs are given in Table I, where they are compared with theoretical calculations at various levels of theory. The peak labeled as X represents the transition between the ground electronic state of the anion and the neutral species, while the higher binding energy features (A, B...) denote transitions to excited electronic states of the neutral species.



FIG. 1. Photoelectron spectra of VB_9^- at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV).

A. VB₉⁻

The 266 nm photoelectron spectrum of VB_9^- (Fig. 1(a)) displays intense and congested features around 4 eV and a weak feature at lower binding energies (labeled as X'). The congested main spectral region consists of at least five relatively sharp bands, labeled as X, A, B, C, and D. The C and D bands are very closely spaced. The adiabatic detachment energy (ADE) of the ground state detachment transition is 3.64 eV, obtained by drawing a straight line along the leading edge of band X and taking the intersection with the binding energy axis plus the spectral resolution. The ADE also represents the electron affinity of neutral VB₉. The vertical detach-



FIG. 2. Photoelectron spectra of NbB_9^- at (a) 266 nm and (b) 193 nm.



FIG. 3. Photoelectron spectra of TaB_9^- at (a) 266 nm and (b) 193 nm.

ment energy of band X measured from the peak maximum is 3.70 eV.

The 193 nm spectrum (Fig. 1(b)) seems to exhibit continuous and relatively weak signals throughout the higher binding energy region. Only one prominent band F with a VDE of 5.03 eV can be identified in this range, whereas congested features appear to be present around 4.5 eV (E). The signalto-noise ratios are too poor beyond the F band to allow identifications of definitive spectral bands. The X' feature at the low binding energy range is probably due to a low-lying isomer. The weak signals throughout the low binding energy range (<3.5 eV) are probably all due to the same weakly populated low-lying isomer.

B. NbB₉⁻

The photoelectron spectra of NbB₉⁻ (Fig. 2) are somewhat similar to those of VB₉⁻. In the 266 nm spectrum, a weak feature (X') at the low binding energy side, probably due to a low-lying isomer, is followed by a series of intense and congested features at higher binding energies around 4 eV. An intense and relatively sharp band X defines the transition from the ground state of NbB₉⁻ to that of neutral NbB₉. The ADE of band X, measured from its leading edge, is 3.58 eV, which represents the electron affinity of NbB₉. The VDE of band X is measured to be 3.64 eV. Beyond band X, the spectral features become more congested and slightly weaker in intensity. Four bands (A, B, C, and D) are assigned. In the 193 nm spectrum (Fig. 2(b)), only one additional broad band is observed at 4.88 eV (E), which is somewhat similar to band F of VB₉⁻.

C. TaB₉⁻

The spectra of TaB_9^- (Fig. 3) are almost identical to those of NbB₉⁻, except the spectral features are slightly better separated and resolved. In addition, the weak low

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TABLE I. Observed vertical electron detachment energies (VDEs) of VB_9^- , NbB_9^- , and TaB_9^- compared with the calculated values for the lowest energy isomer in each case. All energies are in eV.

Observed bands	VDE (exp) ^a	Final state and electronic configuration	VDE (theoretical)		
			PBE0 ^b	CCSD(T) ^c	EOM-CCSD ^d
		$VB_9^-(C_{2v}, {}^2B_2)$			
Х	3.70 (3)	${}^{3}B_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{1}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$	3.72	3.79	e
А	3.79 (3)	${}^{3}B_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{1}6b_{2}{}^{1}$	3.87	3.98	e
В	3.93 (3)	${}^{3}A_{1} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{1}8a_{1}{}^{2}6b_{2}{}^{1}$	3.86	3.98	e
С	4.03 (3)	${}^{1}A_{1} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{0}$	4.17	4.09	4.04
D	4.10 (3)	${}^{1}B_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{1}6b_{2}{}^{1}$			4.14
Е	~ 4.6	${}^{1}B_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{1}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$			4.57
		${}^{1}A_{1} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{1}8a_{1}{}^{2}6b_{2}{}^{1}$			4.57
F	4.94 (4)	${}^{3}A_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{1}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$	4.92	5.14	e
		${}^{3}B_{1} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{1}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$	4.92		e
		${}^{1}A_{2} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{2}2b_{1}{}^{1}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$			5.22
		${}^{1}B_{1} \dots {}^{1}b_{1}{}^{2}1a_{2}{}^{1}2b_{1}{}^{2}7a_{1}{}^{2}5b_{2}{}^{2}8a_{1}{}^{2}6b_{2}{}^{1}$			5.22
		${}^{1}A_{2} \dots {}^{1}b_{1}{}^{1}1a_{2}{}^{2}2b_{1}{}^{2}7a_{1}{}^{2}5b^{2}8a^{2}6b_{2}{}^{1}$			5.45
		NbB ₉ ⁻ $(C_s, {}^2A')$			
Х	3.64 (3)	${}^{3}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{1}10a'^{1}$	3.65	3.73	3.67
		${}^{3}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{1}7a''^{2}10a'^{1}$	3.64	3.78	3.67
А	3.84 (3)	${}^{3}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{1}9a'^{2}7a''^{2}10a'^{1}$	3.77	3.78	3.74
В	3.93 (3)	${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{0}$	4.06	3.97	3.98
С	4.12 (4)	${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{1}9a'^{2}7a''^{2}10a'^{1}$			4.08
D	~4.4	${}^{1}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{1}10a'^{1}$			4.38
		${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{1}7a''^{2}10a'^{1}$			4.38
Ε	4.88 (5)	${}^{3}A' \dots 7a'^{2}5a''^{2}8a'^{1}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$	4.94	5.06	5.01
		${}^{3}A'' \dots 7a'^{2}5a''^{1}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$	4.94		5.01
		${}^{3}A' \dots 7a'{}^{1}5a''{}^{2}8a'{}^{2}6a''{}^{2}9a'{}^{2}7a''{}^{2}10a'{}^{1}$			5.26
		${}^{1}A'' \dots 7a'^{2}5a''^{1}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$			5.32
		${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{1}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$			5.32
		${}^{1}A' \dots 7a'{}^{1}5a''{}^{2}8a'{}^{2}6a''{}^{2}9a'{}^{2}7a''{}^{2}10a'{}^{1}$			5.40
		$TaB_9^-(C_5, {}^2A')$			
Х	3.64 (3)	${}^{3}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{1}10a'^{1}$	3.72	3.71	3.70
А	3.89 (4)	${}^{3}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{1}7a''^{2}10a'^{1}$	3.70	3.85	3.75
		${}^{3}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{1}9a'^{2}7a''^{2}10a'^{1}$	3.70	3.85	3.75
В	4.03 (3)	${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{0}$	4.04	3.89	3.90
С	4.36 (5)	${}^{1}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{2}7a''^{1}10a'^{1}$			4.01
D	4.68 (5)	${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{2}9a'^{1}7a''^{2}10a'^{1}$			4.54
		${}^{1}A'' \dots 7a'^{2}5a''^{2}8a'^{2}6a''^{1}9a'^{2}7a''^{2}10a'^{1}$			4.54
Ε	5.07 (5)	${}^{3}A' \dots 7a'^{2}5a''^{2}8a'^{1}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$	f	5.08	5.06
		${}^{3}A'' \dots 7a'^{2}5a''^{1}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$	f	5.08	5.06
		${}^{1}A' \dots 7a'^{2}5a''^{2}8a'^{1}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$			5.32
		${}^{1}A'' \dots 7a'^{2}5a''^{1}8a'^{2}6a''^{2}9a'^{2}7a''^{2}10a'^{1}$			5.32
		${}^{3}A' \dots 7a'{}^{1}5a''{}^{2}8a'{}^{2}6a''{}^{2}9a'{}^{2}7a''{}^{2}10a'{}^{1}$	5.26	5.38	5.50
		${}^{1}A' \dots 7a'{}^{1}5a''{}^{2}8a'{}^{2}6a''{}^{2}9a'{}^{2}7a''{}^{2}10a'{}^{1}$			5.61

^aNumbers in parentheses represent the uncertainty in the last digit. The ADEs of the X band or the electron affinities of the neutral VB₉, NbB₉, and TaB₉ clusters are measured to be 3.64 ± 0.04 eV, 3.58 ± 0.04 eV, and 3.57 ± 0.04 eV, respectively.

^bVDEs were calculated at ROPBE0/V, Nb, Ta/Stuttgart/B/aug-cc-pVTZ//(RO)PBE0/V, Nb, Ta/Stuttgart/B/aug-cc-pVTZ/.

^cVDEs were calculated at ROCCSD(T)/V, Nb, Ta/Stuttgart/B/aug-cc-pVTZ//(RO)PBE0/V, Nb, Ta/Stuttgart/B/aug-cc-pVTZ.

^dVDEs were calculated at EOM-CCSD/V, Nb, Ta/Stuttgart/B/6-311+G(*d*)//(RO)PBE0/V, Nb, Ta/Stuttgart/B/aug-cc-pVTZ.

^eEOM-CCSD values for triplet states of VB₉⁻ are not presented because of high spin contamination observed in the calculations.

^fVDEs could not be calculated at this level of theory.

binding energies features, attributed to a low-lying isomer, are almost negligible in the spectra of TaB_9^- . The 266 nm spectrum of TaB_9^- displays three intense bands (X, A, and B) and a weaker, broader band C. The ADE of band X, measured to be 3.57 eV, defines the electron affinity of neutral TaB₉, which is identical to that of NbB₉ within our uncertainty. The 193 nm spectrum (Fig. 3(b)) reveals two more bands, a relatively weak band D, and a broad band E, both of

which are similar to those observed in the 193 nm spectrum of NbB_9^{-} .

IV. THEORETICAL RESULTS

Our global minimum search and geometry optimization show that the wheel-like structures are the global minima for all the MB_9^- clusters considered here, as presented in Fig. 4.



FIG. 4. Global minimum structures of VB₉⁻, NbB₉⁻, and TaB₉⁻. Bond lengths are given in Å at the (RO)PBE0/V,Nb,Ta/Stuttgart/B/aug-cc-pVTZ level.

The boron rings in all clusters are slightly distorted from a perfect circle, because of the Jahn-Teller effect. VB_9^- has a planar C_{2v} structure, while NbB_9^- and TaB_9^- both have nonplanar C_s structures with the Nb and Ta atoms located approximately 0.7 Å out of the averaged boron plane. Extensive sets of alternative low-lying isomers are shown in Figs. S1–S3 of the supplementary material⁵⁰ for MB_9^- (M = V, Nb, and Ta), respectively, at the PBE0 level. Energies from single-point CCSD(T) calculations are given for selected low-lying isomers, assuring that the M©B_9^- molecular wheel structures are the global minimum in each case.

Geometry optimization of the neutral M $\textcircled{O}B_9$ (M = V, Nb, Ta) clusters in the D_{9h} symmetry leads to an imaginary frequency corresponding to out-of-plane distortions of the central metal atom in each case. Following the imaginary mode, C_{9v} structures were obtained (Fig. 5, upper row) for all three clusters with an open-shell triplet ground electronic state. Consequently, we considered the closed-shell doubly charged M $\textcircled{O}B_9^{2-}$ clusters (Fig. 5, lower row). The V $\vcenter{O}B_9^{2-}$ cluster was found to be a perfect D_{9h} planar cluster, whereas NbB $_9^{2-}$ and TaB $_9^{2-}$ were found to have C_{9v} symmetry with the central metal atom slightly out-of-plane.

Because of the open-shell nature of the anion and neutral ground states, both singlet and triplet final states can be ac-



FIG. 5. Optimized structures of neutral VB₉, NbB₉, and TaB₉ and the doubly charged VB₉²⁻, NbB₉²⁻, and TaB₉²⁻ clusters. Bond lengths are given in Å at the PBE0/V,Nb,Ta/Stuttgart/ B/ aug-cc-pVTZ level.

cessed during photodetachment, consistent with the complicated photoelectron spectra observed experimentally. In particular, the open-shell anions and neutrals make it challenging to compute the detachment channels. Thus, we calculated the VDEs for the global minimum structures of $M \odot B_9^-$ using three different methods: PBE0, CCSD(T), and EOM-CCSD. The theoretical results are compared with the experimental data in Table I. We found that the three methods give consistent results and together they allow almost quantitative interpretation of the experimental data.

V. DISCUSSION AND INTERPRETATION OF THE PHOTOELECTRON SPECTRA

A. The X' feature and possible presence of low-lying isomers

According to the relative energies calculated at the CCSD(T) level of theory, the global minima of these clusters are significantly more stable compared to the nearest low-lying isomers (see Figs. S1-S3 of the supplementary material).⁵⁰ Despite the relatively high energies of the "boat"like isomers found at the CCSD(T) level, we find that their calculated VDEs are in agreement with the experimental values for the peaks labeled as X' in the spectra of VB_9^- and NbB₉⁻, suggesting that the boat-like isomers were weakly populated in the cluster beams. These observations are similar to the case of NbB₁₀⁻, which has a perfect D_{10h} global minimum with a boat-like low-lying isomer being 5.4 kcal/mol higher in energy. Despite the relatively high energy of the boat-like isomer, it was substantially populated in the cluster beam, giving rise to low binding energy features in the photoelectron spectra of NbB₁₀^{-.37} The fact that the boat-like isomers were present in all of the current cases suggests that the stability of the boat-like isomers relative to the global minima was probably underestimated. Nevertheless, the trend is consistent with the experimental observation: the energy of the boat-like isomer relative to the molecular wheel global minimum increases from VB_9^- to TaB_9^- , and experimentally, the relative intensities of the weak low binding energy features due to the boat-like isomer decrease in the same direction (Figs. 1-3).

We focus our discussion on the global minimum molecular-wheel structures (Fig. 4), which are responsible for the main spectral features observed experimentally. The photoelectron spectral data are compared with the calculated VDEs in Table I, where the final states and MO configurations for the final states are also given.

B. The MOs and bonding in the closed-shell $M \odot B_9^{2-}$ (M = V, Nb, Ta) dianions

Given the similarity of the electronic and the geometrical structures of these clusters, we will discuss in more detail the assignments of the photoelectron spectra of VB₉⁻. The geometry of VB₉⁻ can be best understood by considering one electron removal from the closed-shell V \bigcirc B₉²⁻ cluster. The valence MOs of the *D*_{9h} V \bigcirc B₉²⁻ cluster are plotted in Fig. 6 and they can be understood as follows: the degenerate HOMO



FIG. 6. Molecular orbital plots of $V \odot B_9^{2-}$ (D_{9h} , ${}^2A_1'$) at the PBE0/V/Stuttgart/B/aug-cc-pVTZ level.

(2e₂') and HOMO-1 (2e₁'), plus HOMO-4 (2a₁'), are delocalized σ bonding orbitals between the central V atom and the B₉ ring; the degenerate HOMO-2 (1e₁") and HOMO-3 (1a₂") are delocalized π bonding orbitals between the V atom and the B₉ ring; and remaining nine valence orbitals are responsible for the nine 2c-2e peripheral B–B bonds. Thus, V $(\bigcirc$ B₉²⁻ is doubly aromatic, with 10 σ ($N_{\sigma} = 2$) and 6 π ($N_{\pi} = 1$) electrons and the formal valence of V in V $(\bigcirc$ B₉²⁻ is 5. Thus, V $(\bigcirc$ B₉²⁻ obeys the modified electronic design principle devised for Nb $(\bigcirc$ B₁₀⁻ and Ta $(\bigcirc$ B₁₀⁻, Eq. (2), where x = 5, n = 9, and q = 2.

For the closed-shell Nb \odot B₉²⁻ and Ta \odot B₉²⁻ clusters, we found that the size of the central metal atom is too big to fit inside a B₉ ring and these clusters have quasi-planar structures and a C_{9v} symmetry (Fig. 5, bottom), even though they obey the modified electronic design principle [Eq. (2)] and display bonding features almost identical to the non-distorted D_{9h} structure. The MOs of Nb \odot B₉²⁻ and Ta \odot B₉²⁻ (not shown) are similar to those of V \odot B₉²⁻.

C. Interpretation of the photoelectron spectra of $M \odot B_9^-$ (M = V, Nb, Ta)

Removal of one electron from the degenerate $2e_2'$ HOMO of the D_{9h} V \odot B₉²⁻ results in the low symmetry C_{2v} $V(c)B_9^-$, owing to the Jahn-Teller effect. The MOs of the $C_{2\nu}$ $V(c)B_9^-$ are shown in Fig. 7 and they bear close resemblance to those of $V(\hat{c})B_9^{2-}$, except that its $6b_2$ HOMO is now singly occupied to give the ${}^{2}B_{2}$ ground electronic state (Fig. 4). The other component of the degenerate $2e_2'$ orbital becomes the 7a₁ (HOMO-3) orbital in $V \odot B_9^-$ (Fig. 7). Similarly, removal of an electron from the doubly degenerate HOMO orbitals of Nb(c)B₉²⁻ and Ta(c)B₉²⁻ results in slightly distorted pyramidal structures with C_s symmetry for Nb $\bigcirc B_9^$ and $Ta(c)B_9^-$ (Fig. 4), due to the Jahn-Teller effect. The MOs of Nb(\hat{c})B₉⁻ and Ta(\hat{c})B₉⁻ are given in Figs. 8 and 9, respectively, and their similarities to those of $V(\widehat{c})B_9^-$ (Fig. 4) are evident. In the case of $NbCB_9^-$, the degenerate HOMOs in the closed-shell dianion transform into 10a' (HOMO) and 6a" (HOMO-3) (Fig. 8), whereas in $Ta \odot B_9^-$ they transform into



FIG. 7. Valence canonical molecular orbital plots of $V \odot B_9^-$ (ROPBE0/V/Stuttgart/B/aug-cc-pVTZ).

10a' (HOMO) and 7a'' (HOMO-1) (Fig. 9). These MOs together with the calculated VDEs in Table I are used to interpret the photoelectron spectra.

The calculated neutral states all have C_{9v} symmetry and triplet spin state (${}^{3}A_{2}$, Fig. 5), with their doubly degenerate σ HOMOs half-occupied. The lack of a HOMO-LUMO gap in the photoelectron spectra (Figs. 1-3) is consistent with the triplet configuration of the neutral clusters for all three cases. Therefore, the first detachment channel from $M(\widehat{c})B_9^-$ should be from electron removal from the fully occupied σ delocalized orbital that corresponds to one of the $2e_2'$ orbitals in $V(\hat{c})B_9^{2-}$ (Fig. 6), i.e., the 7a₁ orbital in $V(\hat{c})B_9^{-}$, the 6a'' orbital in Nb $\textcircled{O}B_9^-$, and the 7a" orbital in Ta $\textcircled{O}B_9^-$. The calculated first VDE in each case is in very good agreement with the experimental data, except for the case of Nb(\hat{c})B₉⁻, where the calculated VDE from the 9a' orbital is the same as the first VDE (Table I). In reality, the top four molecular orbitals in all $M(\hat{c})B_9^-$ anions (Figs. 7–9) lie very close in energy and they give rise to seven detachment channels in a narrow energy range, accounting for the congested spectral features from about 3.6 eV to 4.8 eV in the photoelectron spectra (Figs. 1-3



FIG. 8. Valence canonical molecular orbital plots of Nb©B9⁻ (ROPBE0/Nb/Stuttgart/B/aug-cc-pVTZ).



FIG. 9. Valence canonical molecular orbital plots of Ta©B9 (ROPBE0/Ta/Stuttgart/B/aug-cc-pVTZ).

and Table I). Overall, the calculated spectral features are in good agreement with the observed features in these congested spectral regions, as shown in Table I. Remarkably, the feature around 5 eV (band F in Fig. 1(b) and band E in Figs. 2(b) and 3(b)) is very similar in all three cases. As shown in Table I, this feature is from detachment from the same orbitals in all three cases, i.e., the $2b_1$ and $1a_2$ orbitals in V(\hat{c})B₉⁻ (Fig. 7) and 8a' and 5a'' for Nb $(c)B_9^-$ (Fig. 8) and Ta $(c)B_9^-$ (Fig. 9), which correspond to the degenerate delocalized π orbitals $(1e_1'' \text{ in Fig. 6})$. The splitting of these MOs in the $M(\hat{c})B_9^-$ anions seems to be very small, giving rise to the same calculated VDEs, consistent with the experimental band around 5 eV in each case. The excellent agreement and consistency between theory and experiment for this feature in all three anions provide an anchoring point for the validity of the spectral assignment. Overall, the agreement between the calculated VDEs and the experimental data, as shown in Table I, is almost quantitative, confirming unequivocally the obtained global minima for all three clusters.

D. Electronic vs. geometrical factors in determining the structures of $M \odot B_9$, $M \odot B_9^-$, and $M \odot B_9^{2-}$ (M = V, Nb, Ta)

The $M {\textcircled{C}} B_9{}^{2-}$ dianions are all closed-shell species and obey the electronic design principle, as discussed above in Sec. V B. However, only $V(\widehat{c})B_9^{2-}$ is a perfect planar molecular wheel according to our calculations, whereas both Nb $(c)B_9^{2-}$ and Ta $(c)B_9^{2-}$ have C_{9v} symmetry (Fig. 5). These species provide another example of the interplay between electronic and geometrical factors in determining the structures of the $M(\widehat{c})B_n^{q-}$ type molecular wheels. The covalent radii of V, Nb, and Ta are 1.53, 1.64, and 1.79 Å, respectively.⁶¹ Clearly, the V atom fits perfectly inside a B₉ ring in $V(c)B_9^{2-}$, but the B_9 ring is too small to accommodate Ta and Nb, so that they are squeezed out of the ring center slightly to give the C_{9v} Nb \odot B₉²⁻ and Ta \odot B₉²⁻, as well as in the singly charged or neutral species of these clusters. These are in contrast to the MB_{10}^{-} systems (M = V, Nb, Ta), which all obey the modified electronic design principle [Eq. (2)] for planar doubly aromatic $M \odot B_{10}^{-}$ molecular wheels. However, the B_{10} ring has only the right size to fit Ta and Nb comfortably to give rise to the perfectly planar Nb $\odot B_{10}^{-}$ and Ta $\odot B_{10}^{-}$ molecular wheels,³⁷ whereas the V atom is too small to form stable wheel-type V $\odot B_{10}^{-}$ and the global minimum of V B_{10}^{-} has a boat-like 3D structure.³⁸ Thus, we show again that both electronic and geometric factors are important to form perfectly planar M $\odot B_n^{q-}$ type molecular wheels. The C_{2v} distortion in V $\odot B_9^{-}$ is due to the Jahn-Teller effect, as discussed above in Sec. V C. The C_{9v} distortion in the triplet V $\odot B_9$ is due to a pseudo Jahn-Teller effect.⁶²

VI. CONCLUSIONS

We have investigated a new group of clusters, MB9⁻, MB₉, and MB₉²⁻ (M = V, Nb, Ta) and demonstrated that, for the design of $M(\widehat{c})B_n^{q-}$ type molecular wheel borometallic compounds, both electronic and geometric factors should be taken into account. Photoelectron spectroscopy of MB9⁻ (M = V, Nb, Ta) was combined with theoretical calculations to show that the global minimum of VB₉⁻ has a planar C_{2v} V \odot B₉⁻ structure, whereas NbB₉⁻ and TaB₉⁻ possess M \odot B₉⁻ pyramidal type structures with C_s symmetry. Theoretical calculations show that the VB₉²⁻ anion has a perfect planar D_{9h} V(\hat{c})B₉²⁻ molecular wheel structure, whereas NbB₉²⁻ and TaB₉²⁻ have C_{9v} M©B₉²⁻ type structures. All the MB_9^{2-} dianions obey the electronic design principle [Eq. (2) for $M(\hat{c})B_n^{q-}$ type doubly aromatic molecular wheels. But only the V atom can fit perfectly inside the B₉ ring, whereas, because of the larger sizes of Nb and Ta, they get squeezed out of the B₉ ring slightly. The lower symmetries of the $M(\hat{c})B_9^-$ monoanions are all due to the Jahn-Teller effect. All the MB₉ neutrals (M = V, Nb, Ta) are found to have triplet C_{9v} structures. The C_{9v} symmetry of the triplet V \odot B₉ neutral is due to a pseudo Jahn-Teller effect. The current study provides another example of the importance of the interplay between electronic and geometric factors in designing $M(c)B_n^{q-1}$ type molecular wheel type systems.

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