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Structural and electronic properties of V_2B_n ($n = 1–10$) clusters

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ABSTRACT

Inspired by the discovery of a series of Ta_2B_n clusters, the geometric structures, stabilities, and electronic properties of V_2B_n clusters up to $n = 10$ have been systematically investigated based on the density-functional B3LYP method and the CCSD(T) method. Among the small size clusters, the V_2B_5 cluster was observed to have different geometric motif than Sc_2B_5, Ti_2B_5 and Ta_2B_5. For V_2B_n clusters with an $n \geqslant 6$, the bipyramidal structure is energetically favored, as for Sc_2B_n and Ti_2B_n. The second-order difference of energies, binding energies, dissociation energies, vertical ionization potentials, vertical electron affinities and chemical hardness of the V_2B_n clusters were calculated and analyzed. The V_2B_6 cluster was determined to be stable thermodynamically and might be observed in a future experiment. To understand the stability of the V_2B_6 cluster, a detailed inspection of its occupied valence orbitals was performed.

1. Introduction

Transition metal (TM) doped B_n nanostructures have attracted a considerable attention due to their potential to elucidate the fundamental properties of the chemical bond in basic research, as well as their potential applications in the field of multi-functional materials [1–13]. The novel and rich geometric and electronic structures of pure B_n and TM doped B_n were believed to relate to the electron-deficient nature of the B element. For example, a carbon atom can bond to 4 other atoms in most cases, but hepta- and octa-coordinate boron atoms were observed in molecular wheels of eight- and nine-atom boron clusters [14,15]. In recent years, Wang and coworkers have successfully produced a new class of borometallic compounds, namely transition-metal-centered monocyclic boron wheel clusters [9–12,16–18]. For these TM@B_n clusters, $n = 8–10$ are the most promising size range. Both electronic and geometric factors are important in determining the ground state (GS) structure of these TM-doped wheel clusters. The bonding analysis revealed that σ and π double aromaticity is a key factor in stabilizing the planar TM@B_n wheel clusters [10]. A more complicated electronic structure that involves special double aromaticity was reported in TM centered double-ring boron clusters M@B_{2n}, where M = Ti, Cr, Fe, Ni, Zn and $n = 6–8$ [19].

The growth pattern of the TM doped B_n clusters is another interesting problem, which has been addressed in many theoretical investigations [8,20–23]. For 3d TM doped neutral clusters, the TMB_n clusters with $n \leqslant 6$ have planar or quasi-planar geometries. Starting from $n = 7$, bowl-like structures that have the TM atom hosted inside were found to be more stable than the planar structures [22]. For example, we found that for TiB_n and ScB_n ($n = 7–12$), the bowl-like structures were energetically favorable [8,20]. Li [23] and his coworkers have investigated the growth pattern of TMB_n ($n = 8–14$, TM = Cr, Mn, Fe, Co) clusters. They also found that the GS isomers have bowl-like structures when $n = 8–12$. When $n = 14$, the tire-shaped TMB_n (TM = Mn, Fe, Co) isomers were found to be more stable than the bowl-like isomers. As n increases further, fullerene-like isomers with an *endo* TM atom become more stable. For example, Tam et al. [1] have explored the structures of FeB_n (n = 14, 16, 18 and 20). They found that FeB_{14} and FeB_{16} have a tire-shaped GS structure, while FeB_{18} and FeB_{20} have a fullerene-like GS structure.

The structures of TM doped B_n clusters with two metal atoms, TM_2B_n, were also included in some reports. Wang and his coworkers [24] observed the first TM_2B_n cluster, $Au_2B_7^-$, in 2006. Based on experimental results as well as theoretical calculations, they reported that the $Au_2B_7^-$ cluster possesses a planar structure similar to that of $B_7H_2^-$, where two H atoms are substituted by two Au atoms. Ta_2B_n ($n = 2–5$) clusters are another class of TM_2B_n clusters and have been observed by photoelectron spectroscopy [6]. Based on the photoelectron spectra and theoretical calculations, Wang and coworkers have suggested that the GS structures of $Ta_2B_n^-$ and Ta_2B_n ($n = 2–5$) clusters should be incomplete bipyramids, in which the boron atoms form an equatorial belt around the Ta–Ta dimer [6]. A Ta_2B_6 cluster with hexagonal bipyramidal geometry

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was observed by the same group [25]. Recently, we have investigated the growth patterns of Sc_2B_n and Ti_2B_n (n = 1–10). The bipyramidal structure was also found to be energetically preferable for these two series of clusters. Among them, Sc_2B_7 and Ti_2B_6 were found to be the magically stable clusters [4,26].

In the present paper, the structures of V_2B_n clusters (n = 1–10) were investigated based on theoretical calculations to extend our knowledge about the structures of TM_2B_n clusters. The V and Ta elements belong to the same group in the periodic table. We focused on the growth pattern of V_2B_n clusters and compared it with the growth patterns of Ta_2B_n, Sc_2B_n and Ti_2B_n clusters. We are also interested in the evolution of their electronic structures with increasing n. To the best of our knowledge, theoretical investigations regarding the structures and stabilities of V_2B_n clusters are still lacking.

2. Computational details

All of the geometries for the V_2B_n (n = 1–10) isomers that we considered were initially optimized using the B3LYP method [27,28] under the framework of density functional theory (DFT) using the 6-31 + G* basis set. For V_2B_n with an even n, the multiplicities of 1, 3 and 5 were tested, and for an odd n, the multiplicities of 2, 4 and 6 were considered. All of the geometric optimizations were performed without symmetry restriction. The selected stable isomers were further refined with a large 6-311 + G* basis set. The frequency calculations were carried out at the B3LYP/6-311 + G* level to confirm that all of the clusters reported in the text are geometrically stable and to obtain the zero-point vibration energies (ZPE). To obtain more reliable electronic energies, we performed single point energy calculations with the CCSD(T) method for the most stable and second most stable V_2B_n isomers obtained at the B3LYP/6-311 + G* level. The 6-311 + G* basis set was chosen as a compromise between the quality of the theoretical method and the computational cost in the CCSD(T) calculations. If not otherwise mentioned, all of the energies reported in the following sections were obtained at the CCSD(T)/6-311 + G* level with ZPE corrections from the B3LYP/6-311 + G* level. The population analyses and orbital analyses were based on the B3LYP/6-311 + G* results because of the lack of CCSD(T) density. All of the calculations were performed with the Gaussian 09 program [29].

In addition to optimizing the independent configurations, we also considered other initial isomers by replacing two B atoms from some of the stable B_{n+2} clusters [30–32] with two V atoms, or by putting two V atoms on possible locations for the stable B_n clusters to identify the best GS isomers for the V_2B_n clusters. The stable isomers of TMB_n [8,20,22] were also used to generate the initial V_2B_n clusters by replacing the TM with a V atom and adding another V atom. The stable isomers of Sc_2B_n [4] and Ti_2B_n [26] were also considered by replacing the Sc and Ti atoms with V atoms. For larger clusters ($n \geqslant 6$), a global search based on a particle swarm optimization algorithm within an evolutionary scheme was carried out using the CALYPSO package [33], in addition to the methods mentioned above. By using all of these methods, we tried our best to obtain the GS structures of V_2B_n clusters. The most stable isomers obtained from CALYPSO were consistent with those from other methods.

3. Results and Discussion

We explored the low-lying isomers of V_2B_n up to n = 10 with the computational scheme described in Section 2. Fig. 1 shows the most stable and second most stable isomers for all of the V_2B_n (n = 1–10). Their symmetries, spin multiplicities and relative energies (compared to the most stable isomer) are also presented. Geometric coordinates, electronic energies and ZPE are given in the supporting information. These isomers were optimized for both geometry and spin. The most stable V_2B and V_2B_3 isomers have spin multiplicities of 4. For the other V_2B_n clusters, the GS isomers are all singlets (even n) or doublets (odd n). In Fig. 1, we also list the relative energies at the B3LYP/6-311 + G* level (in parentheses). In most cases, the stability orders calculated at the B3LYP/6-311 + G* level are the same as those calculated at the CCSD(T)/6-311 + G*//B3LYP/6-311 + G* level. It is believed that the CCSD(T) energy is more reliable. In the following sections, our discussions are based on the energies obtained at the CCSD(T)/B3LYP level.

A three-membered ring isomer was found to be the most stable V_2B (1a in Fig. 1) and is more stable than the linear isomer 1b by 0.71 eV. The V–V distance in 1a is 2.19 Å and is remarkably longer than the bond length of V_2 dimer (1.77 Å in exp. [34] and 1.71 Å at B3LYP/6-311 + G(d)). For V_2B_2, the GS isomer is a bent rhombus (2a in Fig. 1) with C_{2v} symmetry. In 2a, the V–V distance is 2.95 Å. A rhombic isomer (2b in Fig. 1) is higher in energy than 2a by 0.79 eV. In the case of V_2B_3, the GS isomer is 3a with a V–V bond length of 2.44 Å. The second most stable isomer 3b is higher in energy than 3a by 0.23 eV. The GS isomer 4a of V_2B_4 is similar to its Sc_2B_4 and Ti_2B_4 counterparts, which prefer an incomplete bipyramid. In 4a, the V–V bond length is 2.37 Å. Isomer 4b is higher in energy than 4a by only 0.13 eV. The GS isomer of V_2B_5 is an irregular polyhedron (5a in Fig. 1). In isomer 5a, the V–V bond length is 2.26 Å. The incomplete bipyramidal structure of isomer 5b is the second most stable V_2B_5 isomer and is higher in energy than 5a by only 0.22 eV. It should be mentioned that for Ti_2B_5, Sc_2B_5 and Ta_2B_5, isomers similar to 5b are the GS isomers [4,6,26].

For V_2B_n with n = 6–8, the structures of the GS isomers are similar to their Ti_2B_n and Sc_2B_n counterparts. All of the GS isomers possess the bipyramidal structure, with the two metal atoms occupying apex sites. The GS isomer of V_2B_6 (6a in Fig. 1) has C_2 symmetry, in which the six-membered B_6 ring distorts to a non-planar structure. The V–V distance in 6a is 2.77 Å. It should be noted that Ta_2B_6 is a perfect hexagonal bipyramid with D_{6h} symmetry [25]. The most stable structure for V_2B_7 (7a in Fig. 1) is a heptagonal bipyramid with C_{7v} symmetry, in which the V–V distance is 2.81 Å. In 7a, two V atoms have different distances to the center of B_7 ring. By adding a B atom on the six-membered B_6 ring of 6a, we obtain the isomer 7b as the second most stable isomer of V_2B_7, which is less stable than 7a by 1.30 eV. In the GS isomer 8a of V_2B_8, all B atoms form a zigzag eight-membered ring. Isomer 8a possesses D_{4d} symmetry with a V–V distance of 2.25 Å. The second most stable isomer 8b is higher in energy than 8a by 0.38 eV. V_2B_9 and V_2B_{10} also favor the bipyramidal structure. The most stable V_2B_9 (9a in Fig. 1) is generated by adding two adjacent B atoms on the B_7 ring of 7a. The second most stable isomer, 9b, is formed by inserting a B atom into the boron ring of 8b and is higher in energy than 9a by 0.57 eV. By adding two B atoms onto the B_8 ring of 8a, we obtain the GS isomer of V_2B_{10} (10a in Fig. 1). Isomer 10a has C_s symmetry with a V–V distance of 2.35 Å. By adding one B atom to isomer 9a, we obtain isomer 10b, which is higher in energy than 10a by 0.38 eV.

Now, we discuss the growth pattern of V_2B_n clusters. Both electronic and geometric factors are important in determining the structure of a cluster. For example, VB_9^{2-}, NbB_9^{2-} and TaB_9^{2-} all obey the electronic design principle to form doubly aromatic molecular wheels [10]. However, only VB_9^{2-} is a planar molecule with perfect D_{9h} symmetry. In NbB_9^{2-} and TaB_9^{2-}, the center metals are slightly out of plane due to their large atomic radii. The GS structures of V_2B_5 are obviously different than their Sc_2B_5, Ti_2B_5 and Ta_2B_5 counterparts. For Sc_2B_5, Ti_2B_5 and Ta_2B_5, the GS structures can be viewed as incomplete bipyramids. The GS structures of V_2B_5 can be viewed as irregular polyhedrons in which the V atoms prefer