Hyperhalogen properties of early-transition-metal borates†

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The equilibrium structures, stability and magnetic properties of Sc(BO2)n−/0 (n = 1−4) clusters were investigated on the basis of density functional theory calculations. The BO2 ligands prefer to stretch out in the most stable Sc(BO2)−/ anions but tend to come together in the lowest-lying Sc(BO2)3 structure. According to the MP2 results, the Sc(BO2)4− species could be classified as hyperhalogen anions since they have larger vertical electron detachment energies (VDEs, 5.44−8.85 eV) than that of the superhalogen anion BO2−. With titanium and vanadium playing the role of central atom, the Ti(BO2)n−/0 (n = 1−5) and V(BO2)n−/0 (n = 1−6) clusters were studied in a similar manner. In these cases, the central transition metal atoms are inclined to keep their intrinsic spin. In addition, the hyperhalogen identity of the Ti(BO2)n− (n = 4, 5) and V(BO2)n− (n = 3−6) species were also confirmed by the calculated VDE values.

1. Introduction

It is well-known that halogen atoms possess the highest electron affinities (EAs) in the periodic table, and the chlorine atom possesses the maximum value, namely 3.61 eV.1 Atoms and clusters with high EA usually show remarkable oxidation capacity in chemical reactions. Bartlett and co-workers found that PtF6 could even oxidize a Xe atom,2 and then confirmed that the PtF6 molecule possesses a very high EA of 6.8 eV.2 Such molecules that have higher EAs than the chlorine atom were termed superhalogen by Boldyrev and Gutsev in 1981.3 Besides, they recommended a simple formula MXn− for constructing superhalogens, where M is a main group or transition metal atom, X is a halogen atom, and n is the maximal formal valence of M.4 The first experimental evidence of such species, namely MX5− (M = Li, Na, and X = Cl, Br, I), was obtained by Wang’s group in 1999.5 Afterwards, an increasing number of superhalogen anions have been theoretically predicted or experimentally detected, such as MXn− (M = Be, Mg, Ca; X = Cl, Br)5−8 and MCln− (M = Sc, Y, La).9 Recently, many kinds of superhalogens that are beyond the MXn− formula have been proposed and characterized. To facilitate extra-electron delocalization, multinuclear superhalogen anions have been designed such as P2F11− and As2F11−,10 Mg2F5−,11 Al2F7−,12 and H3F13−.13 As a result, higher vertical electron detachment energy can be achieved. By introducing non-halogen ligands, the scope of superhalogen has been further extended to include the chalcogen-based MnO4,14 CrO4,14 BO2−,15 AlO2−,16 VO3−,17 BrO3−,18 IO3−,19 IO4−,19 BSO− and BrSO− molecules, and those involving electrophilic substituent,9 organic group,20 and acidic functional group21 as ligands.

Superhalogens are strong electron-acceptors and can be used to oxidize systems with high ionization potential, such as benzene22 and small water clusters.23 They may combine with superalkalis to form ionic compounds that are predicted to possess excellent nonlinear optical response.24 Recent studies have also shown that MnCl3, one of the experimentally synthesized superhalogens, could be used to tune the electronic and magnetic properties of silicone,25 and that the AlF4 superhalogen can initiate a radical-substitution chain reaction as the trigger-compound.26 In 2015, Jena predicted that superhalogens could serve as a bridge between complex metal hydrides and electrolytes in Li-ion battery.27 Soon after, the suitability of superhalogen salt for Mg battery electrolyte was experimentally proved.28 The extensive application prospects of superhalogens make them promising agents in chemistry and material science and attract more and more attention.29,30

Hyperhalogens, another series of electronegative clusters whose EA values are even higher than those of their superhalogen ligands, were proposed by Jena and coworkers in 2010.31 Au(BO2)n was reported as the first member of this type of molecules. Thereafter, the strategy of using superhalogen as ligands was employed to design a great many high EA species, e.g., Cu(BO2)m [m = 1, 2],12 Al(BO2)m,31 Ag(BO2),34 Na(BF4)2,35 Mg(BF4)2,36 Al(BF4)3,37 Al(H2F3)3,37 and M(IO3)2− (M = H, Li, Na,

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† Electronic supplementary information (ESI) available: Selected molecular orbitals of the studied borate anions, and VDE values of some related cluster anions. See DOI: 10.1039/c7ra10238k
K). Furthermore, Jena et al. proposed the concept of "magnetic hyperhalogens" by studying the Fe(BO2)₆ and Mn(BO2)₆ clusters. Recently, two series of hyperhalogen anions involving planar and cage-like hyperhalogen ligands were reported, respectively, and the concept of aromatic hyperhalogen was brought forward as well.⁴⁰,⁴¹

In this work, theoretical investigation of borates of the first three subgroup elements, namely scandium, titanium, and vanadium, was presented. On the one hand, these transition metal (TM) elements have unfilled d orbitals, which may render the resulting compounds magnetism. On the other hand, they have multivalent properties, so it is interesting to make clear the minimum number of BO₂ ligands they need to exhibit hyperhalogen character with. Besides, our study also aims to (1) reveal the geometrical feature of the resulting Sc(BO₂)₆⁻⁻ (n = 1–4), Ti(BO₂)₆⁻⁻ (n = 1–5), and V(BO₂)₆⁻⁻ (n = 1–6) clusters; (2) detect their stability through examining their dissociation energies of predetermined dissociation pathways; (3) explore the spin state evolution of central atoms and VDE values of the TM(BO₂)₆⁻⁻ (TM = Sc, Ti, V) anions.

2. Computational details

With different spin multiplicity taken into account, the optimized geometries of the Sc(BO₂)₆⁻⁻ (n = 1–4), Ti(BO₂)₆⁻⁻ (n = 1–5), and V(BO₂)₆⁻⁻ (n = 1–6) species were obtained by using the M06 functional of density functional theory. Frequency and natural bond orbital (NBO) analyses⁴⁴ were performed at the same level. Single point energies were computed by using the second-order Møller–Plesset (MP2) method. For all calculations, the 6-311+G(3df) basis set was used for B and O atoms, while the Los Alamos set of the double-zeta type LANL2DZ basis set and effective core potential (ECP) were used for the Sc, Ti, and V atoms.

The vertical detachment energies (VDEs) of the Sc(BO₂)₆⁻⁻ (n = 1–4), Ti(BO₂)₆⁻⁻ (n = 1–5), and V(BO₂)₆⁻⁻ (n = 1–6) anions were obtained by two methods. First, the VDE values were indirectly computed as the energy difference between the neutral and the anion both at the anion’s geometry by using the MP2 method. Second, the restricted outer valence Green function (OVGF)⁴⁵–⁴⁶ method was used to estimate the VDE values. For all investigated anions, the pole strengths (Ps) are greater than 0.85, justifying the validity of OVGF approximation. For comparison, the adiabatic detachment energy (ADE) of each anion was also obtained by using the MP2 method, which was computed as the difference in total energy between the neutral and anion at their respective optimized geometries.

All calculations were performed using the GAUSSIAN 09 program package.⁴⁸ Dimensional plots of the molecular structures were generated with the GaussView program.⁴⁹

3. Results and discussion

3.1 Sc(BO₂)₆⁻⁻ and Sc(BO₂)₆⁻⁻ (n = 1–4)

3.1.1 Equilibrium geometries and relative stability. We considered all possible configurations of Sc(BO₂)₆⁻⁻ and Sc(BO₂)₆⁻⁻ and show their optimized structures in Fig. 1 and 2, respectively. Their relative energies are listed in Tables 1 and 2, respectively. The nomenclature uses Arabic numeral from 1 to 4 to indicate the number of BO₂ ligands in the Sc(BO₂)₆⁻⁻ clusters, followed by a, b, c… indicating the increasing MP2 single point energy order of different isomers. As for the neutral Sc(BO₂)₆⁻⁻ anions, their structures are named after corresponding anionic ones.

As shown in Fig. 1, isomer 1a of ScBO₂⁻⁻ is linear and similar to the reported structures of FeBO₂⁻⁻, MnBO₂⁻⁻, and MnBO₂⁻⁻.⁴⁸ The other isomer 1b has C₃v symmetry, where the BO₂ ligand bends to 156.6° and binds with the Sc atom via two O atoms. Both 1a and 1b have magnetic moment of 1 µ₆, However, the neutral ScBO₂⁻⁻ (see Fig. 2) has variable magnetism. The most stable isomer 1a of ScBO₂⁻⁻ has a magnetic moment of 2 µ₆, which is similar to the case of ScCl and ScF.⁴⁹ Isomer 1a also has a linear configuration, only it has a magnetic moment of 0 µ₆ and slightly shorter Sc–O bond length of 1.867 Å. For as for 1b and 1b', which share similar structural features with 1b, they possess different Sc–O bond lengths (2.225 Å and 2.114 Å, respectively) and magnetic moments (2 µ₆ and 0 µ₆, respectively).

As one more BO₂ ligand is introduced, four isomers have been obtained for both anionic Sc(BO₂)₆⁻⁻ and neutral Sc(BO₂)₆⁻⁻. The spin multiplicities of Sc(BO₂)₆⁻⁻ and Sc(BO₂)₆⁻⁻ are 1 and 2, respectively. 2a, the lowest-energy isomer of Sc(BO₂)₆⁻⁻, has a linear structure, in which each BO₂ ligand is attached to the middle Sc atom through a Sc–O bond. The same case was reported for the ground states of Mn(BO₂)₆⁻⁻ and Fe(BO₂)₆⁻⁻. The Sc–O bond length (1.979 Å) of 2a is slightly shorter than that of 1a (2.006 Å). Isomer 2b has a planar structure, where the two BO₂ ligands combine with each other, forming a B₂O₄ unit that shows a similar structure to the recently reported (BO₂)₂⁻⁻ anion.⁵⁰ In the next isomer 2c, two BO₂ ligands bind with the Sc atom via one and two Sc–O bonds, respectively. The ∆O1B102 angle of 2c is 147.5°, indicating a larger ligand distortion relative to structure 1b. As for the last isomer 2d, it has a D₃ᵥ-symmetric structure where each BO₂ unit is linked to the center Sc atom by two Sc–O bonds. The Sc atom is coplanar with each BO₂ ligand in this structure and the two BO₂ planes are perpendicular to each other. The ∆O B102 angle in 2d is 148.5°, which is close to that of 2c. From Fig. 2 and Table 2, the neutral Sc(BO₂)₆⁻⁻ isomers share similar structures and the same total energy order with their corresponding anions.

Sc(BO₂)₆⁻⁻ and Sc(BO₂)₆⁻⁻ have magnetic moments of 1 µ₆ and 0 µ₆, respectively. Seven structures were obtained for Sc(BO₂)₆⁻⁻, and the D₃ᵥ-symmetric structure 3a is the most stable one. In 3a, each BO₂ ligand binds with the center Sc atom via one Sc–O bond of 1.990 Å. In contrast, a ScBO₂ quadrilateral forms in the rest isomers. The Cᵥ-symmetric isomer 3b can be viewed as one more BO₂ ligand attaching to structure 2c, which is supported by NBO analysis. Both isomers 3c and 3d can be obtained by adding a BO₂ ligand to structure 2b. The difference is that the additional BO₂ ligand bonds with the Sc atom via one O atom in the former but via two O atoms in the latter. In Cᵥ-symmetric 3e, three BO₂ ligands get together and form a B₃O₆ unit, which is similar to the structure of (BO₂)₆⁻⁻. In the next isomer 3f, a B₂O₄ unit forms and is linked to Sc through three Sc–O bonds.

The least favorable structure of Sc(BO₂)₆⁻⁻ is 3g with C₃v.
symmetry, which contains a different B$_2$O$_6$ unit compared with 3e. As for neutral Sc(BO$_2$)$_3$, all isomers possess a similar structure to their corresponding anions but their stability follows a different order. The largest structural difference is found between 3e and its neutral counterpart, namely 3c where one of the BO$_2$ ligands deviates 45.7° from the horizontal.

Six optimized configurations (μ$_B$ = 0) were obtained for Sc(BO$_2$)$_3$ and all of them can be considered derived from the Sc(BO$_2$)$_3$ structures. The $T_d$-symmetric 4a is the most stable isomer of Sc(BO$_2$)$_3$, in which each BO$_2$ ligand connects to the Sc atom via one O atom, forming four Sc–O bonds of 1.958 Å. The four BO$_2$ ligands keep away from each other and retain their linear geometry in this isomer. In contrast, two or more BO$_2$ units are combined together in the higher-lying isomers. Isomer 4b lies 6.9 kcal mol$^{-1}$ higher in energy than 4a. It can be obtained by attaching one more BO$_2$ ligand to the vertex boron atom of 3b. With two B$_2$O$_4$ units linked to the Sc atom separately, the $C_2$-symmetric 4c is generated. A trimeric BO$_2$ (B$_3$O$_6$) unit forms in both 4d and 4e isomers, and the energy difference between them is 6.7 kcal mol$^{-1}$. From Fig. 1, 4d and 4e basically inherit the structures of 3e and 3g, respectively, apart from an additional BO$_2$ ligand being attached to the Sc atom of their precursors. In the least stable isomer 4f, four BO$_2$ ligands polymerize to form a tetrameric B$_4$O$_8$, which is bound to the Sc atom through five Sc–O bonds. Note that all anionic Sc(BO$_2$)$_3$ have corresponding neutral Sc(BO$_2$)$_3$ structures (μ$_B$ = 1), only the latter has different total energy order from the former. For instance, the most stable isomer of Sc(BO$_2$)$_3$, namely 4d,
a similar structure to 4d, a low-lying isomer of Sc(BO2)4−. Meanwhile, the lowest-energy isomer of Sc(BO2)4− is corresponding to the least favorable configuration (4a′) of Sc(BO2)4−. This reflects the fact that the loss of extra electron only slightly affects geometry of the studied anions, but varies their relative stability.

3.1.2 Dissociation energy. To explore the thermodynamic stability of the Sc(BO2)2n− anions, two fragmentation paths were considered, namely Sc(BO2)n− → Sc(BO2)n−1 + BO2− and Sc(BO2)n− → Sc(BO2)n−1 + BO2. The zero-point-corrected dissociation energies of the Sc(BO2)2n− anions are listed in Table 1. From the table, these dissociation reactions are highly endothermic. Hence, all Sc(BO2)2n− anions are stable when it comes to emission of a BO2− or BO2 fragment. Besides, the dissociation of a neutral BO2 ligand requires more energy than detaching a BO2− anion from Sc(BO2)2n−. As far as the lowest-energy Sc(BO2)2n− isomers are concerned, it gets more difficult for them to lose a BO2− unit as n becomes larger. For neutral Sc(BO2)n, we also considered two fragmentation pathways, namely Sc(BO2)n → Sc(BO2)n−1 + BO2 and Sc(BO2)n → Sc(BO2)n−2 + BO2. From Table 2, their corresponding zero-point-corrected dissociation energies vary in the range of 33.7–132.5 kcal mol−1 and 120.7–209.4 kcal mol−1, respectively, indicating the stability of Sc(BO2)n. It is also noted that there is not much chance for Sc(BO2)n to eliminate a B2O4 dimer in view of the high dissociation energies.
3.1.3 Hyperhalogen characteristics. Jena and coworkers have reported that MP2 is a reliable method for estimating the vertical detachment energies (VDEs) of metal borate anion and yields results close to those from the CCSD(T) method.33 On the other hand, the OVGF method is also very popular in assessing the VDEs of anions.5,8,10–12,19,21,23,39–40 Take the ScCl4− anion as an example. Its VDE value calculated by the OVGF method is 7.18 eV, which agrees quite well with the experimental result of 7.14 eV.9 Hence, the VDEs of the Sc(BO2)n− anions were obtained by using the MP2 and OVGF methods, respectively. Besides, the adiabatic detachment energies (ADEs) of Sc(BO2)n− were also calculated at the MP2 level. All results are given in Table 1. From the table, the results of MP2 and OVGF calculations are basically consistent. According to the MP2 results, the Sc(BO2)n− anions exhibit high VDE values ranging from 5.44 to 8.85 eV, which are larger than the VDE of 4.46 eV for the Bo2− anion. Therefore, the Sc(BO2)n− species could be classified as hyperhalogen anions. Among the Sc(BO2)n− anions, the first three isomers 4a–c possess larger VDEMP2 values (7.98–8.85 eV) than the rest ones 4d–f (5.44–7.08 eV). This could be attributed to the polymerization of Bo2 units, which is a disadvantage for Sc(BO2)n− to distribute the extra negative charge. Besides, it can be seen from Table 1 that the VDE values show an increasing order of 1a < 2a < 3a < 4a, indicating the VDE dependence of Sc(BO2)n− on the number of Bo2 ligands. In particular, the VDEs show a sharp increase from Sc(BO2)3− to Sc(BO2)4−, which can be related to the maximum valence state of +3 of the Sc atom.

For comparison, the previously reported VDE values of Al(BO2)3−, Sc(BH4)3−, and ScF3− (ref. 50) are shown in ES1.† Given that ScFe4− is a superhalogen anion with halogen as ligands, it is not surprising that it possesses a smaller VDE value of 7.74 eV than that of Sc(BO2)4− (8.69 eV in the present work). Note that ScFe4− also outperforms other hyperhalogen anions. From Table S1,† the VDE value of Sc(BO2)4− is much larger than that of Sc(BH4)− (6.47 eV), although Bo2− has a smaller VDE value compared with BH4− (4.57 eV). Likewise, Sc(BO2)4− is probably a stronger oxidizing agent than Al(BO2)4− (whose VDE = 8.28 eV) where a trivalent main group atom plays the role of central core.

3.2 Ti(BO2)n− (n = 1–5) and V(BO2)n− (n = 1–6)

Next to Sc, the Ti and V atoms have electron configurations of [Ar]3d24s2 and [Ar]3d44s2 and possess maximum valence of +4

TABLE 1 Relative energy (Erel in kcal mol−1), vertical detachment energies (VDEs, in eV), and adiabatic detachment energies (ADEs, in eV) of the Sc(BO2)n− isomers. Pole strengths (PS) in parentheses. Dissociation energies (in kcal mol−1) of the Sc(BO2)n− → Sc(BO2)n−1 + Bo2− (D1) and Sc(BO2)n− → Sc(BO2)n−2 + Bo2− (D2) reactions

| Cluster | Isomer | Erel | VDEOGVF | VDEMP2 | ADE MP2 | D1 | D2 |
|---------|--------|------|---------|---------|---------|-----|-----|
| Sc(BO2)− | 1a | 0.0 | 1.70 (0.888) | 1.41 | 53.6 | 163.9 |
| | 1b | 17.6 | 1.21 (0.896) | 1.28 | 1.26 | 31.7 | 142.0 |
| | 2a | 0.0 | 2.21 (0.882) | 1.94 | 1.91 | 82.0 | 149.7 |
| | 2b | 15.6 | 1.68 (0.881) | 1.56 | 1.50 | 64.6 | 132.3 |
| | 2c | 21.7 | 1.44 (0.852) | 1.59 | 1.27 | 63.0 | 130.8 |
| | 2d | 44.1 | 0.80 (0.817) | 0.82 | 0.79 | 43.3 | 111.1 |
| Sc(BO2)3− | 3a | 0.0 | 2.94 (0.940) | 2.39 | 2.45 | 94.3 | 134.8 |
| | 3b | 9.0 | 3.87 (0.933) | 3.46 | 2.35 | 84.7 | 125.2 |
| | 3c | 13.2 | 2.36 (0.946) | 2.10 | 2.03 | 83.3 | 123.8 |
| | 3d | 20.2 | 3.40 (0.933) | 3.02 | 1.90 | 73.8 | 114.3 |
| | 3e | 27.1 | 3.19 (0.980) | 2.97 | 2.84 | 61.5 | 102.0 |
| | 3f | 27.3 | 3.37 (0.934) | 3.21 | 1.75 | 66.4 | 106.9 |
| | 3g | 36.5 | 2.00 (0.977) | 1.84 | 1.77 | 53.0 | 93.5 |
| Sc(BO2)4− | 4a | 0.0 | 9.08 (0.917) | 8.69 | 8.67 | 103.0 | 142.7 |
| | 4b | 6.9 | 8.40 (0.915) | 8.85 | 7.09 | 98.6 | 138.4 |
| | 4c | 17.5 | 7.87 (0.913) | 7.98 | 6.63 | 88.6 | 128.4 |
| | 4d | 23.5 | 5.82 (0.929) | 5.44 | 4.45 | 79.9 | 119.7 |
| | 4e | 30.2 | 6.93 (0.922) | 7.08 | 5.64 | 74.3 | 114.1 |
| | 4f | 49.2 | 6.02 (0.921) | 6.02 | 4.91 | 54.3 | 94.1 |

TABLE 2 Relative energy (Erel in kcal mol−1) of the Sc(BO2)n− isomers and dissociation energies (in kcal mol−1) of the Sc(BO2)n− → Sc(BO2)n−1 + Bo2− (D1) and Sc(BO2)n− → Sc(BO2)n−2 + Bo2− (D2) reactions

| Cluster | Isomer | Erel | D1 | D2 |
|---------|--------|------|----|----|
| Sc(BO2) | 1a′ | 0.0 | 112.2 | — |
| | 1a− | 10.2 | 121.3 | — |
| | 1b− | 19.8 | 99.4 | — |
| | 1b′ | 28.4 | 108.8 | — |
| Sc(BO2)2 | 2a | 0.0 | 122.5 | 206.8 |
| | 2b | 6.1 | 124.0 | 208.3 |
| | 2c | 6.8 | 120.4 | 204.7 |
| | 2d | 18.1 | 111.7 | 196.1 |
| Sc(BO2)3 | 3a | 0.0 | 130.7 | 207.7 |
| | 3b | 6.8 | 125.3 | 202.2 |
| | 3c | 3.5 | 132.5 | 209.4 |
| | 3d | 7.5 | 127.6 | 204.5 |
| | 3e | 35.9 | 101.3 | 178.2 |
| | 3f | 11.2 | 122.4 | 199.3 |
| | 3g | 20.8 | 117.6 | 194.5 |
| Sc(BO2)4 | 4a | 73.8 | 33.7 | 120.7 |
| | 4b | 44.4 | 44.3 | 131.3 |
| | 4c | 44.3 | 46.1 | 133.1 |
| | 4d | 0.0 | 82.1 | 169.1 |
| | 4e | 34.2 | 50.6 | 137.6 |
| | 4f | 36.4 | 54.1 | 141.1 |
and +5, respectively. To reveal how many BO₂ ligands Ti and V require to qualify their borates for being classified as hyperhalogens, the evolution of DVE values of the Ti(BO₂)ₙ⁻ (n = 1–5) and V(BO₂)ₙ⁻ (n = 1–6) systems were also studied in this work. Based on above analysis, all the lowest-lying Sc(BO₂)ₙ⁻ isomers feature a structure where the BO₂ ligands spread apart and each binds with the central Sc atom through a Sc–O bond. In view of this, only the isomers with separated BO₂ ligands were considered for the Ti(BO₂)ₙ⁻ (n = 1–5) and V(BO₂)ₙ⁻ (n = 1–6) anions. These structures, together with their corresponding neutral ones, were optimized by the M06 method. Different spin multiplicities were taken into account during optimizations. They are possibly local, but not global minima on the potential energy surfaces.

3.2.1 Geometry and magnetism. The optimized structures of Ti(BO₂)ₙ⁻ and their corresponding neutral Ti(BO₂)ₙ are shown in Fig. 3 and 4, respectively, while those of the anionic V(BO₂)ₙ⁻ and neutral V(BO₂)ₙ are presented in Fig. 5 and 6, respectively. The nomenclature uses symbol of element plus Arabic numerals from 1 to 6 to indicate the number of involved BO₂ ligands, followed by s, d, t, q, quintet, and sextet to denote the spin state (singlet, doublet, ...). To illuminate electronic structure of the resulting borates, some selected molecular orbitals are shown in Fig. S1 (ESI†).

Three structures with different spin states (singlet, triplet, quintet) were found for Ti(BO₂)⁻. The singlet isomer is linear, while the other two are slightly bent. It can be found from Fig. 3 and Table 3 that, the isomer where the Ti atom maintains its spin is the most stable, followed by that in a higher spin state, while the one with a total spin state of zero is the least favorable. For example, the stability order is Ti₁⁻⁻ > Ti₁-quintet > Ti₁⁻⁻. The same is valid for the Ti(BO₂)₁⁻⁻ and Ti(BO₂)₂⁻⁻ isomers. That is, the Ti₂⁻⁻ and Ti₃⁻⁻ isomers with two unpaired d electrons from Ti are 3.0 and 17.3 kcal mol⁻¹ more stable than Ti₂⁻⁻ and Ti₃⁻⁻, respectively. Due to Jahn–Teller effect, Ti₃⁻⁻ has C₂ᵥ instead of D₃h symmetry and the symmetry of Ti₄⁻⁻ is lowered to D₂d compared with the lowest-lying structure of Sc(BO₂)₄⁻⁻. In contrast, Ti₃⁻⁻ and its corresponding neutral Ti₃⁻⁻ hold D₃h symmetry. Likewise, Ti₅⁻⁻ possesses a trigonal bipyramidal geometry with D₃₃h symmetry. The structures of neutral Ti(BO₂)₅ basically resemble those of their corresponding anions. The only exception here is Ti₅⁻⁻, in which two BO₂ ligands are combined together.

From Fig. 5 and Table 3, the V atom maintains its spin in the lowest-lying isomer of V(BO₂)⁻, namely V₁⁻⁻. Consequently, it has a magnetic moment of 3 μB. High-spin isomer V₁⁻⁻⁻ and low-spin isomer V₁⁻⁻ are 5.8 and 71.7 kcal mol⁻¹ higher in energy than V₁⁻⁻, respectively. All three structures of V(BO₂)₂⁻ are linear with D₃₃h symmetry. The magnetic moment is 4 μB for the lowest-energy configuration V₂⁻⁻⁻. The electronic structure characteristics of both Ti(BO₂)ₙ⁻ and V(BO₂)ₙ⁻ species indicate that the central transition metal atoms are inclined to keep the intrinsic electronic state in their borates. For V(BO₂)ₙ⁻ (n = 3–6), the BO₂ ligands are distributed individually in each cluster. Obviously, Jahn–Teller distortion also appears in the

![Fig. 3 Optimized structures of the Ti(BO₂)ₙ⁻ (n = 1–5) clusters. (Color legend: Ti, blue; O, red; B, light pink; symmetry and magnetic moment in parentheses.)](image-url)
V(BO2)$_n$C$_0$ series. The geometry of V3-q is still of D$_{3h}$-symmetry. In contrast, both V4-t and V4-s are distorted to D$_{2d}$-symmetry as the V atom possesses two d electrons therein. V5-d is lowered to C$_2$-symmetry because the V atom has one d electron left. Similar to the case of Ti(BO$_2$)$_n$C$_0$, V6-s does not have d electron from the central metal atom, so it appears to be a regular octahedron with O$_h$-symmetry. As for the neutral V(BO$_2$)$_n$ clusters, the BO$_2$ ligands are also isolated in every structure except that two BO$_2$ ligands dimerized in V6'-d.

From Table 3, the zero-point-corrected dissociation energies of Ti(BO$_2$)$_n$C$_0$ and V(BO$_2$)$_n$C$_0$ are in the range of 26.3–141.6 kcal mol$^{-1}$ and 14.6–139.5 kcal mol$^{-1}$, respectively, indicating the stability of Ti(BO$_2$)$_n$C$_0$ and V(BO$_2$)$_n$C$_0$ with respect to emission of a BO$_2$ unit.

3.2.2 Vertical electron detachment energy. The VDE and ADE values of Ti(BO$_2$)$_n$C$_0$ and V(BO$_2$)$_n$C$_0$ calculated at the MP2 level are listed in Table 3, where the VDE values from the OVGF method are also listed for comparison. From the table, Ti3-t, Ti4-d, Ti5-s, Ti6-d, V2-t, V3-q, V4-s, V4-t, V5-d, and V6-s can be classified as superhalogen anions, among which the Ti3-t, Ti4-d, V2-t, V3-q, V4-t, V5-d isomers with nonzero magnetic moment can be considered as magnetic superhalogens. Besides, the Ti4-d, Ti5-

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**Fig. 4** Optimized structures of the Ti(BO$_2$)$_n$ ($n = 1–5$) clusters. (Color legend: Ti, blue; O, red; B, light pink; symmetry and magnetic moment in parentheses.)

**Fig. 5** Optimized structures of the V(BO$_2$)$_n$ (n = 1–6) clusters. (Color legend: V, purple; O, red; B, light pink; symmetry and magnetic moment in parentheses.)
s, V3-q, V4-s, V4-t, V5-d and V6-s species possess larger VDE values than that of BO2− and can be termed hyperhalogen anions. In a word, with Sc, Ti, and V as central atoms, it requires at least four, four, and three BO2 ligands, respectively, to qualify the resulting TM(BO2)n− (TM = Sc, Ti, and V) clusters to be considered as hyperhalogens. From Table 3, it is noted that the VDEMP2 values of Ti(BO2)n− show a sharp increase from Ti(BO2)4− to Ti(BO2)5−. Such a sudden rise of VDE value is believed to root in the maximum valence state of +4 of the Ti atom. However, the same increase doesn’t appear in the V(BO2)n− series. From Table S1,† the VDE values of TMFₙ₋₀ (TM = Sc, Ti, V) can be more or less enhanced by replacing fluorine with BO2 ligands.

4. Conclusions

The structural, electronic and magnetic properties of three series of early-transition-metal borates, namely Sc(BO2)n−₀ (n = 1–4), Ti(BO2)n−₀ (n = 1–5), and V(BO2)n−₀ (n = 1–6), were studied by performing density functional theory and ab initio calculations. In view of the positive dissociation energies, all studied anionic clusters are stable against the loss of a BO2 ligand. The lowest-lying Sc(BO2)n−₀ isomers feature a structure where the BO2 ligands spread apart, whereas the BO2 ligands begin to combine into a trimer in the lowest-energy Sc(BO2)4− structure. This can be related to the maximum valence state of +3 of the Sc atom. By the same token, there is a sharp increase in VDE value from Sc(BO2)3− to Sc(BO2)4−, and the latter species can be classified as hyperhalogens since they possess larger VDE values than that of its superhalogen ligand BO2−. As for Ti and V atoms, they require four and three BO2 ligands, respectively, to enable their borates to be termed hyperhalogen. Besides, the Ti4−, V3-q, V4-t, and V5-d species can be considered as magnetic hyperhalogens owing to their nonzero magnetic moment.

Conflicts of interest

There are no conflicts of interest to declare.
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