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# Hyperhalogen properties of early-transition-metal borates†

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The equilibrium structures, stability and magnetic properties of  $\text{Sc}(\text{BO}_2)_n^{-/0}$  ( $n = 1-4$ ) clusters were investigated on the basis of density functional theory calculations. The  $\text{BO}_2$  ligands prefer to stretch out in the most stable  $\text{Sc}(\text{BO}_2)_n^-$  anions but tend to come together in the lowest-lying  $\text{Sc}(\text{BO}_2)_4$  structure. According to the MP2 results, the  $\text{Sc}(\text{BO}_2)_4^-$  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  $\text{BO}_2^-$ . With titanium and vanadium playing the role of central atom, the  $\text{Ti}(\text{BO}_2)_n^{-/0}$  ( $n = 1-5$ ) and  $\text{V}(\text{BO}_2)_n^{-/0}$  ( $n = 1-6$ ) 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  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 4, 5$ ) and  $\text{V}(\text{BO}_2)_n^-$  ( $n = 3-6$ ) species were also confirmed by the calculated VDE values.

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## 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.<sup>1</sup> Atoms and clusters with high EA usually show remarkable oxidation capacity in chemical reactions. Bartlett and co-workers found that  $\text{PtF}_6$  could even oxidize a Xe atom,<sup>2</sup> and then confirmed that the  $\text{PtF}_6$  molecule possesses a very high EA of 6.8 eV.<sup>3</sup> Such molecules that have higher EAs than the chlorine atom were termed superhalogen by Boldyrev and Gutsev in 1981.<sup>4</sup> Besides, they recommended a simple formula  $\text{MX}_{k+1}$  for constructing superhalogens, where M is a main group or transition metal atom, X is a halogen atom, and  $k$  is the maximal formal valence of M.<sup>4</sup> The first experimental evidence of such species, namely  $\text{MX}_2^-$  (M = Li, Na, and X = Cl, Br, I), was obtained by Wang's group in 1999.<sup>5</sup> Afterwards, an increasing number of superhalogen anions have been theoretically predicted or experimentally detected, such as  $\text{MX}_3^-$  (M = Be, Mg, Ca; X = Cl, Br)<sup>6-8</sup> and  $\text{MCl}_4^-$  (M = Sc, Y, La).<sup>9</sup> Recently, many kinds of superhalogens that are beyond the  $\text{MX}_{k+1}$  formula have been proposed and characterized. To facilitate extra-electron delocalization, multinuclear superhalogen anions have been designed such as  $\text{P}_2\text{F}_{11}^-$  and  $\text{As}_2\text{F}_{11}^-$ ,<sup>10</sup>  $\text{Mg}_2\text{F}_5^-$ ,<sup>11</sup>  $\text{Al}_2\text{F}_7^-$ ,<sup>10</sup> and

$\text{H}_{12}\text{F}_{13}^-$ .<sup>12</sup> 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  $\text{MnO}_4$ ,<sup>13</sup>  $\text{CrO}_4$ ,<sup>14</sup>  $\text{BO}_2$ ,<sup>15</sup>  $\text{AlO}_2$ ,<sup>16</sup>  $\text{VO}_3$ ,<sup>16</sup>  $\text{BrO}_3$ ,<sup>17</sup>  $\text{IO}_3$ ,<sup>17</sup>  $\text{IO}_4$ ,<sup>17</sup>  $\text{BS}_2$ ,<sup>18</sup> and  $\text{BSO}$ <sup>18</sup> molecules, and those involving electrophilic substituent,<sup>19</sup> organic group,<sup>20</sup> and acidic functional group<sup>21</sup> as ligands.

Superhalogens are strong electron-acceptors and can be used to oxidize systems with high ionization potential, such as benzene<sup>22</sup> and small water clusters.<sup>23</sup> They may combine with superalkalis to form ionic compounds that are predicted to possess excellent nonlinear optical response.<sup>24</sup> Recent studies have also shown that  $\text{MnCl}_3$ , one of the experimentally synthesized superhalogens, could be used to tune the electronic and magnetic properties of silicone,<sup>25</sup> and that the  $\text{AlF}_4$  superhalogen can initiate a radical-substitution chain reaction as the trigger-compound.<sup>26</sup> In 2015, Jena predicted that superhalogens could serve as a bridge between complex metal hydrides and electrolytes in Li-ion battery.<sup>27</sup> Soon after, the suitability of superhalogen salt for Mg battery electrolyte was experimentally proved.<sup>28</sup> The extensive application prospects of superhalogens make them promising agents in chemistry and material science and attract more and more attention.<sup>29,30</sup>

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.<sup>31</sup>  $\text{Au}(\text{BO}_2)_2$  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.,  $\text{Cu}_n(\text{BO}_2)_m$  ( $n, m = 1, 2$ ),<sup>32</sup>  $\text{Al}(\text{BO}_2)_m$ ,<sup>33</sup>  $\text{Ag}(\text{BO}_2)_2$ ,<sup>34</sup>  $\text{Na}(\text{BF}_4)_2$ ,<sup>35</sup>  $\text{Mg}(\text{BF}_4)_3$ ,<sup>36</sup>  $\text{Al}(\text{BF}_4)_4$ ,<sup>37</sup>  $\text{Al}(\text{BH}_4)_4$ ,<sup>37</sup> and  $\text{M}(\text{IO}_3)_2^-$  (M = H, Li, Na,

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K).<sup>38</sup> Furthermore, Jena *et al.* proposed the concept of “magnetic hyperhalogens” by studying the  $\text{Fe}(\text{BO}_2)_n$  and  $\text{Mn}(\text{BO}_2)_n$  clusters.<sup>39</sup> Recently, two series of hyperhalogen anions involving planar and cage-like superhalogen ligands were reported, respectively, and the concept of aromatic hyperhalogen was brought forward as well.<sup>40,41</sup>

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  $\text{BO}_2$  ligands they need to exhibit hyperhalogen character with. Besides, our study also aims to (1) reveal the geometrical feature of the resulting  $\text{Sc}(\text{BO}_2)_n^{-/0}$  ( $n = 1-4$ ),  $\text{Ti}(\text{BO}_2)_n^{-/0}$  ( $n = 1-5$ ), and  $\text{V}(\text{BO}_2)_n^{-/0}$  ( $n = 1-6$ ) 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  $\text{TM}(\text{BO}_2)_n^-$  (TM = Sc, Ti, V) anions.

## 2. Computational details

With different spin multiplicity taken into account, the optimized geometries of the  $\text{Sc}(\text{BO}_2)_n^{-/0}$  ( $n = 1-4$ ),  $\text{Ti}(\text{BO}_2)_n^{-/0}$  ( $n = 1-5$ ), and  $\text{V}(\text{BO}_2)_n^{-/0}$  ( $n = 1-6$ ) species were obtained by using the M06 functional<sup>42</sup> of density functional theory. Frequency and natural bond orbital (NBO) analyses<sup>43</sup> 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  $\text{Sc}(\text{BO}_2)_n^-$  ( $n = 1-4$ ),  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 1-5$ ), and  $\text{V}(\text{BO}_2)_n^-$  ( $n = 1-6$ ) 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)<sup>44-46</sup> method was used to estimate the VDE values. For all investigated anions, the pole strengths (PSs) are greater than 0.85, justifying the validity of OVGF approximation.<sup>47</sup> 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.<sup>48</sup> Dimensional plots of the molecular structures were generated with the GaussView program.<sup>49</sup>

## 3. Results and discussion

### 3.1 $\text{Sc}(\text{BO}_2)_n^-$ and $\text{Sc}(\text{BO}_2)_n$ ( $n = 1-4$ )

**3.1.1 Equilibrium geometries and relative stability.** We considered all possible configurations of  $\text{Sc}(\text{BO}_2)_n^-$  and  $\text{Sc}(\text{BO}_2)_n$  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  $\text{BO}_2$  ligands in the  $\text{Sc}(\text{BO}_2)_n^-$  clusters, followed by a, b, c... indicating the increasing MP2 single point energy order of different isomers. As for the neutral  $\text{Sc}(\text{BO}_2)_n$  series, their structures are named after corresponding anionic ones.

As shown in Fig. 1, isomer **1a** of  $\text{ScBO}_2^-$  is linear and similar to the reported structures of  $\text{FeBO}_2$ ,  $\text{MnBO}_2$ , and  $\text{MnBO}_2^-$ .<sup>39</sup> The other isomer **1b** has  $C_{2v}$  symmetry, where the  $\text{BO}_2$  ligand bends to  $156.6^\circ$  and binds with the Sc atom *via* two O atoms. Both **1a** and **1b** have magnetic moment of  $1 \mu_B$ . However, the neutral  $\text{ScBO}_2$  (see Fig. 2) has variable magnetism. The most stable isomer **1a'** of  $\text{ScBO}_2$  has a magnetic moment of  $2 \mu_B$ , which is similar to the case of  $\text{ScCl}$  and  $\text{ScF}$ .<sup>50</sup> Isomer **1a''** also has a linear configuration, only it has a magnetic moment of  $0 \mu_B$  and slightly shorter Sc–O bond length of  $1.867 \text{ \AA}$ . As for **1b'** and **1b''**, which share similar structural features with **1b**, they possess different Sc–O bond lengths ( $2.225 \text{ \AA}$  and  $2.114 \text{ \AA}$ , respectively) and magnetic moments ( $2 \mu_B$  and  $0 \mu_B$ , respectively).

As one more  $\text{BO}_2$  ligand is introduced, four isomers have been obtained for both anionic  $\text{Sc}(\text{BO}_2)_2^-$  and neutral  $\text{Sc}(\text{BO}_2)_2$ . The spin multiplicities of  $\text{Sc}(\text{BO}_2)_2^-$  and  $\text{Sc}(\text{BO}_2)_2$  are 1 and 2, respectively. **2a**, the lowest-energy isomer of  $\text{Sc}(\text{BO}_2)_2^-$ , has a linear structure, in which each  $\text{BO}_2$  ligand is attached to the middle Sc atom through a Sc–O bond. The same case was reported for the ground states of  $\text{Mn}(\text{BO}_2)_2^-$  and  $\text{Fe}(\text{BO}_2)_2^-$ .<sup>39</sup> The Sc–O bond length ( $1.979 \text{ \AA}$ ) of **2a** is slightly shorter than that of **1a** ( $2.006 \text{ \AA}$ ). Isomer **2b** has a planar structure, where the two  $\text{BO}_2$  ligands combine with each other, forming a  $\text{B}_2\text{O}_4$  unit that shows a similar structure to the recently reported  $(\text{BO}_2)_2^-$  anion.<sup>51</sup> In the next isomer **2c**, two  $\text{BO}_2$  ligands bind with the Sc atom *via* one and two Sc–O bonds, respectively. The  $\angle \text{O1B1O2}$  angle of **2c** is  $147.5^\circ$ , indicating a larger ligand distortion relative to structure **1b**. As for the last isomer **2d**, it has a  $D_{2d}$ -symmetric structure where each  $\text{BO}_2$  unit is linked to the center Sc atom by two Sc–O bonds. The Sc atom is coplanar with each  $\text{BO}_2$  ligand in this structure and the two  $\text{BO}_2$  planes are perpendicular to each other. The  $\angle \text{OBO}$  angle in **2d** is  $148.5^\circ$ , which is close to that of **2c**. From Fig. 2 and Table 2, the neutral  $\text{Sc}(\text{BO}_2)_2$  isomers share similar structures and the same total energy order with their corresponding anions.

$\text{Sc}(\text{BO}_2)_3^-$  and  $\text{Sc}(\text{BO}_2)_3$  have magnetic moments of  $1 \mu_B$  and  $0 \mu_B$ , respectively. Seven structures were obtained for  $\text{Sc}(\text{BO}_2)_3^-$ , and the  $D_{3h}$ -symmetric structure **3a** is the most stable one. In **3a**, each  $\text{BO}_2$  ligand binds with the center Sc atom *via* one Sc–O bond of  $1.990 \text{ \AA}$ . In contrast, a  $\text{ScOBO}$  quadrilateral forms in the rest isomers. The  $C_{2v}$ -symmetric isomer **3b** can be viewed as one more  $\text{BO}_2$  ligand attaching to structure **2c**, which is supported by NBO analysis. Both isomers **3c** and **3d** can be obtained by adding a  $\text{BO}_2$  ligand to structure **2b**. The difference is that the additional  $\text{BO}_2$  ligand bonds with the Sc atom *via* one O atom in the former but *via* two O atoms in the latter. In  $C_{2v}$ -symmetric **3e**, three  $\text{BO}_2$  ligands get together and form a  $\text{B}_3\text{O}_6$  unit, which is similar to the structure of  $(\text{BO}_2)_3^-$ .<sup>51</sup> In the next isomer **3f**, a  $\text{B}_2\text{O}_4$  unit forms and is linked to Sc through three Sc–O bonds. The least favorable structure of  $\text{Sc}(\text{BO}_2)_3^-$  is **3g** with  $C_s$



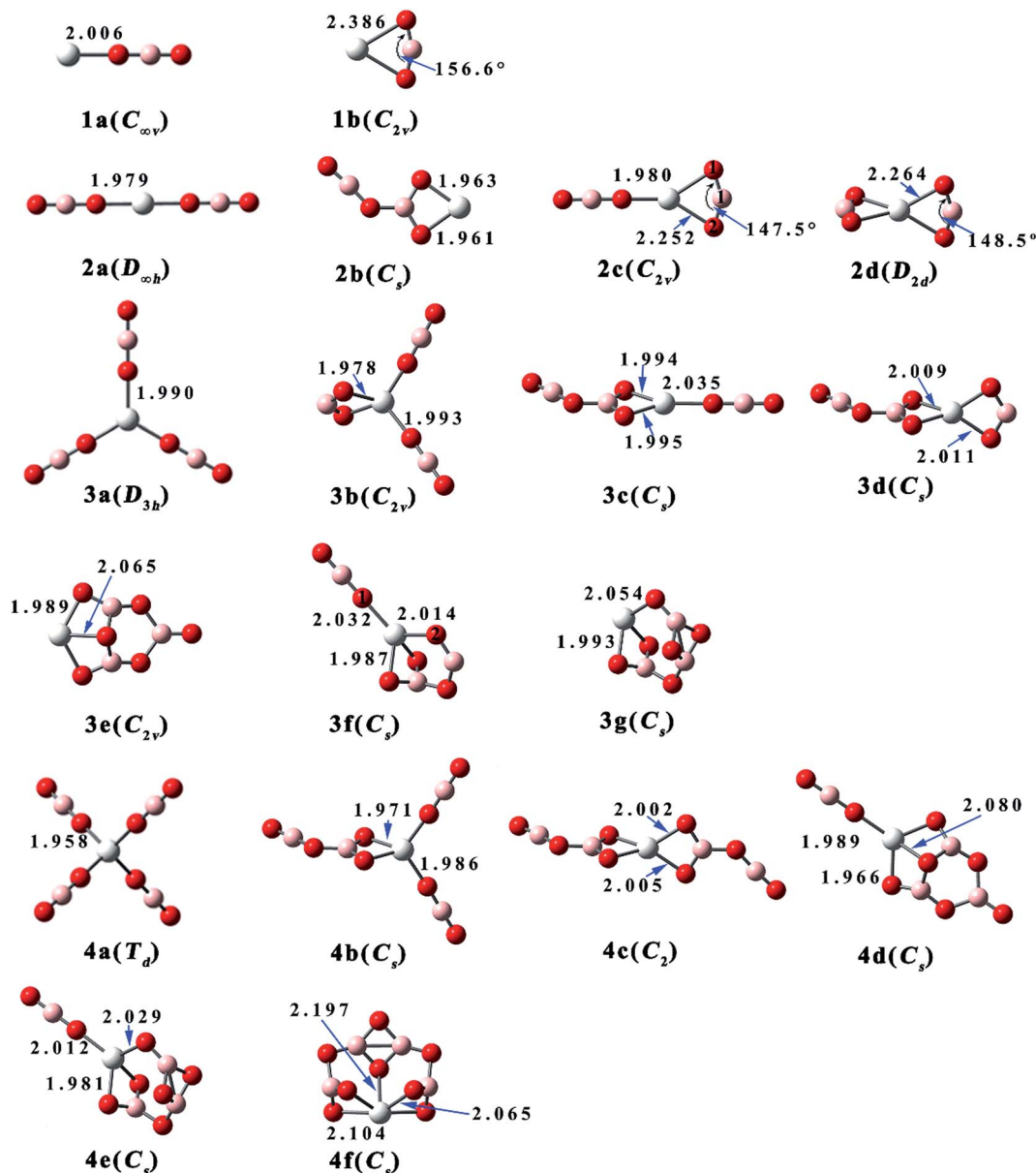


Fig. 1 Equilibrium structures and critical bond lengths (in Å) of the  $\text{Sc}(\text{BO}_2)_n^-$  ( $n = 1-4$ ) clusters. (Color legend: Sc, grey; O, red; B, light pink. Symmetry in parentheses.)

symmetry, which contains a different  $\text{B}_3\text{O}_6$  unit compared with **3e**. As for neutral  $\text{Sc}(\text{BO}_2)_3$ , all isomers possess a similar structure to their corresponding anions but their stability follows a different order. The largest structural difference is found between **3c** and its neutral counterpart, namely **3c'** where one of the  $\text{BO}_2$  ligands deviates  $45.7^\circ$  from the horizontal.

Six optimized configurations ( $\mu_{\text{B}} = 0$ ) were obtained for  $\text{Sc}(\text{BO}_2)_4^-$  and all of them can be considered derived from the  $\text{Sc}(\text{BO}_2)_3^-$  structures. The  $T_d$ -symmetric **4a** is the most stable isomer of  $\text{Sc}(\text{BO}_2)_4^-$ , in which each  $\text{BO}_2$  ligand connects to the Sc atom *via* one O atom, forming four Sc–O bonds of 1.958 Å. The four  $\text{BO}_2$  ligands keep away from each other and retain their linear geometry in this isomer. In contrast, two or more  $\text{BO}_2$  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  $\text{BO}_2$  ligand to the vertex boron atom of **3b**. With two  $\text{B}_2\text{O}_4$  units linked to the Sc atom separately, the  $C_2$ -symmetric **4c** is generated. A trimeric  $\text{BO}_2$  ( $\text{B}_3\text{O}_6$ ) 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  $\text{BO}_2$  ligand being attached to the Sc atom of their precursors. In the least stable isomer **4f**, four  $\text{BO}_2$  ligands polymerize to form a tetrameric  $\text{B}_4\text{O}_8$ , which is bound to the Sc atom through five Sc–O bonds. Note that all anionic  $\text{Sc}(\text{BO}_2)_4^-$  have corresponding neutral  $\text{Sc}(\text{BO}_2)_4$  structures ( $\mu_{\text{B}} = 1$ ), only the latter has different total energy order from the former. For instance, the most stable isomer of  $\text{Sc}(\text{BO}_2)_4$ , namely **4d'**, has



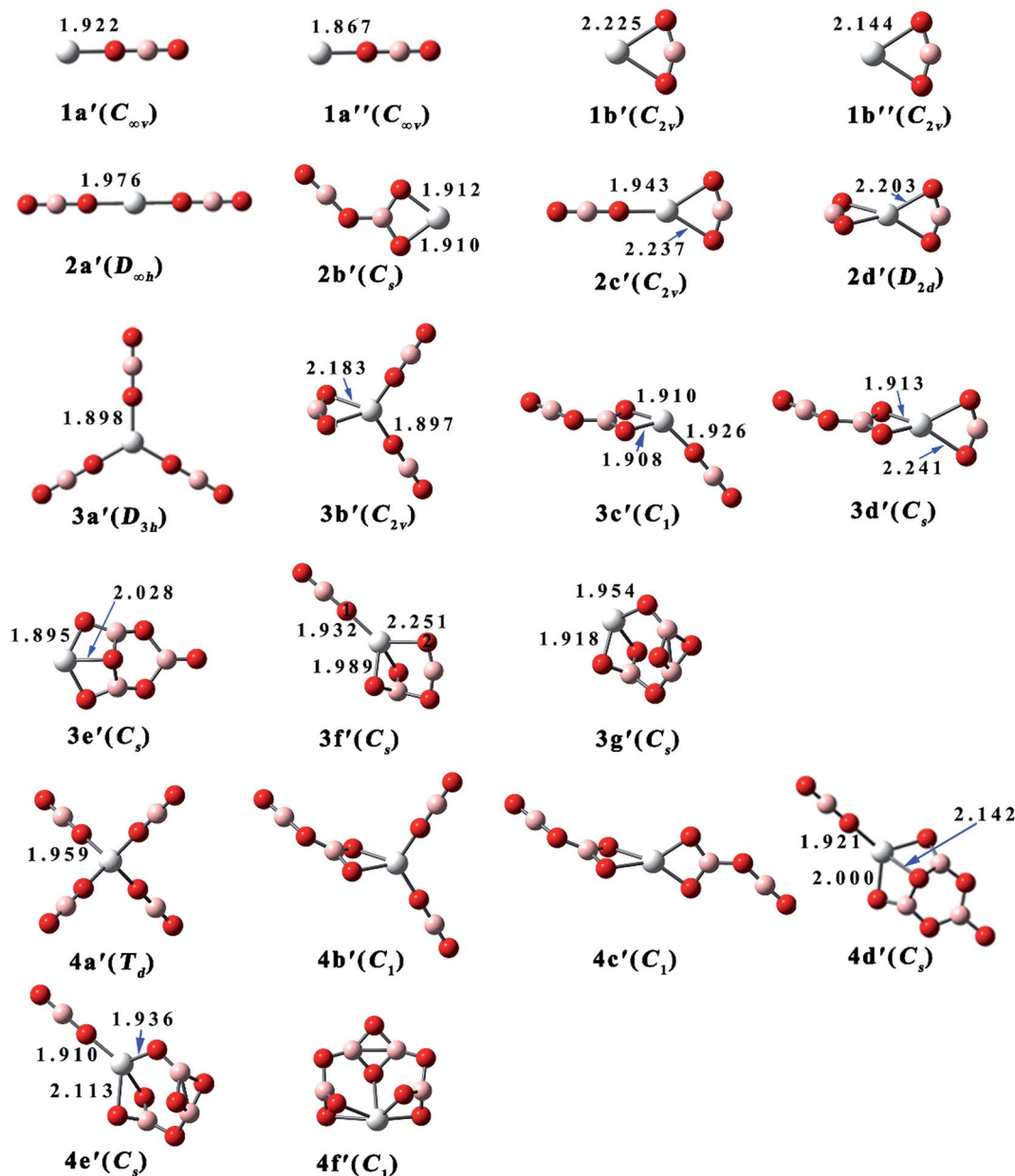


Fig. 2 Equilibrium structures and critical bond lengths (in Å) of the Sc(BO<sub>2</sub>)<sub>n</sub> (n = 1–4) clusters. (Color legend: Sc, grey; O, red; B, light pink. Symmetry in parentheses.)

a similar structure to **4d**, a low-lying isomer of Sc(BO<sub>2</sub>)<sub>4</sub><sup>−</sup>. Meanwhile, the lowest-energy isomer of Sc(BO<sub>2</sub>)<sub>4</sub><sup>−</sup> is corresponding to the least favorable configuration (**4a'**) of Sc(BO<sub>2</sub>)<sub>4</sub>. 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(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> anions, two fragmentation paths were considered, namely Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> → Sc(BO<sub>2</sub>)<sub>n−1</sub> + BO<sub>2</sub><sup>−</sup> and Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> → Sc(BO<sub>2</sub>)<sub>n−1</sub><sup>−</sup> + BO<sub>2</sub>. The zero-point-corrected dissociation energies of the Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> anions are listed in Table 1. From the table, these dissociation reactions are highly endothermic. Hence, all Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> anions are stable when it

comes to emission of a BO<sub>2</sub><sup>−</sup> or BO<sub>2</sub> fragment. Besides, the dissociation of a neutral BO<sub>2</sub> ligand requires more energy than detaching a BO<sub>2</sub><sup>−</sup> anion from Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup>. As far as the lowest-energy Sc(BO<sub>2</sub>)<sub>n</sub><sup>−</sup> isomers are concerned, it gets more difficult for them to lose a BO<sub>2</sub><sup>−</sup> unit as n becomes larger. For neutral Sc(BO<sub>2</sub>)<sub>n</sub>, we also considered two fragmentation pathways, namely Sc(BO<sub>2</sub>)<sub>n</sub> → Sc(BO<sub>2</sub>)<sub>n−1</sub> + BO<sub>2</sub> and Sc(BO<sub>2</sub>)<sub>n</sub> → Sc(BO<sub>2</sub>)<sub>n−2</sub> + B<sub>2</sub>O<sub>4</sub>. From Table 2, their corresponding zero-point-corrected dissociation energies vary in the range of 33.7–132.5 kcal mol<sup>−1</sup> and 120.7–209.4 kcal mol<sup>−1</sup>, respectively, indicating the stability of Sc(BO<sub>2</sub>)<sub>n</sub>. It is also noted that there is not much chance for Sc(BO<sub>2</sub>)<sub>n</sub> to eliminate a B<sub>2</sub>O<sub>4</sub> dimer in view of the high dissociation energies.



**Table 1** Relative energy ( $E_{\text{rel}}$ , in kcal mol<sup>-1</sup>), vertical detachment energies (VDEs, in eV), and adiabatic detachment energies (ADEs, in eV) of the Sc(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> isomers. Pole strengths (PS) in parentheses. Dissociation energies (in kcal mol<sup>-1</sup>) of the Sc(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> → Sc(BO<sub>2</sub>)<sub>*n*-1</sub><sup>-</sup> + BO<sub>2</sub><sup>-</sup> ( $D_1$ ) and Sc(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> → Sc(BO<sub>2</sub>)<sub>*n*-1</sub><sup>-</sup> + BO<sub>2</sub> ( $D_2$ ) reactions

Cluster	Isomer	$E_{\text{rel}}$	VDE <sup>OVGF</sup>	VDE <sup>MP2</sup>	ADE (MP2)	$D_1$	$D_2$
Sc(BO <sub>2</sub> ) <sup>-</sup>	<b>1a</b>	0.0	1.70 (0.888)	1.41	1.23	53.6	163.9
	<b>1b</b>	17.6	1.21 (0.896)	1.28	1.26	31.7	142.0
Sc(BO <sub>2</sub> ) <sub>2</sub> <sup>-</sup>	<b>2a</b>	0.0	2.21 (0.882)	1.94	1.91	82.0	149.7
	<b>2b</b>	15.6	1.68 (0.881)	1.56	1.50	64.6	132.3
	<b>2c</b>	21.7	1.44 (0.852)	1.59	1.27	63.0	130.8
	<b>2d</b>	44.1	0.80 (0.817)	0.82	0.79	43.3	111.1
Sc(BO <sub>2</sub> ) <sub>3</sub> <sup>-</sup>	<b>3a</b>	0.0	2.94 (0.940)	2.59	2.45	94.3	134.8
	<b>3b</b>	9.0	3.87 (0.933)	3.46	2.35	84.7	125.2
	<b>3c</b>	13.2	2.36 (0.946)	2.10	2.03	83.3	123.8
	<b>3d</b>	20.2	3.40 (0.933)	3.02	1.90	73.8	114.3
	<b>3e</b>	27.1	3.19 (0.980)	2.97	2.84	61.5	102.0
	<b>3f</b>	27.3	3.57 (0.934)	3.21	1.75	66.4	106.9
	<b>3g</b>	36.5	2.00 (0.977)	1.84	1.77	53.0	93.5
Sc(BO <sub>2</sub> ) <sub>4</sub> <sup>-</sup>	<b>4a</b>	0.0	9.08 (0.917)	8.69	8.67	103.0	142.7
	<b>4b</b>	6.9	8.40 (0.915)	8.85	7.09	98.6	138.4
	<b>4c</b>	17.5	7.87 (0.913)	7.98	6.63	88.6	128.4
	<b>4d</b>	23.5	5.82 (0.929)	5.44	4.45	79.9	119.7
	<b>4e</b>	30.2	6.93 (0.922)	7.08	5.64	74.3	114.1
	<b>4f</b>	49.2	6.02 (0.921)	6.02	4.91	54.3	94.1

**Table 2** Relative energy ( $E_{\text{rel}}$ , in kcal mol<sup>-1</sup>) of the Sc(BO<sub>2</sub>)<sub>*n*</sub> isomers and dissociation energies (in kcal mol<sup>-1</sup>) of the Sc(BO<sub>2</sub>)<sub>*n*</sub> → Sc(BO<sub>2</sub>)<sub>*n*-1</sub> + BO<sub>2</sub> ( $D'_1$ ) and Sc(BO<sub>2</sub>)<sub>*n*</sub> → Sc(BO<sub>2</sub>)<sub>*n*-2</sub> + B<sub>2</sub>O<sub>4</sub> ( $D'_2$ ) reactions

Cluster	Isomer	$E_{\text{rel}}$	$D'_1$	$D'_2$
Sc(BO <sub>2</sub> )	<b>1a'-t</b>	0.0	112.2	—
	<b>1a'-s</b>	10.2	121.3	—
	<b>1b'-t</b>	19.8	99.4	—
	<b>1b'-s</b>	28.4	108.8	—
Sc(BO <sub>2</sub> ) <sub>2</sub>	<b>2a'</b>	0.0	122.5	206.8
	<b>2b'</b>	6.1	124.0	208.3
	<b>2c'</b>	6.8	120.4	204.7
	<b>2d'</b>	18.1	111.7	196.1
Sc(BO <sub>2</sub> ) <sub>3</sub>	<b>3a'</b>	0.0	130.7	207.7
	<b>3b'</b>	6.8	125.3	202.2
	<b>3c'</b>	3.5	132.5	209.4
	<b>3d'</b>	7.5	127.6	204.5
	<b>3e'</b>	35.9	101.3	178.2
	<b>3f'</b>	11.2	122.4	199.3
Sc(BO <sub>2</sub> ) <sub>4</sub>	<b>3g'</b>	20.8	117.6	194.5
	<b>4a'</b>	73.8	33.7	120.7
	<b>4b'</b>	44.4	44.3	131.3
	<b>4c'</b>	44.3	46.1	133.1
	<b>4d'</b>	0.0	82.1	169.1
	<b>4e'</b>	34.2	50.6	137.6
	<b>4f'</b>	36.4	54.1	141.1

**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.<sup>33</sup> On the other hand, the OVGf method is also very popular in assessing the VDEs of anions.<sup>5-8,10-12,19,21,33,50</sup> Take the ScCl<sub>4</sub><sup>-</sup> 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.<sup>9</sup> Hence, the VDEs of the Sc(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> anions were

obtained by using the MP2 and OVGf methods, respectively. Besides, the adiabatic detachment energies (ADEs) of Sc(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> 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(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> 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 BO<sub>2</sub><sup>-</sup> anion. Therefore, the Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> species could be classified as hyperhalogen anions. Among the Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> anions, the first three isomers **4a-c** possess larger VDE<sup>MP2</sup> 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 BO<sub>2</sub> units, which is a disadvantage for Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> 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(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> on the number of BO<sub>2</sub> ligands. In particular, the VDEs show a sharp increase from Sc(BO<sub>2</sub>)<sub>3</sub><sup>-</sup> to Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup>, which can be related to the maximum valence state of +3 of the Sc atom.

For comparison, the previously reported VDE values of Al(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup>,<sup>33</sup> Sc(BH<sub>4</sub>)<sub>*n*</sub><sup>-</sup>,<sup>52</sup> and ScF<sub>*n*</sub><sup>-</sup> (ref. 50) are shown in ESI.† Given that ScF<sub>4</sub><sup>-</sup> 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(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> (8.69 eV in the present work). Note that Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> also outperforms other hyperhalogen anions. From Table S1,† the VDE value of Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> is much larger than that of Sc(BH<sub>4</sub>)<sub>4</sub><sup>-</sup> (6.47 eV), although BO<sub>2</sub><sup>-</sup> has a smaller VDE value compared with BH<sub>4</sub><sup>-</sup> (4.57 eV). Likewise, Sc(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> is probably a stronger oxidizing agent than Al(BO<sub>2</sub>)<sub>4</sub><sup>-</sup> (whose VDE = 8.28 eV) where a trivalent main group atom plays the role of central core.

### 3.2 Ti(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> (*n* = 1–5) and V(BO<sub>2</sub>)<sub>*n*</sub><sup>-</sup> (*n* = 1–6)

Next to Sc, the Ti and V atoms have electron configurations of [Ar]3d<sup>2</sup>4s<sup>2</sup> and [Ar]3d<sup>3</sup>4s<sup>2</sup> and possess maximum valence of +4



and +5, respectively. To reveal how many  $\text{BO}_2$  ligands Ti and V require to qualify their borates for being classified as hyperhalogens, the evolution of VDE values of the  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 1-5$ ) and  $\text{V}(\text{BO}_2)_n^-$  ( $n = 1-6$ ) systems were also studied in this work. Based on above analysis, all the lowest-lying  $\text{Sc}(\text{BO}_2)_n^-$  isomers feature a structure where the  $\text{BO}_2$  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  $\text{BO}_2$  ligands were considered for the  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 1-5$ ) and  $\text{V}(\text{BO}_2)_n^-$  ( $n = 1-6$ ) anions. These structures, together with their corresponding neutral ones, were optimized by the M06 method. Different spin multiplicities were taken into account during optimizations. Note that the neutral  $\text{Ti}(\text{BO}_2)_n$  ( $n = 1-5$ ) and  $\text{V}(\text{BO}_2)_n$  ( $n = 1-6$ ) configurations were obtained on the basis of their corresponding anionic structures instead of a thorough structure searching. They are possibly local, but not global minima on the potential energy surfaces.

**3.2.1 Geometry and magnetism.** The optimized structures of  $\text{Ti}(\text{BO}_2)_n^-$  and their corresponding neutral  $\text{Ti}(\text{BO}_2)_n$  are shown in Fig. 3 and 4, respectively, while those of the anionic  $\text{V}(\text{BO}_2)_n^-$  and neutral  $\text{V}(\text{BO}_2)_n$  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  $\text{BO}_2$  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  $\text{Ti}(\text{BO}_2)^-$ . 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-t** > **Ti1-quintet** > **Ti1-s**. The same is valid for the  $\text{Ti}(\text{BO}_2)_2^-$  and  $\text{Ti}(\text{BO}_2)_3^-$  isomers. That is, the **Ti2-q** and **Ti3-t** isomers with two unpaired d electrons from Ti are 3.0 and 17.3 kcal mol<sup>-1</sup> more stable than **Ti2-d** and **Ti3-s**, respectively. Due to Jahn–Teller effect, **Ti3-t** has  $C_{2v}$  instead of  $D_{3h}$  symmetry and the symmetry of **Ti4-d** is lowered to  $D_{2d}$  compared with the lowest-lying structure of  $\text{Sc}(\text{BO}_2)_4^-$ . In contrast, **Ti3-s** and its corresponding neutral **Ti3'-d** hold  $D_{3h}$  symmetry. Likewise, **Ti5-s** possesses a trigonal bipyramidal geometry with  $D_{3h}$  symmetry. The structures of neutral  $\text{Ti}(\text{BO}_2)_n$  basically resemble those of their corresponding anions. The only exception here is **Ti5'-d**, in which two  $\text{BO}_2$  ligands are combined together.

From Fig. 5 and Table 3, the V atom maintains its spin in the lowest-lying isomer of  $\text{V}(\text{BO}_2)^-$ , namely **V1-q**. Consequently, it has a magnetic moment of 3  $\mu_B$ . High-spin isomer **V1-sextet** and low-spin isomer **V1-d** are 5.8 and 71.7 kcal mol<sup>-1</sup> higher in energy than **V1-q**, respectively. All three structures of  $\text{V}(\text{BO}_2)_2^-$  are linear with  $D_{\infty h}$  symmetry. The magnetic moment is 4  $\mu_B$  for the lowest-energy configuration **V2-quintet**. The electronic structure characteristics of both  $\text{Ti}(\text{BO}_2)_n^-$  and  $\text{V}(\text{BO}_2)_n^-$  species indicate that the central transition metal atoms are inclined to keep the intrinsic electronic state in their borates. For  $\text{V}(\text{BO}_2)_n^-$  ( $n = 3-6$ ), the  $\text{BO}_2$  ligands are distributed individually in each cluster. Obviously, Jahn–Teller distortion also appears in the

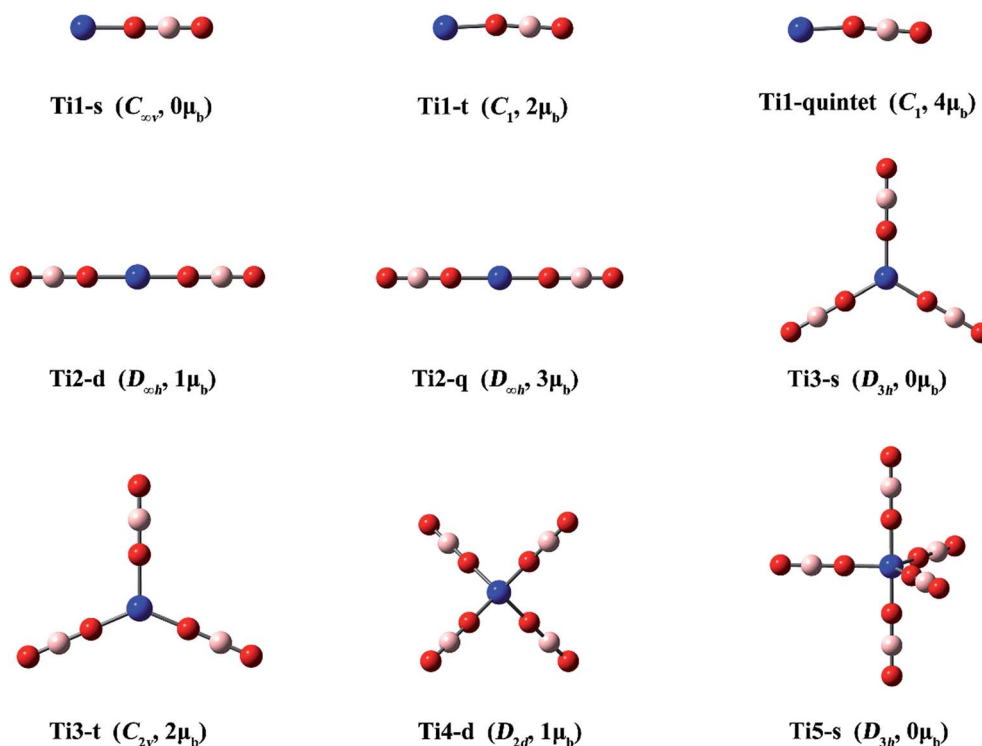


Fig. 3 Optimized structures of the  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 1-5$ ) clusters. (Color legend: Ti, blue; O, red; B, light pink; symmetry and magnetic moment in parentheses.)



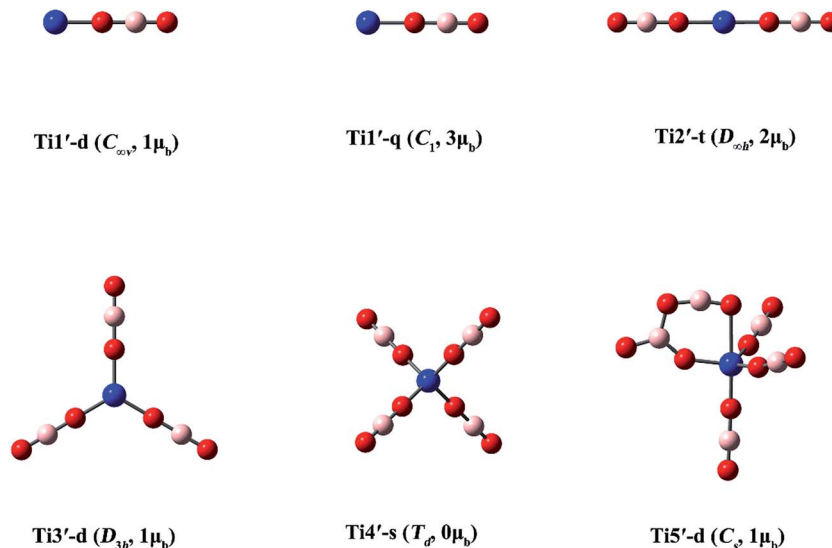


Fig. 4 Optimized structures of the  $\text{Ti}(\text{BO}_2)_n$  ( $n = 1-5$ ) clusters. (Color legend: Ti, blue; O, red; B, light pink; symmetry and magnetic moment in parentheses.)

$\text{V}(\text{BO}_2)_n^-$  series. The geometry of  $\text{V3}\text{-q}$  is still of  $D_{3h}$ -symmetry. In contrast, both  $\text{V4}\text{-t}$  and  $\text{V4}\text{-s}$  are distorted to  $D_{2d}$ -symmetry as the V atom possesses two d electrons therein.  $\text{V5}\text{-d}$  is lowered to  $C_2$ -symmetry because the V atom has one d electron left. Similar to the case of **4a** and  $\text{Ti5}\text{-s}$ ,  $\text{V6}\text{-s}$  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  $\text{V}(\text{BO}_2)_n$  clusters, the  $\text{BO}_2$  ligands are also isolated in every structure except that two  $\text{BO}_2$  ligands dimerized in  $\text{V6}'\text{-d}$ .

From Table 3, the zero-point-corrected dissociation energies of  $\text{Ti}(\text{BO}_2)_n^-$  and  $\text{V}(\text{BO}_2)_n^-$  are in the range of 26.3–

141.6 kcal mol<sup>-1</sup> and 14.6–139.5 kcal mol<sup>-1</sup>, respectively, indicating the stability of  $\text{Ti}(\text{BO}_2)_n^-$  and  $\text{V}(\text{BO}_2)_n^-$  with respect to emission of a  $\text{BO}_2$  unit.

**3.2.2 Vertical electron detachment energy.** The VDE and ADE values of  $\text{Ti}(\text{BO}_2)_n^-$  and  $\text{V}(\text{BO}_2)_n^-$  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**, **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-**

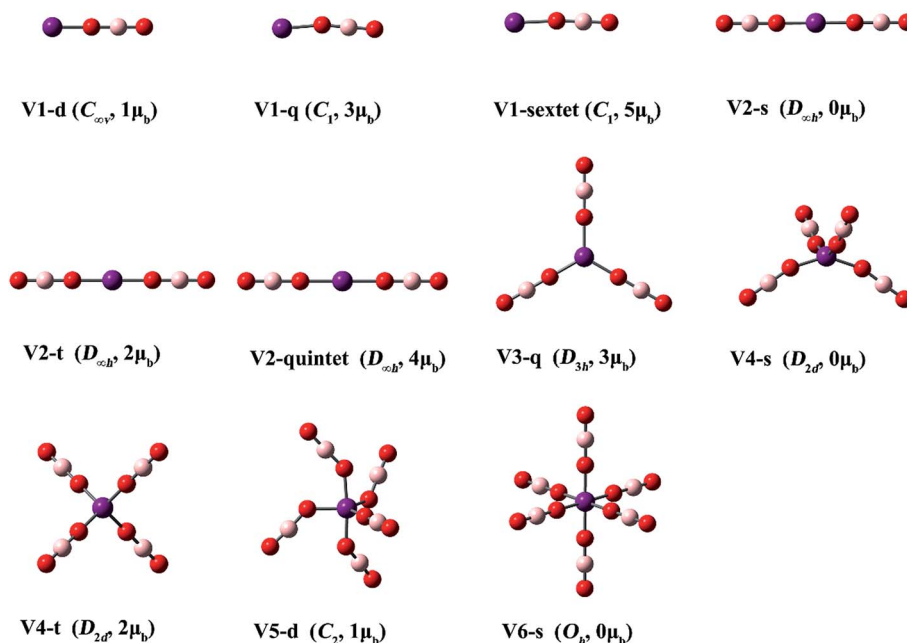


Fig. 5 Optimized structures of the  $\text{V}(\text{BO}_2)_n^-$  ( $n = 1-6$ ) clusters. (Color legend: V, purple; O, red; B, light pink; symmetry and magnetic moment in parentheses.)



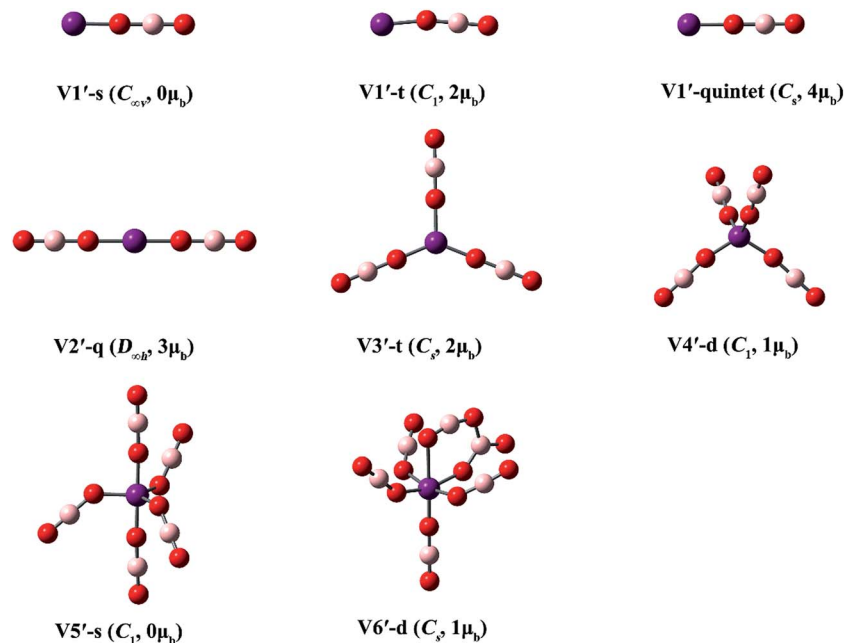


Fig. 6 Optimized structures of the  $V(\text{BO}_2)_n$  ( $n = 1-6$ ) clusters. (Color legend: V, purple; O, red; B, light pink; symmetry and magnetic moment in parentheses.)

Table 3 Relative energy ( $E_{\text{rel}}$ , in kcal mol<sup>-1</sup>), vertical detachment energies (VDEs, in eV), and adiabatic detachment energies (ADEs, in eV) of  $\text{Ti}(\text{BO}_2)_n^-$  ( $n = 1-5$ ) and  $\text{V}(\text{BO}_2)_n^-$  ( $n = 1-6$ ). Pole strengths (PS) in parentheses. Dissociation energies ( $D_e$ , in kcal mol<sup>-1</sup>) of the  $\text{TM}(\text{BO}_2)_n^- \rightarrow \text{TM}(\text{BO}_2)_{n-1}^- + \text{BO}_2$  (TM = Ti, V) reactions

Species	$E_{\text{rel}}$	VDE <sup>OVGF</sup>	VDE <sup>MP2</sup>	ADE <sup>MP2</sup>	$D_e$
Ti1-s	23.5	1.57 (0.885)	1.25	0.66	28.5
Ti1-t	0.0	1.77 (0.864)	1.76	1.68	53.4
Ti1-quintet	9.9	1.26 (0.922)	0.62	0.61	26.3
Ti2-d	3.0	3.08 (0.815)	3.67	3.58	141.6
Ti2-q	0.0	2.06 (0.960)	1.65	1.61	136.1
Ti3-s	17.3	2.95 (0.878)	2.58	2.07	126.9
Ti3-t	0.0	4.20 (0.922)	3.71	2.82	130.1
Ti4-d	—	6.66 (0.889)	4.86	4.11	126.3
Ti5-s	—	9.23 (0.911)	9.30	6.29	94.1
V1-d	71.7	2.01 (0.854)	0.93	0.91	14.6
V1-q	0.0	1.95 (0.858)	3.03	2.98	59.5
V1-sextet	5.8	1.49 (0.983)	0.97	0.86	45.6
V2-s	44.3	2.49 (0.849)	2.54	2.44	107.5
V2-t	24.6	4.46 (0.811)	3.62	3.30	139.5
V2-quintet	0.0	2.38 (0.957)	2.11	2.06	134.2
V3-q	—	5.18 (0.908)	5.10	4.02	127.9
V4-s	49.7	7.38 (0.882)	7.23	3.68	68.1
V4-t	0.0	8.44 (0.906)	8.72	5.84	95.5
V5-d	—	9.09 (0.909)	9.27	5.62	93.6
V6-s	—	9.44 (0.910)	8.23	5.87	46.2

s, V3-q, V4-s, V4-t, V5-d and V6-s species possess larger VDE values than that of  $\text{BO}_2^-$  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  $\text{BO}_2$  ligands, respectively, to qualify the resulting  $\text{TM}(\text{BO}_2)_n^-$  (TM = Sc, Ti, and V) clusters to be considered as hyperhalogens. From Table 3, it is noted that the VDE<sup>MP2</sup> values of  $\text{Ti}(\text{BO}_2)_n^-$  show a sharp increase from

$\text{Ti}(\text{BO}_2)_4^-$  to  $\text{Ti}(\text{BO}_2)_5^-$ . 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  $\text{V}(\text{BO}_2)_n^-$  series. From Table S1,<sup>†</sup> the VDE values of  $\text{TMF}_n^-$  (TM = Sc, Ti, V) can be more or less enhanced by replacing fluorine with  $\text{BO}_2$  ligands.<sup>50</sup>

## 4. Conclusions

The structural, electronic and magnetic properties of three series of early-transition-metal borates, namely  $\text{Sc}(\text{BO}_2)_n^{-/0}$  ( $n = 1-4$ ),  $\text{Ti}(\text{BO}_2)_n^{-/0}$  ( $n = 1-5$ ), and  $\text{V}(\text{BO}_2)_n^{-/0}$  ( $n = 1-6$ ), 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  $\text{BO}_2$  ligand.

The lowest-lying  $\text{Sc}(\text{BO}_2)_n^-$  isomers feature a structure where the  $\text{BO}_2$  ligands spread apart, whereas the  $\text{BO}_2$  ligands begin to combine into a trimer in the lowest-energy  $\text{Sc}(\text{BO}_2)_4$  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  $\text{Sc}(\text{BO}_2)_3^-$  to  $\text{Sc}(\text{BO}_2)_4^-$ , and the latter species can be classified as hyperhalogens since they possess larger VDE values than that of its superhalogen ligand  $\text{BO}_2^-$ . As for Ti and V atoms, they require four and three  $\text{BO}_2$  ligands, respectively, to enable their borates to be termed hyperhalogen. Besides, the Ti4-d, 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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