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Does the Valence State Index Reflect the Stability of Neutral Boron Subhalide Clusters?

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The numbers of valence structures (NVS) and the valence state indexes (VSI) have been determined for a series of $2n$ framework electron clusters *viz.* polyhedral boron subhalides B_nX_n ($n=6$–12) and compared with those obtained for the parent $B_nH_n^{2-}$ dianions. The VSI does not reflect the experimental stabilities.

Key words: Valence state index – Boron subhalide cluster – Valence structures – Stability.

1. Introduction

Quite recently the thermal stabilities of neutral polyhedral boron subbromides B_nX_n have been determined [7] and, for these $2n$ framework electron clusters, the following sequence has been obtained

$$B_9Br_9 > B_{10}Br_{10} > B_8Br_8 \simeq B_7Br_7.$$

Furthermore, mass spectral evidence has been reported for the B_7, B_{10}, B_{11} and B_{12} chlorides [8].

Therefore, we would like to show in this paper how the method described in Refs. 1–5 can be used to determine the number of valence structures (NVS) of the $2n$ framework electron clusters B_nX_n.

2. The B_6X_6 Case

Using Lipscomb's rules [5] it is easy to show that the boron framework of B_nX_n is held together through n central three-center bonds. The systematic search is

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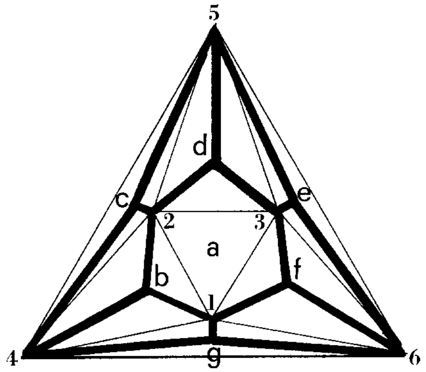

Fig. 1. The valence structure of B_6X_6 shown on a Schlegel diagram (face 456 is named *h*)

very simple in the case of the octahedral B_6X_6 cluster because only four equivalent ways [$n_x = 4$, see Refs. 1–4)] to place the six BBB bonds are possible, shown in Fig. 1.

It is easy to show that there are no other ways to put the six framework three-center bonds for this octahedral cluster: if atom 1 is saturated by three BBB bonds located in faces *b*, *f* and *g* for instance (see Fig. 1), then face *a* cannot be used and there is only *one* way to saturate atoms 2 and 3 – that is to put BBB bonds in faces *c*, *d* and *e* which also saturates atoms 4, 5 and 6. Only three other ways to saturate atom 1 are possible, i.e. to put the three-center bonds in faces *a*, *b*, *g*; *a*, *f*, *g* or *a*, *b*, *f*, which are symmetry equivalent to the case which is described above. Therefore the NVS of B_6X_6 is 4.

3. The B_7X_7 Case

The B_7X_7 boron halide cluster cannot be described by central three-center bonds: if three adjacent BBB bonds are placed to saturate atom 1, for instance in the triangular faces *b*, *c* and *d* (see Fig. 2), then faces *a* and *e* may not be used because atom 1 is already saturated. Atoms 5 and 6 may be saturated by using faces *i* and *j*, and 4 and 7 by using face *g*. We still have one BBB bond not

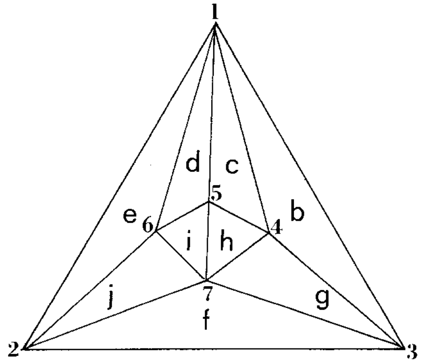

Fig. 2. Numbering convention and names of the triangular faces shown on the Schlegel diagram of the bipyramidal B_7X_7 boron subhalide cluster (face 123 is named l)

accounted for and atoms 2 and 3 unsaturated. However, face *a* cannot be used (atom 1 is already saturated) nor can face *f* (7 is already saturated); if three *non*-adjacent bonds are used to saturate atom 1, for instance in faces *b*, *d* and *e*, then faces *a* and *c* may not be used and BBB bonds must be put in faces *g*, *h* and *i* to saturate atoms 4 and 5. Atom 6 and 7 being saturated, faces *f* and *j* may not be used and atoms 2 and 3 cannot be saturated. However, B_7X_7 can be described by using open and central three-center bonds.

The numbering convention of Ref. 1 has been used to allow an easy comparison of this case with the parent $B_nH_n^{2-}$ case.

4. The B_8X_8 Case

For the dodecahedral [10] B_8H_8 cluster, there is only one acceptable way of positioning the eight BBB bonds (in the triangular faces *abcegikl*, see Fig. 3) and these may be found systematically as in the preceeding cases

The numbering convention of Ref. 12 has been used to allow an easy comparison of this case with the parent $B_nH_n^{2-}$ case instead of the better numbering proposed recently [9].

Indeed if atom 8 is saturated by putting BBB bonds in faces *a*, *b* and *c*, then face *d* may not be used[1]. There are two ways to saturate atom 7: by putting a BBB bond either in face *g* or in face *h*. If this fourth three-center bond is put in face *h*, then atom 4 is saturated too and faces *i* and *j* may not be used. This means that atom 2 cannot be saturated because only two faces to which atom 2 belongs are free.

If the fourth three-center bond is put in face *g*, then face *h* cannot be used. There are then two ways to saturate atom 6: by putting the fifth BBB bond

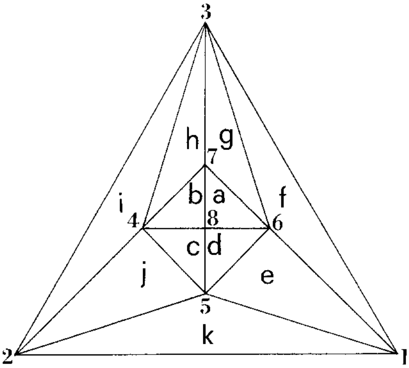

Fig. 3. Numbering convention and names of the triangular faces shown on the Schlegel diagram of the dodecahedral B_8X_8 boron subhalide cluster (face 123 is named 1)

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[1] If atom 8 is saturated by putting the central BBB bonds in faces *bcd* or *acd*, atom 2 or atom 1 resp. cannot be saturated; if the bonds are put in the triangular faces *abcfgjkl*, two couples of adjacent atoms (3, 4 and 5, 6) are linked by no bond; furthermore if they are put in *abdehikl* the same is true for 3, 8 and 4, 5; finally if they are put in *abdfhjkl*, atoms 4 and 5 are linked by no bond.

either in face *f* or in face *e*. If this fifth three-center bond is put in face *f*, then face *e* may not be used, then there is only one way to saturate atom 5 – by putting two BBB bonds in faces *k* and *j* which also saturates atom 4. Therefore face *i* cannot be used. Three atoms are still not saturated (atoms 1, 2 and 3); this can be achieved by putting the last BBB bond in face *l*. If the fifth three-center bond is put in face *e* then face *f* may not be used and then, there is only one way to saturate atoms 1 and 3, that is to put three-center bonds in faces *i*, *k* and *l* which also saturates atoms 5 and 4[1].

5. The B_9X_9 Case

For the tricapped trigonal prismatic [11] B_9X_9 cluster, atom 8 (see Fig. 4) can be saturated in four different ways. If the three BBB bonds are put in faces *c*, *d* and *e*, then face *f* cannot be used. If the fourth BBB bond is put in face *g* then atoms 2 and 5 are saturated and faces *b*, *h* and *j* may not be used but then, atom 9 cannot be saturated because only face *i* is available there. This means that atom 9 must be saturated by putting the three BBB bonds in faces *i*, *j* and *h*, which saturates 2 and 5 too. This means that faces *g*, *b* and *a* are no more available. Analogously a three-center bond may not be put in face *k* because it would saturate atoms 3 and 6 and consequently faces *l* and *n* would not be available with, as a consequence, that atom 7 could never be saturated. Therefore, atom 6 must be saturated by putting a three-center bond in face *n*; face *k* cannot be used and two BBB bonds placed in faces *l* and *m* are sufficient to saturate atoms 4, 7, 1 and 3. An analogous start with BBB bonds in faces *c*, *e* and *f* leads to an analogous valence structure. Therefore the NVS of B_9X_9 is equal to 2^2. Indeed, if atom 8 is saturated by BBB bonds either in faces *d*, *e* and *f* or *c*, *d* and *f*, then the 6 other three center bonds cannot be placed[2] following the topological rules [5].

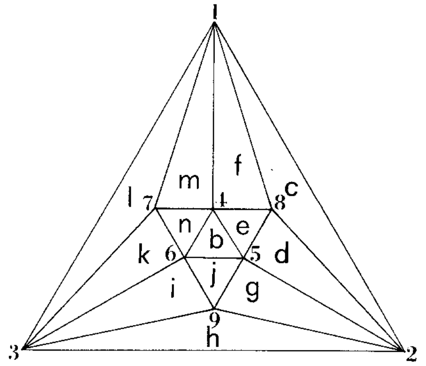

Fig. 4. Numbering convention and names of the triangular faces shown on the Schlegel diagram of the tricapped trigonal prismatic B_9X_9 boron subhalide cluster (face 123 is called face *a*)

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[2] Mention may be made of symmetry relationships, i.e. that the two VS's derived are symmetry equivalent, as are the two prohibited.

The numbering convention of Ref. 1 has been used instead of the better numbering proposed recently [9], to allow an easy comparison between this case and the parent $B_9H_9^{2-}$ case.

6. The $B_{10}X_{10}$ Case

The NVS can be determined analogously for the bicapped anticube $B_{10}X_{10}$. It is easy to see that there are four equivalent ways to saturate atom 1 by using three of the four triangular faces of the upper pyramid. Analogously, there are also four ways to saturate atom 2.

If atom 1 is saturated by putting BBB bonds in faces *a*, *b* and *c* (see Fig. 5) and atom 2 by putting three-center bonds in faces *n*, *o* and *p*, then faces *d* and *m* may not be used and there is only one way to saturate atom 10, i.e. to put BBB bonds in faces *f* and *h*. This saturates atoms 4, 5 and 9 too. Therefore faces *e*, *g*, *i* and *j* may not be used and atom 6 can never be saturated. (An analogous situation is encountered if the BBB bonds are initially put in faces *a*, *b*, *c*; *m*, *o* and *p*).

If atoms 1 and 2 are saturated by putting three-center bonds in faces *a*, *b*, *c*; *m*, *n*, *o*, then there is only one way compatible with the topological rules [5] to saturate atom 10, i.e. to put the seventh BBB bond in face *f*. Then atom 4 is saturated too and faces *e*, *g* and *h* may not be used. There is only one way to saturate atom 5 i.e. by putting a three-center bond in face *i*, which saturates atom 9 too. Face *j* may not be used and atoms 6, 3, 8 and 7 are saturated if the last two BBB bonds are put in faces *k* and *l* but then atoms 5 and 10 are linked by no bond. Therefore this valence structure is not acceptable. An analogous situation is encountered if the BBB bonds are initially put in *abc*, *mnp*, and when atom 1 is saturated by three-center bonds located in faces *b*, *c* and *d*; *c*, *d* and *a* or *d*, *a* and *b*. Therefore the NVS of $B_{10}X_{10}$ is equal to 0.

The numbering convention of Ref. 1 has been used instead of the better numbering proposed recently [9], to allow an easy comparison of this case with the parent $B_{10}H_{10}^{2-}$ case.

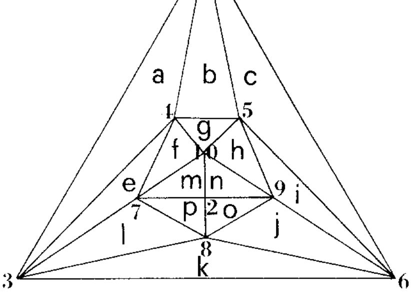

Fig. 5. Numbering convention and names of the triangular faces shown on a Schlegel diagram of the $B_{10}X_{10}$ boron subhalide cluster (face 136 is called face *d*)

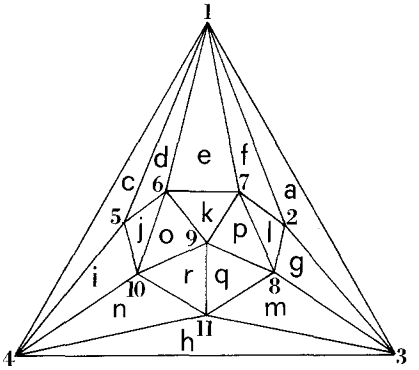

Fig. 6. Numbering convention and names of the triangular faces shown on a Schlegel diagram of the $B_{11}X_{11}$ boron subhalide cluster (face 134 is called face *b*)

7. The $B_{11}X_{11}$ Case

An analogous systematic search can be quite easily undertaken for the $B_{11}X_{11}$ case if one realises that atoms 2 and 5 are the tops of "square" pyramids so that there are only four ways to saturate them. Therefore no more than 16 cases have to be examined which readily show that only six valence structures are possible for this particular case, called *AA*, *DD*, *AC*, *CA*, *BD* and *DB*. The first two are achiral valence structures, whereas *AC*, *CA* and *BD*, *DB* are two enantiomeric pairs. The locations of the three-center bonds are described below (see Fig. 6) as follows:

$AA = aceghijklqr$; $DD = bdfghijklqr$; $AC = acdghjklnpr$;

$CA = acfhijklmoq$; $BD = adfghijknpq$; $DB = cdfghiklmor$.

However only the first two are acceptable because two couples of adjacent atoms are not directly bonded in the four other ones (1, 7 and 8, 11 for *AC*, 1, 4 and 9, 10 in *BD*).

Therefore the NVS of the $C_{2v}B_{11}X_{11}$ cluster is equal to 2.

The numbering convention of Ref. 3 has been used instead of the better numbering proposed recently [9], to allow an easy comparison between this case and the parent $B_{11}H_{11}^{2-}$ case.

8. The $B_{12}X_{12}$ Case

The case of the icosahedral $B_{12}X_{12}$ cluster is simple because it is symmetrical but complicated because of the higher number of faces. First of all it must be seen that there are only two energetically different ways to saturate any of the boron atoms of $B_{12}X_{12}$ because there are two *different* ways to put three BBB bonds on the triangular faces of a pentagonal pyramid: either adjacently (*A*) or not (*B*).

Keeping this in mind and using the same systematic search [1–4] as that one described above it is possible to find one C_3 valence structure called (1) allowed

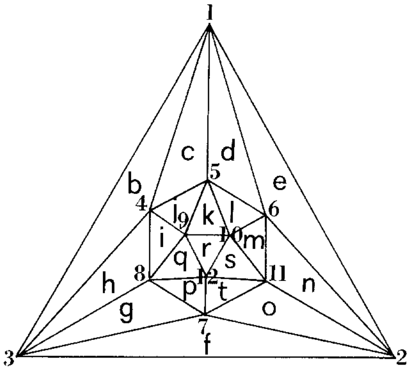

Fig. 7. Numbering convention and names of the triangular faces shown on a Schlegel diagram [4] of the $B_{12}X_{12}$ boron subhalide cluster (face 123 is called face *a*)

according to the topological rules [5], with twelve BBB bonds giving 12 times the B-type pattern and two other D_3 enantiomeric valence structures, (2) and (3), with twelve three-center bonds giving 6 times the A-, and 6 times the B-type pattern. The locations of the BBB bonds for the three possible valence structures, (1), (2) and (3), are given below (see Fig. 7): (1) *abdgijlnoprs*; (2) *bcdfgilnoqrs*; (3) *abegijklnpst*. However, only the first is acceptable because for the other two, three couples of adjacent atoms are not directly bonded [for (2): 1, 2; 5, 9 and 7, 12]. The number n_x of symmetry equivalent structures being equal to 20 for the C_3 valence structure (and 10 for the D_3 ones) the NVS is equal to 20 for the icosahedral $B_{12}X_{12}$.

The numbering convention of Ref. 4) has been used to allow an easy comparison between this case and the parent $B_{12}H_{12}^{2-}$ case.

9. Discussion

The results of the systematic search described above are summarized in Table 1 and compared with those obtained for the parent $B_nH_n^{2-}$ structures. From the NVS, the valence state index VSI (= (log NVS)/$n_{\text{tr.f.}}$ where $n_{\text{tr.f.}}$ is the number of triangular faces) [6] has been calculated and included in Table 1.

Table 1. Number of valence structures (NVS) and valence structure index (VSI) of B_nX_n and $B_nH_n^{2-}$ boron ompounds

	B_nX_n		$B_nH_n^{2-}$			$VSI(B_nH_n^{2-})$
n	NVS	VSI	NVS	VSI	Ref.	$VSI(B_nH_n)$
6	4	0.0753	32	0.1881	5, 6	2.5
7	0	$-\infty$	20	0.1301	5, 6	0
8	1	0	14	0.0955	2	∞
9	2	0.0215	16	0.0860	5, 6	4
10	0	$-\infty$	72	0.1161	5, 6	0
11	2	0.0167	16	0.0669	5, 6	4
12	20	0.0651	240	0.1191	2	1.8

It is obvious that the stability of the B_nX_n clusters estimated from their VSI ($6 > 12 > 9 > 11 > 8 > 10 \simeq 7$) is not in good agreement with the experimental sequence ($9 > 10 > 8 \simeq 7$) [7] whereas the VSI's of $B_nH_n^{2-}$ which are polyhedral boranes are much larger than those of the parent B_nX_n compounds as expected.

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