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BORATE CLUSTERS AND FUNDAMENTAL BUILDING BLOCKS CONTAINING FOUR POLYHEDRA: WHY FEW CLUSTERS ARE UTILIZED AS FUNDAMENTAL BUILDING BLOCKS OF STRUCTURES

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ABSTRACT

The fundamental building blocks (FBBs) of the structures of borate minerals and synthetic inorganic compounds commonly contain four borate polyhedra. Although there are twenty-one chemically feasible borate clusters that contain four polyhedra, only two occur as the FBBs of crystal structures: these are the 4□:<4□> (one example) and 2Δ2□:<Δ2□>=<Δ2□> (seventeen examples) FBBs. There are nine borate clusters of the form 4B:<3B>=<3B>, but of these, only the 2Δ2□:<Δ2□>=<Δ2□> cluster occurs as the FBB of structures. Molecular-orbital (Hartree–Fock) calculations have been done using the 3–21G* basis-set on all atoms, and including full symmetry-unrestricted geometry optimization, for the nine clusters of the form 4B:<3B>=<3B>. The calculated geometry of the 2Δ2□:<Δ2□>=<Δ2□> cluster is in excellent agreement with the average geometry of FBBs of structures. These calculations demonstrate that the 2Δ2□:<Δ2□>=<Δ2□> cluster is the most stable cluster of the general form 4B:<3B>=<3B>, in accord with its dominance as a structure FBB. The results indicate that the 2Δ2□:<Δ2□>=<Δ2□> cluster is favored as a structure FBB owing to local bonding considerations. Factors that determine the relative stabilities of borate clusters of the form 4B:<3B>=<3B> are discussed.

Keywords: borate, borate mineral, fundamental building block, crystal structure, molecular orbital, Hartree–Fock, structure stability.

SOMMAIRE

Les blocs structuraux fondamentaux utilisés dans la charpente de minéraux boratés et les composés inorganiques synthétiques contiennent assez couramment quatre polyèdres de borate. Quoiqu'il y ait vingt-et-un agencements de borate qui soient chimiquement possibles, deux seulement semblent utilisés dans les structures cristallines: on connait un exemple de l'agencement 4□:<4□>, et dix-sept de l'agencement 2Δ2□:<Δ2□>=<Δ2□>. Il y a neuf agencements de polyèdres de borate de la forme 4B:<3B>=<3B>, mais parmi ceux-ci, seul l'agencement 2Δ2□:<Δ2□>=<Δ2□> semble utilisé comme bloc structural fondamental. Des calculs d'orbites moléculaires (méthode de Hartree–Fock) ont été effectués en utilisant le système de référence 3–21G* pour tous les atomes, avec provision pour optimisation de la géométrie des agencements sans restrictions imposées par la symétrie, pour neuf agencements de la forme 4B:<3B>=<3B>. La géométrie calculée pour l'agencement 2Δ2□:<Δ2□>=<Δ2□> concorde très étroitement avec la géométrie moyenne des blocs structuraux fondamentaux observés. Ces calculs démontrent que l'agencement 2Δ2□:<Δ2□>=<Δ2□> est le plus stable parmi ceux qui répondent à la formule générale 4B:<3B>=<3B>, ce qui rend compte de sa dominance dans les structures connues. Ces résultats montrent que l'agencement 2Δ2□:<Δ2□>=<Δ2□> est favorisé dans les structures à cause de considérations locales des liaisons. Les facteurs importants pour assurer la stabilité relative des agencements de polyèdres de borate de forme générale 4B:<3B>=<3B> sont évalués.

(Traduit par la Rédaction)

Mots-clés: borate, minéral boraté, bloc structural fondamental, structure cristalline, orbite moléculaire, Hartree–Fock, stabilité structurale.

INTRODUCTION

The polymerization of borate triangles and tetrahedra in the structures of borate minerals and synthetic inorganic compounds gives rise to great structural diversity. In general, a borate structure contains clusters of corner-sharing $B\phi_3$ and $B\phi_4$ polyhedra (ϕ: O^{2-}, OH^-), which occur as discrete polyanions or polymerize to form larger clusters, chains, sheets or frameworks. Thus, borate structures readily lend themselves to classification based on the geometry of the clusters of borate polyhedra. Recently, Burns *et al.*

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(1995) have developed a descriptor for the borate fundamental building blocks (FBBs) of structures, and Grice *et al.* (in prep.) have proposed a classification scheme for borate minerals that is based upon the identity of the structure FBB and the degree of polymerization involving the FBBs.

As part of their work on borate clusters and fundamental building blocks, Burns *et al.* (1995) identified all chemically feasible borate clusters that contain three to six polyhedra and are formed by corner-sharing of borate triangles and tetrahedra, with the restriction that all polyhedra are at least two-connected. Burns *et al.* (1995) found that borate clusters with three to six polyhedra may have thirty-nine different polyhedral connectivities (not discriminating between triangles and tetrahedra, within the above boundary-constraints), but the FBBs of mineral structures show only six of these connectivities. Also, the frequency of three-membered rings of polyhedra in borate structures is remarkable; of the fifty-one borate mineral structures that are based on FBBs with three to six polyhedra, only one FBB is not based solely upon three-membered rings of polyhedra, and thirty-five of the structures are based on FBBs that contain only <Δ2□> rings, *i.e,* a ring containing one triangle and two tetrahedra. Three factors may affect the frequency of occurrence of borate clusters as the FBBs of the structures of borate minerals: (1) considerations of local bonding may restrict the number of borate clusters that are utilized as FBBs of a crystal structure (on the basis of stability), (2) long-range structural effects may favor the inclusion of specific FBBs, and (3) some borate clusters may be favored in the precursor fluid medium (*i.e.,* owing to Eh, pH conditions), thereby making them readily available for incorporation as structural FBBs of a growing crystal.

Various types of molecular-orbital calculations have been used to examine the details of borate clusters, and the results have been invaluable for the interpretation of experimental results (*i.e.,* Vaughan & Tossell 1973, Snyder *et al.* 1976, Gupta & Tossell 1981, 1990, Gupta *et al.* 1981, Tossell & Lazzeretti 1988, Zha *et al.* 1993). Also, numerous studies have used molecular-orbital calculations to predict the equilibrium geometries of various borate clusters; early calculations tended to be semi-empirical (*i.e.,* Schlenker *et al.* 1978, Uchida *et al.* 1985), but more recently, the calculations have been *ab initio* (*i.e.,* Gupta & Tossell 1981, 1983, Gupta *et al.* 1981, Geisinger *et al.* 1985, Zhang *et al.* 1985, Zha *et al.* 1993). These studies have invariably considered borate clusters that contain three or less polyhedra, and show that *ab initio* Hartree–Fock calculations give bond lengths and bond angles that are in good agreement with experiment, as long as the charge on the cluster remains small.

In this work, borate clusters containing four polyhedra are considered in detail. Burns *et al.* (1995) showed that only a few of the possible borate clusters that contain four polyhedra occur as FBBs of the structures of minerals, and this is also the case for synthetic inorganic compounds. However, to understand the stability of the clusters that do occur as FBBs of structures, and to evaluate the reliability of stability criteria, all possible clusters (within certain boundary-constraints) must be examined, and not just those that have been observed in structures (Hawthorne 1983). Initially, borate clusters with four polyhedra that are FBBs of structures of minerals and synthetic inorganic compounds were identified and tabulated. Hartree–Fock calculations were then done for all possible borate clusters with the general form 4B:<3B>=<3B>, allowing the investigation of stability of individual clusters.

Throughout this paper, the descriptor proposed by Burns *et al.* (1995) for borate clusters and FBBs is used. Each FBB has a descriptor of the form *A:B,* where *A* gives the number of borate triangles (Δ) and tetrahedra (□) in the FBB in the form *i*Δ*j*□, where *i* and *j* are the numbers of triangles and tetrahedra, respectively. The *B* part is a character string that contains information on the connectivity of the polyhedra. The string is written such that adjacent Δ or □ (or both) represent polyhedra that share corners, and the delimiters < > indicate that the polyhedra within share corners to form a ring. The sharing of polyhedra between rings is indicated by the symbols –, =, ≡, *etc.* for one, two, three or more polyhedra, respectively. Thus, the FBB with the descriptor 2Δ2□: <Δ2□>=<Δ2□> contains two triangles and two tetrahedra. There are two three-membered rings of

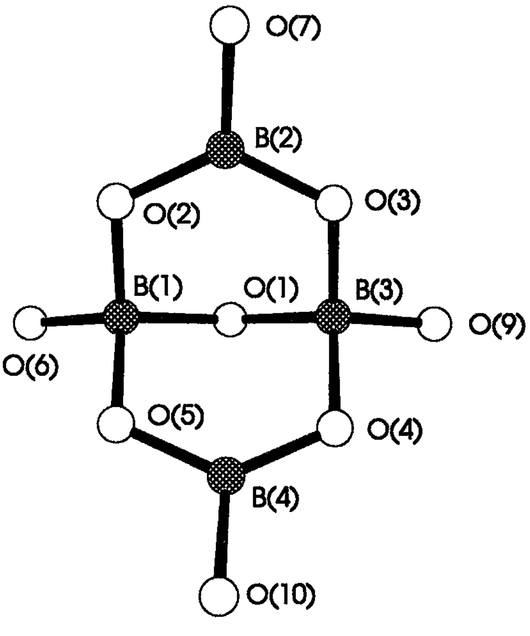

FIG. 1. The FBB 2Δ2□:<Δ2□>=<Δ2□>.

polyhedra, each of which contains one triangle and two tetrahedra, and the rings have two tetrahedra in common, as shown in Figure 1. Further details of the descriptor for FBBs are given in Burns *et al.* (1995).

OBSERVED STEREOCHEMISTRY OF FBBs WITH FOUR POLYHEDRA

The structures of seven borate minerals are based on FBBs that have four polyhedra. The structure of borcarite is the only structure that is based on the FBB 4□:<4□>, a four-membered ring of corner-sharing borate tetrahedra (Burns & Hawthorne 1995a). The structures of the other minerals are all based on the FBB 2Δ2□:<Δ2□>=<Δ2□> (Fig. 1). The geometrical details of the FBB of borax, hungchaoite, roweite, tincalconite and diomignite, 2Δ2□:<Δ2□>=<Δ2□>, are given in Table 1. Fedorovskite is isostructural with roweite, thus it is based on the same FBB, but the structure has not been refined. In addition, the structures of ten synthetic inorganic compounds are based on a total of twelve FBBs that contain four polyhedra. Each of these structures is based on the FBB 2Δ2□:<Δ2□>=<Δ2□>, and the geometrical details of each of the FBBs are listed in Table 2.

TABLE 1. OBSERVED 2Δ2□:<Δ2□>=<Δ2□> STEREOCHEMISTRY IN MINERALS*

	Brx	Hung	Row	Tinc	Diom
B(1)-O(1)**	1.465	1.458	1.417	1.468	1.454
B(1)-O(2)	1.485	1.493	1.506	1.467	1.507
B(1)-O(5)	1.501	1.498	1.506	1.497	1.496
B(1)-O(6)	1.439	1.459	1.493	1.448	1.448
<B(1)-O>	1.472	1.477	1.480	1.470	1.476
Σb.v.	3.04	3.01	2.99	3.06	3.02
δ x 1000	0.248	0.158	0.626	0.141	0.302
B(2)-O(2)	1.364	1.367	1.364	1.362	1.385
B(2)-O(3)	1.370	1.366	1.393	1.332	1.386
B(2)-O(7)	1.375	1.373	1.367	1.386	1.349
<B(2)-O>	1.370	1.369	1.375	1.360	1.373
Σb.v.	3.01	3.02	2.97	3.10	2.98
δ x 1000	0.011	0.005	0.090	0.264	0.157
B(3)-O(1)	1.465	1.457	1.469	1.468	1.454
B(3)-O(3)	1.501	1.499	1.495	1.497	1.496
B(3)-O(4)	1.484	1.501	1.495	1.467	1.507
B(3)-O(9)	1.439	1.445	1.446	1.448	1.448
<B(3)-O>	1.472	1.475	1.476	1.470	1.476
Σb.v.	3.05	3.02	3.01	3.06	3.02
δ x 1000	0.248	0.284	0.191	0.141	0.302
B(4)-O(4)	1.364	1.366	1.367	1.386	1.349
B(4)-O(5)	1.370	1.367	1.364	1.362	1.385
B(4)-O(10)	1.375	1.368	1.393	1.332	1.386
<B(4)-O>	1.370	1.367	1.375	1.360	1.373
Σb.v.	3.01	3.03	2.97	3.10	2.98
δ x 1000	0.011	0.000	0.090	0.264	0.157
B(1)-O(1)-B(3)	110.9	111.5	108.8	111.4	108.0
B(1)-O(2)-B(2)	117.0	117.3	118.7	117.4	116.2
B(2)-O(3)-B(3)	120.6	119.6	120.7	121.1	119.8
B(3)-O(4)-B(1)	117.0	117.0	120.7	117.4	116.2
B(1)-O(5)-B(1)	120.6	120.6	118.7	121.1	119.8

*Brx: borax (Levy & Lisensky 1978); Hung: hungchaoite (Wan & Ghose 1977); Row: roweite (Moore & Araki 1974); Tinc: tincalconite (Giacovazzo *et al.* 1973); Diom: diomignite (Radaev *et al.* 1989)
**atom labels are as in Figure 1.

The bond-valence sums and polyhedral distortions are reported for each polyhedron in the FBBs listed in Tables 1 and 2. Bond-valences were calculated using the parameters of Brown & Altermatt (1985). The polyhedral distortions were calculated using the formulae:

$$\delta = \tfrac{1}{4}\Sigma[(L-L_O)/L_O]^2 \qquad (1)$$

for tetrahedra, and

$$\delta = \tfrac{1}{3}\Sigma[(L-L_O)/L_O]^2 \qquad (2)$$

for triangles; the summations are over all bond lengths of the polyhedron, L is the individual bond-length, and L_O is the average bond-length for the polyhedron.

CHEMICALLY FEASIBLE CLUSTERS BASED ON FOUR BORATE POLYHEDRA

Burns *et al.* (1995) identified all chemically feasible clusters that contain four borate polyhedra based on corner-sharing of borate triangles or tetrahedra (or both), with the boundary constraint that each polyhedron must be at least two-connected. The graphs of the twenty-one chemically feasible clusters are shown in Figure 2.

An important observation is that of the twenty-one clusters, *only two* occur as the FBB of a crystal structure; these are the FBB 4□:<4□>, upon which the structure of borcarite is based, and the FBB 2Δ2□:<Δ2□>=<Δ2□>, upon which the structures of six mineral species (those in Table 1 plus fedorovskite) and the structures of ten synthetic inorganic compounds (Table 2) are based. There is no *a priori* nor even *a posteriori* explanation for this remarkable preference of these two clusters as FBBs of crystal structures.

There are nine borate clusters that have the general form 4B:<3B>=<3B>; these are shown in Figure 2. All but one of the structure FBBs that contain four polyhedra are 2Δ2□:<Δ2□>=<Δ2□>, which is of the general form 4B:<3B>=<3B>. Notably, none of the other eight borate clusters of the form 4B:<3B>=<3B> occurs as the FBB of a structure. Molecular-orbital calculations have been done for each of the nine clusters with the general form 4B:<3B>=<3B> to investigate their relative stabilities.

MOLECULAR-ORBITAL CALCULATIONS

Molecular-orbital calculations have been done for many molecular clusters of various size as an approximation of local conditions in a crystal structure (*i.e.*, Newton & Gibbs 1980, Gupta & Tossell 1981, 1983, Gupta *et al.* 1981, Gibbs 1982, Geisinger *et al.* 1985,

TABLE 2. OBSERVED 2Δ2□:<Δ2□>=<Δ2□> STEREOCHEMISTRY IN SYNTHETIC COMPOUNDS*

	SC1	SC2	SC3a	SC3b	SC4	SC5	SC6	SC7a	SC7b	SC8	SC9	SC10
B(1)-O(1)**	1.451	1.441	1.641	1.574	1.445	1.474	1.470	1.454	1.467	1.466	1.468	1.454
B(1)-O(2)	1.495	1.503	1.473	1.502	1.512	1.441	1.487	1.495	1.495	1.491	1.536	1.553
B(1)-O(5)	1.481	1.508	1.537	1.536	1.509	1.458	1.511	1.505	1.507	1.491	1.633	1.505
B(1)-O(6)	1.469	1.465	1.338	1.345	1.435	1.470	1.448	1.442	1.442	1.448	1.407	1.462
<B(1)-O>	1.474	1.479	1.497	1.489	1.475	1.461	1.479	1.474	1.478	1.474	1.511	1.493
Σb.v.	3.03	2.99	2.97	2.99	3.03	3.14	2.99	3.04	3.00	3.03	2.81	2.89
δ x 1000	0.120	0.349	5.374	3.420	0.577	0.077	0.243	1.474	0.292	0.152	3.085	0.698
B(2)-O(2)	1.372	1.379	1.410	1.392	1.378	1.359	1.372	1.368	1.370	1.362	1.305	1.366
B(2)-O(3)	1.361	1.366	1.355	1.445	1.390	1.321	1.312	1.363	1.371	1.372	1.443	1.323
B(2)-O(7)	1.360	1.365	1.383	1.310	1.382	1.407	1.401	1.373	1.371	1.373	1.425	1.432
<B(2)-O>	1.364	1.370	1.383	1.382	1.383	1.362	1.362	1.368	1.371	1.369	1.391	1.374
Σb.v.	3.05	3.01	2.91	2.94	2.90	3.08	3.09	3.02	3.00	3.02	2.88	3.00
δ x 1000	0.016	0.022	0.264	1.614	0.013	0.667	0.741	0.009	0.000	0.013	1.939	1.065
B(3)-O(1)	1.452	1.462	1.381	1.419	1.434	1.495	1.472	1.457	1.454	1.466	1.430	1.430
B(3)-O(3)	1.500	1.501	1.473	1.409	1.512	1.517	1.502	1.506	1.484	1.491	1.549	1.535
B(3)-O(4)	1.462	1.499	1.467	1.472	1.507	1.443	1.498	1.485	1.485	1.491	1.625	1.495
B(3)-O(9)	1.462	1.438	1.544	1.479	1.468	1.435	1.447	1.446	1.461	1.448	1.442	1.482
<B(3)-O>	1.469	1.475	1.466	1.445	1.480	1.472	1.480	1.473	1.471	1.474	1.511	1.485
Σb.v.	3.07	3.03	3.13	3.29	2.99	3.05	2.99	3.04	3.05	3.03	2.89	2.95
δ x 1000	0.156	0.321	1.553	0.462	0.458	0.549	0.224	0.255	0.087	0.152	2.820	0.638
B(4)-O(4)	1.361	1.369	1.386	1.318	1.366	1.349	1.378	1.373	1.362	1.362	1.336	1.353
B(4)-O(5)	1.353	1.381	1.381	1.460	1.363	1.444	1.358	1.368	1.353	1.372	1.416	1.381
B(4)-O(10)	1.390	1.357	1.507	1.416	1.381	1.355	1.384	1.372	1.389	1.373	1.518	1.378
<B(4)-O>	1.368	1.369	1.425	1.398	1.370	1.383	1.373	1.371	1.368	1.369	1.423	1.371
Σb.v.	3.03	3.02	2.63	2.83	3.01	2.93	2.98	3.00	3.03	3.02	2.66	3.00
δ x 1000	0.135	0.051	1.672	1.802	0.033	0.987	0.066	0.002	0.125	0.013	2.738	0.084
B(1)-O(1)-B(3)	108.4	110.2	115.0	111.6	113.3	108.1	111.0	110.1	111.9	111.3	110.3	108.3
B(1)-O(2)-B(2)	117.0	117.3	119.2	124.3	116.3	120.0	118.2	122.2	120.3	120.6	121.6	119.5
B(2)-O(3)-B(3)	117.2	121.2	125.6	127.7	119.5	122.2	118.5	117.4	117.4	117.0	119.5	117.4
B(3)-O(4)-B(1)	117.9	116.8	117.2	120.2	115.8	123.0	117.8	120.7	119.4	120.6	120.3	119.6
B(1)-O(5)-B(1)	120.5	120.1	124.3	124.8	119.7	120.5	119.0	117.0	118.6	117.0	118.6	114.9

*SC1: $Na_2(B_4O_6(OH)_2)$ (Menchetti & Sabelli 1978); SC2: $K_2B_4O_7$ (Krogh-Moe 1972); SC3: $Rb_2Sr(B_4O_5(OH_4)_2)(H_2O)_8$ (Ivchenko & Kurkutova 1975); SC4: $Mn(B_4O_5(OH)_4)(H_2O)_7$ (Berzinya *et al.* 1974); SC5: CdB_4O_7 (Ihara & Krogh-Moe 1966); SC6: $K_2(B_4O_5(OH)_4)(H_2O)_2$ (Marezio *et al.* 1963); SC7: $CaK_2(B_4O_5(OH)_4)_2(H_2O)_8$ (Solans *et al.* 1982); SC8: $K_{1.67}Na_{0.33}B_4O_5(OH)_4(H_2O)_3$ (Smykalla & Behm 1988); SC9: $(NH_4)_2(B_4O_5(OH)_4)(H_2O)_4$ (Janda *et al.* 1981); SC10: CaB_4O_7 (Zayakina & Brovkin 1977).
** atoms labels are as in Figure 1.

Zhang *et al.* 1985, Lasaga & Gibbs 1987, 1988, 1990, 1991, McCammon *et al.* 1991, Zha *et al.* 1993, Burns & Hawthorne 1995b, c). These cluster calculations are only an approximation of the local environment in a crystal structure; there are long-range effects in periodic structures that are ignored by this approach. In the structures of borates, the B–ϕ bonds are of much higher bond-valence (≥ 0.7 *vu*) than the other cation–ϕ bonds (≤ 0.3 *vu*), thus it is expected that molecular-orbital calculations done for borate clusters will be good models for the clusters where they occur as FBBs of crystal structures. An outline of molecular-orbital calculations as applied in this work may be found in Burns & Hawthorne (1995b).

Molecular-orbital calculations were done for the nine clusters shown in Figure 3, each of which is of the general form 4B:<3B>=<3B>. In each cluster, a single hydrogen atom was attached to each terminal

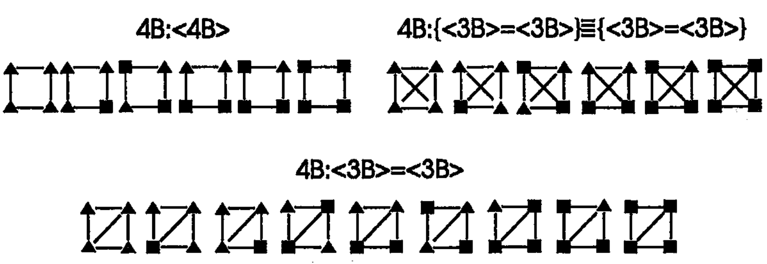

FIG. 2. Chemically feasible clusters containing four borate polyhedra. $B\phi_3$ triangles and $B\phi_4$ tetrahedra are represented by triangles and squares, respectively.

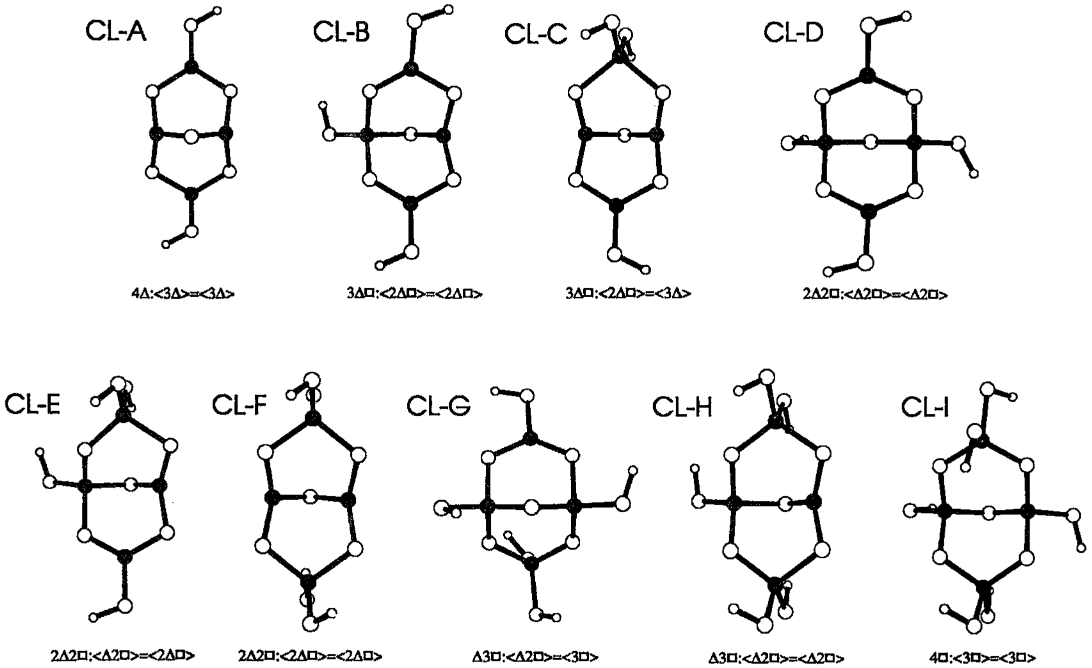

FIG. 3. Each of the nine borate clusters for which molecular-orbital calculations were done. Black circles: boron atoms; large open circles: oxygen atoms; small circles: hydrogen atoms.

oxygen atom to simulate the effects of an extended structure. Each calculation was done using the closed-shell Hartree–Fock method and the 3–21G* basis set (Dobbs & Hehre 1987, Binkley *et al.* 1980, Gordon *et al.* 1982, Pietro *et al.* 1982) on all atoms. Calculations were done using the computer program Gaussian 92 (Frisch *et al.* 1992), version C, installed on an IBM RISC 6000 model 560 computer. The geometry of each cluster was optimized *without* symmetry constraint; the positions of *all atoms* in the cluster were *independently* adjusted using the Berny optimization routine until the maximum forces on any atom did not exceed 0.00045 Hartrees/Bohr, and the maximum displacement of any atom in the previous cycle did not exceed 0.0018 Å. All O–H distances optimized to ~0.97 Å, and calculated B–O–H bond-angles were optimized to ~106°. The B–O bond lengths and bridging-oxygen B–O–B bond angles, together with bond-valence sums for the polyhedra and polyhedron distortion (δ), are given in Table 3. Bond angles in the polyhedra are given in Table 4, and the energy and stoichiometry of each cluster are reported in Table 5.

RESULTS OF CALCULATIONS

Examination of borate structures shows which borate clusters are preferred as FBBs, and which are not, but the question of why specific clusters are not utilized as FBBs of structures remains unanswered. Molecular-orbital calculations are ideally suited for the investigation of this problem, as calculations are equally valid for any cluster, regardless of whether or not the cluster is the FBB of a crystal structure. Also, molecular-orbital calculations done for clusters that are FBBs of borate structures provide very good predictions of the equilibrium geometry of the FBB (*i.e.*, Gupta & Tossell 1981, 1983, Gupta *et al.* 1981, Geisinger *et al.* 1985, Zhang *et al.* 1985, Zha *et al.* 1993).

The molecular-orbital calculations reported here give equilibrium geometries for each of the borate clusters with the general form 4B:<3B>=<3B> (Table 3); of these, eight do not occur as the FBB of a crystal structure. Thus these geometries cannot be obtained from experiment. Each of these clusters is chemically feasible in light of these results, as the calculations have located the equilibrium positions for all atoms within each cluster, and each cluster remains completely connected.

Comparison of calculated-cluster and FBB geometries for 2Δ2□:<Δ2□>=<Δ2□>

The calculated bond-lengths and bond-angles for the 2Δ2□:<Δ2□>=<Δ2□> cluster are compared with the average bond-lengths and bond-angles in the FBBs

TABLE 3. CALCULATED BOND-LENGTHS AND BRIDGING-OXYGEN BOND-ANGLES FOR 4B:<3B>=<3B> CLUSTERS

	*CL-A	CL-B	CL-C	CL-D	CL-E	CL-F	CL-G	CL-H	CL-I
B(1)-O(1)**	1.426	1.543	1.441	1.465	1.541	1.464	1.475	1.566	1.500
B(1)-O(2)	1.396	1.523	1.338	1.520	1.454	1.369	1.446	1.490	1.485
B(1)-O(5)	1.390	1.499	1.472	1.515	1.542	1.368	1.569	1.465	1.488
B(1)-O(6)		1.423		1.469	1.457		1.510	1.495	1.560
<B(1)-O>	1.404	1.497	1.417	1.492	1.498	1.400	1.500	1.504	1.508
Σb.v.	2.747	2.868	2.682	2.890	2.854	2.791	2.845	2.806	2.770
δ x 1000	0.126	0.923	1.634	0.289	0.824	1.034	0.934	0.623	0.406
B(2)-O(2)	1.429	1.357	1.605	1.361	1.490	1.565	1.484	1.479	1.463
B(2)-O(3)	1.419	1.428	1.603	1.374	1.593	1.562	1.483	1.548	1.474
B(2)-O(7)	1.350	1.390	1.423	1.429	1.463	1.451	1.517	1.493	1.542
B(2)-O(8)			1.427		1.467	1.452	1.520	1.491	1.554
<B(2)-O>	1.399	1.392	1.514	1.388	1.503	1.507	1.501	1.503	1.508
Σb.v.	2.791	2.847	2.794	2.874	2.825	2.798	2.819	2.809	2.777
δ x 1000	0.630	0.435	0.349	0.451	1.235	1.380	0.136	0.315	0.709
B(3)-O(1)	1.426	1.369	1.443	1.453	1.397	1.464	1.461	1.422	1.485
B(3)-O(3)	1.390	1.407	1.335	1.512	1.353	1.368	1.443	1.387	1.479
B(3)-O(4)	1.393	1.405	1.428	1.536	1.442	1.370	1.606	1.383	1.511
B(3)-O(9)				1.469			1.508		1.556
<B(3)-O>	1.403	1.394	1.402	1.492	1.397	1.401	1.505	1.397	1.508
Σb.v.	2.754	2.824	2.782	2.891	2.807	2.789	2.828	2.797	2.785
δ x 1000	0.135	0.157	1.161	0.492	0.676	1.022	1.766	0.157	0.405
B(4)-O(4)	1.429	1.415	1.411	1.362	1.397	1.565	1.353	1.550	1.468
B(4)-O(5)	1.419	1.368	1.399	1.371	1.360	1.562	1.365	1.482	1.482
B(4)-O(10)	1.350	1.387	1.377	1.430	1.415	1.451	1.462	1.493	1.544
B(4)-O(11)						1.451		1.488	1.537
<B(4)-O>	1.399	1.390	1.396	1.388	1.391	1.507	1.393	1.503	1.508
Σb.v.	2.791	2.852	2.809	2.878	2.850	2.798	2.848	2.805	2.791
δ x 1000	0.630	0.193	0.357	0.472	0.271	1.380	1.227	0.329	0.485
<Σb.v.>	2.771	2.848	2.767	2.883	2.834	2.794	2.835	2.804	2.781
B(1)-O(1)-B(3)	94.09	102.45	92.19	114.79	99.98	89.84	111.93	97.41	108.46
B(1)-O(2)-B(2)	114.54	124.14	114.95	117.74	123.57	114.48	123.39	121.94	123.04
B(2)-O(3)-B(3)	115.43	109.57	114.92	119.11	106.92	113.99	124.43	108.30	122.77
B(3)-O(4)-B(1)	114.54	109.20	113.24	117.89	110.30	114.48	115.79	109.71	117.47
B(1)-O(5)-B(1)	115.43	124.35	113.42	118.87	119.80	113.98	116.98	121.91	117.28
ζ_{B-O-B}	8.19	9.25	9.26	1.36	9.03	9.65	4.42	9.49	4.32

*CL-A: 4Δ:<3Δ>=<3Δ>
CL-B: 3Δ□:<2Δ□>=<2Δ□>
CL-C: 3Δ□:<2Δ□>=<3Δ>
CL-D: 2Δ2□:<Δ2□>=<Δ2□>
CL-E: 2Δ2□:<Δ2□>=<2Δ□>
CL-F: 2Δ2□:<2Δ□>=<2Δ□>
CL-G: Δ3□:<Δ2□>=<3□>
CL-H: Δ3□:<Δ2□>=<Δ2□>
CL-I: 4□:<3□>=<3□>
**atom labels are as in Figure 1; in addition O(8) bonds to B(2) and O(11) bonds to B(4).

of fifteen structures in Table 6. However, it must be borne in mind that the calculations are for an isolated cluster, whereas the FBBs occur embedded in a crystal structure; thus exact correspondence between calculated and observed parameters is not expected. Nevertheless, calculated B–O bond-lengths are in close agreement with the averages in FBBs; the calculated bond-lengths are all within 4% of the averages in FBBs, and most are within 2%; all but two of the calculated bond-lengths are within 1σ of the average in the FBBs, and the other two are within 2σ. The average calculated $^{[3]}$B-ϕ and $^{[4]}$B-ϕ bond-lengths are consistently ~1% larger than the corresponding averages in FBBs; this is attributed to the charge of –2 on the model cluster. The bond-length trends in the FBBs are reproduced by the calculations: the longest $^{[4]}$B–ϕ bonds occur for the $^{[4]}$B–O–$^{[3]}$B polyhedron-bridging bonds around the four-membered ring, and the shortest $^{[4]}$B–ϕ bond-lengths occur for the two $^{[4]}$B–O(1) bonds that bridge between tetrahedra. The shortest $^{[3]}$B–ϕ bonds are the polyhedron-bridging $^{[4]}$B–ϕ–$^{[3]}$B bonds around the four-membered ring.

TABLE 4. CALCULATED POLYHEDRAL BOND-ANGLES FOR 4B:<3B>=<3B> CLUSTERS

	*CL-A	CL-B	CL-C	CL-D	CL-E	CL-F	CL-G	CL-H	CL-I
O(1)-B(1)-O(2)**	112.6	102.2	116.4	108.2	104.9	112.4	112.6	102.9	110.4
O(1)-B(1)-O(5)	112.8	103.5	109.7	108.1	102.2	112.8	105.4	104.3	107.8
O(1)-B(1)-O(6)		115.5		109.9	114.2		106.8	111.6	103.7
O(2)-B(1)-O(5)	125.6	111.0	127.2	107.4	112.0	130.2	109.7	116.2	113.6
O(2)-B(1)-O(6)		111.7		111.8	113.5		114.3	108.2	109.7
O(5)-B(1)-O(6)		112.3		111.4	109.4		107.5	113.1	111.2
<O-B(1)-O>	117.0	109.4	117.8	109.5	109.4	118.5	109.4	109.4	109.4
O(2)-B(2)-O(3)	115.5	119.6	101.8	124.5	104.8	104.3	111.2	107.3	113.0
O(2)-B(2)-O(7)	122.3	123.7	106.8	119.9	108.8	106.9	106.0	107.9	108.6
O(2)-B(2)-O(8)			111.3		113.5	111.3	113.7	112.7	114.0
O(3)-B(2)-O(7)	112.1	116.6	111.5	115.6	110.8	111.8	113.6	111.3	112.1
O(3)-B(2)-O(8)			109.6		107.7	110.0	106.6	108.2	105.0
O(7)-B(2)-O(8)			115.0		111.0	112.1	105.7	109.3	103.8
<O-B(2)-O>	116.6	120.0	109.3	120.0	109.4	109.4	109.5	109.4	109.4
O(1)-B(3)-O(3)	112.8	117.2	116.4	107.8	120.8	112.8	112.3	116.1	110.1
O(1)-B(3)-O(4)	112.6	117.7	109.4	107.6	113.1	112.5	104.4	116.3	107.2
O(1)-B(3)-O(9)				116.1			113.8		111.8
O(3)-B(3)-O(4)	125.6	120.6	127.7	107.8	123.7	130.0	110.8	126.3	114.9
O(3)-B(3)-O(9)				111.2			113.5		109.5
O(4)-B(3)-O(9)				106.0			101.0		103.1
<O-B(3)-O>	117.0	118.5	117.8	109.4	119.2	118.4	109.3	119.6	109.4
O(4)-B(4)-O(5)	115.5	119.4	118.9	124.6	122.7	104.4	127.1	107.6	111.9
O(4)-B(4)-O(10)	122.3	118.9	119.7	119.5	118.3	111.3	119.0	111.0	113.3
O(4)-B(4)-O(11)						106.9		108.4	109.7
O(5)-B(4)-O(10)	122.1	121.6	121.3	115.9	119.0	110.0	113.9	107.5	104.8
O(5)-B(4)-O(11)						111.8		112.8	110.4
O(10)-B(4)-O(11)						112.1		109.5	106.5
<O-B(4)-O>	120.0	120.0	120.0	120.0	120.0	109.4	120.0	109.5	109.4

*CL-A: 4Δ:<3Δ>=<3Δ>
CL-B: 3Δ□:<2Δ□>=<2Δ□>
CL-C: 3Δ□:<2Δ□>=<3Δ>
CL-D: 2Δ2□:<Δ2□>=<Δ2□>
CL-E: 2Δ2□:<Δ2□>=<2Δ□>
CL-F: 2Δ2□:<2Δ□>=<2Δ□>
CL-G: Δ3□:<Δ2□>=<3□>
CL-H: Δ3□:<Δ2□>=<Δ2□>
CL-I: 4□:<3□>=<3□>
**atom labels are as in Figure 1; in addition O(8) bonds to B(2) and O(11) bonds to B(4).

The calculated polyhedron-bridging $^{[4]}$B–O–$^{[3]}$B bond-angles for the 2Δ2□:<Δ2□>=<Δ2□> cluster are in good agreement with those observed in FBBs in structures; the trends are reproduced, and the calculated $^{[4]}$B–O–$^{[3]}$B bond-angles are within 1σ of the averages in minerals. The calculated $^{[4]}$B–O–$^{[4]}$B bond-angle is wider than the average in FBBs; it is within 2.3σ of the averages in FBBs.

Comparison of calculated geometries

The nine clusters of the form 4B:<3B>=<3B> have five different stoichiometries (Table 5); thus it is not possible to directly compare the calculated energy of each of the nine clusters. However, in the cases

TABLE 5. HARTREE-FOCK ENERGIES, COMPOSITIONS AND B(1)-B(3) SEPARATIONS FOR 4B:<3B>=<3B> CLUSTERS

Cluster	Composition	Energy (Hartrees)	B(1)-B(3) (Å)
CL-A: 4Δ:<3Δ>=<3Δ>	$[B_4O_5(OH)_2]$	-621.1153	2.087
CL-B: 3Δ□:<2Δ□>=<2Δ□>	$[B_4O_5(OH)_3]^{-1}$	-696.2777	2.278
CL-C: 3Δ□:<2Δ□>=<3Δ>	$[B_4O_5(OH)_3]^{-1}$	-696.2184	2.078
CL-D: 2Δ2□:<Δ2□>=<Δ2□>	$[B_4O_5(OH)_4]^{-2}$	-771.2393	2.458
CL-E: 2Δ2□:<Δ2□>=<2Δ□>	$[B_4O_5(OH)_4]^{-2}$	-771.1989	2.252
CL-F: 2Δ2□:<2Δ□>=<2Δ□>	$[B_4O_5(OH)_4]^{-2}$	-771.1755	2.068
CL-G: Δ3□:<Δ2□>=<3□>	$[B_4O_5(OH)_5]^{-3}$	-845.9807	2.433
CL-H: Δ3□:<Δ2□>=<Δ2□>	$[B_4O_5(OH)_5]^{-3}$	-845.9796	2.247
CL-I: 4□:<3□>=<3□>	$[B_4O_5(OH)_6]^{-4}$	-920.5979	2.422

TABLE 6. COMPARISON OF HARTREE-FOCK GEOMETRY AND AVERAGE GEOMETRY OF 2Δ2□:<Δ2□>=<Δ2□> IN STRUCTURES

	CALC.	*OBS.	σ
B(1)-O(1)**	1.465	1.474	0.052
B(1)-O(2)	1.520	1.497	0.024
B(1)-O(5)	1.515	1.511	0.035
B(1)-O(6)	1.469	1.438	0.040
<B(1)-O>	1.492	1.480	
B(2)-O(2)	1.361	1.369	0.020
B(2)-O(3)	1.374	1.369	0.036
B(2)-O(7)	1.429	1.378	0.027
<B(2)-O>	1.388	1.372	
B(3)-O(1)	1.453	1.451	0.025
B(3)-O(3)	1.512	1.498	0.028
B(3)-O(4)	1.536	1.493	0.037
B(3)-O(9)	1.469	1.458	0.025
<B(3)-O>	1.492	1.475	
B(4)-O(4)	1.362	1.361	0.017
B(4)-O(5)	1.371	1.381	0.030
B(4)-O(10)	1.430	1.393	0.047
<B(4)-O>	1.388	1.378	
B(1)-O(1)-B(3)	114.79	110.59	1.85
B(1)-O(2)-B(2)	117.74	117.94	1.99
B(2)-O(3)-B(3)	119.11	121.05	2.41
B(3)-O(4)-B(4)	117.89	118.00	1.77
B(4)-O(5)-B(1)	118.87	120.60	1.58

*average value for all occurences in minerals (Table 1) and synthetic inorganic compounds (Table 2).

**atom labels as in Figure 1.

where more than one cluster does have identical stoichiometry, the calculated energy for each arrangement is an invaluable guide to the relative stability of the clusters.

2Δ2□: Three clusters have the stoichiometry 2Δ2□ (CL–D, CL–E, CL–F) and the composition $[B_4O_5(OH)_4]^{2-}$; these are the 2Δ2□:<Δ2□>= <Δ2□>, 2Δ2□:<Δ2□>=<2Δ□> and 2Δ2□:<2Δ□>= <2Δ□> clusters. The results of the calculations for these clusters are of particular interest, as only the 2Δ2□:<Δ2□>=<Δ2□> cluster occurs as the FBB of a structure, even though all three clusters have identical stoichiometry. The 2Δ2□:<Δ2□>=<Δ2□> cluster has the lowest energy: it is 0.0404 Hartrees (106.1 kJ/mole) more stable than the 2Δ2□:<Δ2□>=<2Δ□> cluster, and 0.0638 Hartrees (167.5 kJ/mole) more stable than the 2Δ2□:<2Δ□>=<2Δ□> cluster (Table 5). Thus, the calculations clearly indicate that the 2Δ2□:<Δ2□>= <Δ2□> cluster is significantly more stable, on the basis that it has the lowest energy. These calculations are for isolated clusters; the lower energy of the 2Δ2□:<Δ2□>=<Δ2□> cluster may only be attributed to *local* effects *within* the clusters.

The calculated equilibrium-geometries for clusters with stoichiometry 2Δ2□ show features that are consistent with the greater stability of the 2Δ2□:<Δ2□>=<Δ2□> cluster. The bond-valences of polyhedra provide an indicator of cluster stability for each cluster. The theoretical value is 3.0 *vu* for a borate polyhedron, and the calculated geometries of clusters that give polyhedron bond-valences closest to 3.0 will be the most stable. In all cases, the sum of bond-valences for each borate polyhedron is somewhat less than 3.0 *vu*. The average sum of polyhedron bond-valences for each cluster (<Σb.v.>) is given in Table 3. The <Σb.v.> for the most stable 2Δ2□:<Δ2□>= <Δ2□> cluster is 2.878 *vu*; the 2Δ2□:<Δ2□>= <2Δ□> and 2Δ2□:<2Δ□>=<2Δ□> clusters have <Σb.v.> = 2.834 and 2.794 *vu*, respectively. There is a linear relationship between the cluster energy and <Σb.v.> in clusters with stoichiometry 2Δ2□ (Fig. 4). The maximum distortion of the polyhedra (δ_{max}) also is an indicator of the relative stability of the clusters, because highly distorted polyhedra are less stable than undistorted polyhedra (in the case of borate polyhedra). The most stable 2Δ2□:<Δ2□>=<Δ2□> cluster has δ_{max} = 0.492, and the 2Δ2□:<Δ2□>=<2Δ□> and 2Δ2□:<2Δ□>=<2Δ□> clusters have δ_{max} = 2.850 and 2.798, respectively. The average deviation of polyhedron-bridging B–O–B bond-angles (ξ_{B-O-B}) from the average of ~119° for <3B> in FBBs is an additional indicator of the stability of the cluster. The most stable 2Δ2□:<Δ2□>=<2Δ□> cluster has ξ_{B-O-B} = 1.36°; the 2Δ2□:<Δ2□>=<2Δ□> and 2Δ2□: <2Δ□>=<2Δ□> clusters have ξ_{B-O-B} equal to 9.02° and 9.65°, respectively.

3Δ□: Two clusters have the stoichiometry 3Δ□ (CL–B and CL–C) and the composition $[B_4O_5(OH)_3]^{1-}$; neither of these clusters occurs as the FBB of a crystal structure. The energy of the 3Δ□:<2Δ□>=<2Δ□> cluster is 0.0593 Hartrees

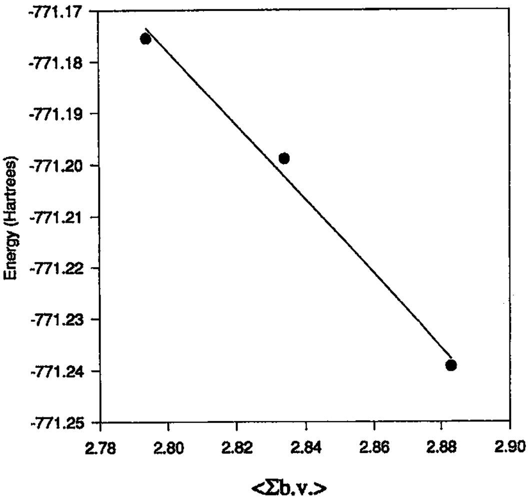

FIG. 4. Cluster energy *versus* the average sum of polyhedra bond-valences (<Σb.v.>) for each cluster with stoichiometry 2Δ2□.

(155.7 kJ/mole) lower than that of the 3Δ□:<2Δ□>=<3Δ> cluster (Table 5). The more stable 3Δ□:<2Δ□>=<2Δ□> cluster has <Σb.v.> = 2.848 *vu*, δ_{max} = 0.923 and $\xi_{B–O–B}$ = 9.25; the less stable 3Δ□:<2Δ□>=<3Δ> cluster has <Σb.v.> = 2.767 *vu*, δ_{max} = 1.634 and $\xi_{B–O–B}$ = 9.26. Thus, the <Σb.v.> and δ_{max} parameters for these clusters effectively distinguish which is the more stable.

Δ3□: Two clusters have the stoichiometry Δ3□ (CL–G and CL–H) and the composition $[B_4O_5(OH)_5]^{3-}$; neither occur as the FBB of a crystal structure. The energy of these two clusters is similar: the energy of the Δ3□:<Δ2□>=<3□> cluster is 0.0011 Hartrees (2.9 kJ/mole) lower than the Δ3□:<Δ2□>=<Δ2□> cluster (Table 5). The slightly more stable Δ3□:<Δ2□>=<3□> cluster has <Σb.v.> = 2.835 *vu* compared to <Σb.v.> = 2.804 *vu* for the Δ3□:<Δ2□>=<Δ2□> cluster. The Δ3□:<Δ2□>=<3□> cluster has δ_{max} = 1.766 and $\xi_{B–O–B}$ = 4.42, the Δ3□:<Δ2□>=<Δ2□> cluster has δ_{max} = 0.623 and $\xi_{B–O–B}$ = 9.49. The energetically preferred cluster has the higher δ_{max} value in this case, but $\xi_{B–O–B}$ is considerably lower for the most stable cluster.

WHY FEW CLUSTERS CONTAINING FOUR POLYHEDRA ARE UTILIZED AS STRUCTURE FBBS

The molecular-orbital calculations have provided equilibrium geometries for each of the nine clusters with the general form 4B:<3B>=<3B>. Comparison of the geometries of the various clusters with identical stoichiometry (for which relative stability is given by the calculated energy) has demonstrated that the parameters <Σb.v.>, δ_{max} and $\xi_{B–O–B}$ are indicators of relative stability of a cluster; the optimal <Σb.v.> is 3.0 *vu*, and optimal values of δ_{max} and $\xi_{B–O–B}$ are zero. Thus, it is now possible to identify which of the nine clusters is the most stable. The best values of <Σb.v.> (2.883 *vu*), Σ_{max} (0.492) and $\xi_{B–O–B}$ (1.36°) all correspond to the same cluster: 2Δ2□:<Δ2□>=<Δ2□>, which is the only cluster of the general form 4B:<3B>=<3B> that occurs as the FBB of structures of minerals and synthetic inorganic compounds.

Previous molecular-orbital calculations done for borate clusters have been limited to clusters that occur as the FBBs of crystal structures. In the current study, however, molecular-orbital calculations have been done for the nine possible borate clusters with the general form 4B:<3B>=<3B>, despite the fact that only one of these clusters occurs as the FBB of a structure. The calculations show that the one cluster that does occur in crystal structures is the most stable of the nine. These calculations include only local effects within the borate cluster; thus the results indicate that, in the case of borate clusters with the general form 4B:<3B>=<3B>, the 2Δ2□:<Δ2□>=<Δ2□> cluster is the only one used as a FBB because it is considerably more favorable on the local (short-range) scale.

WHY THE 2Δ2□:<Δ2□>=<Δ2□> CLUSTER IS THE MOST STABLE

The molecular-orbital calculations indicate that the 2Δ2□:<Δ2□>=<Δ2□> cluster is the most stable borate cluster of the form 4B:<3B>=<3B>, in accord with its occurrence as the FBB of crystal structures. The other clusters of the form 4B:<3B>=<3B> are less stable because: (1) their arrangements of triangles and tetrahedra in some cases require considerable distortion of the polyhedron geometries to facilitate the connectivity of the cluster, (2) B – B separations are short in some clusters, increasing the Coulombic repulsion component of the cluster energy.

Polyhedron geometries of the well-refined structures of eighty minerals have been tabulated; the average $<^{[3]}B–\phi>$ bond-length for 105 triangles is 1.370 Å (σ = 0.017 Å), and the average $<^{[4]}B–\phi>$ bond-length calculated for 127 tetrahedra is 1.476 Å (σ = 0.025 Å). The average bond-angle for an individual tetrahedron is usually in the range 109.4 to 109.5°, and the average bond-angle for an individual triangle is almost invariably 120.0°, indicating that $B\phi_3$ groups have a strong tendency to be planar. The calculated bond-lengths and average polyhedron bond-angles for the 2Δ2□:<Δ2□>=<Δ2□> cluster are close to the averages for polyhedra in minerals (Tables 3, 4, 6). However, some of the calculated geometries of the other eight clusters show highly distorted polyhedron geometries, giving $<B–\phi>$ bond-lengths that are considerably longer than expected. The borate triangles in some of the clusters are very distorted from planarity, as indicated by average polyhedral bond-angles that are less than 120°. The 4Δ:<3Δ>=<3Δ>, 3Δ□:<2Δ□>=<2Δ□>, 3Δ□:<2Δ□>=<3Δ> and 2Δ2□:<2Δ□>=<2Δ□> clusters show average triangular bond-angles that are less than 119°. The borate triangles in the 2Δ2□:<Δ2□>=<2Δ□> and 3Δ□:<Δ2□>=<Δ2□> clusters are also somewhat distorted from planarity. As the calculated geometries correspond to the minimum-energy configuration for each cluster, it may be concluded that it is not possible for these clusters to be assembled using undistorted polyhedra. Only the 2Δ2□:<Δ2□>=<Δ2□>, Δ3□:<Δ2□>=<3□> and 4□:<3□>=<3□> clusters have average bond-angles in the polyhedra that are close to the averages in minerals and that are typical of undistorted polyhedra; these are the clusters that may be assembled without significant distortion of the bond angles in the polyhedra.

The shortest B–B separation in each cluster is invariably between B(1) and B(3) (shown in Fig. 1); these distances are given in Table 5. The B(1)–B(3) separations fall into three groups of three each: those with separations ~2.45 Å occur where B(1) and B(3) are both tetrahedrally coordinated boron, those with separations ~2.25 Å occur where B(1) is tetrahedrally coordinated boron and B(3) is triangularly coordinated boron, and those with separations ~2.07 Å occur in clusters where B(1) and B(3) are both triangularly coordinated boron. Coulombic repulsion will destabilize clusters with short B–B separations. Examination of FBBs of crystal structures indicates that typical B–B separations are greater than 2.40 Å, suggesting that the only clusters of the form 4B:<3B>=<3B> that will be stable are those with both B(1) and B(3) being tetrahedrally coordinated boron. These are the 2Δ2□:<Δ2□>=<Δ2□>, Δ3□:<Δ2□>= <3□> and 4□:<3□>=<3□> clusters.

It may be that the Δ3□:<Δ2□>=<3□> and 4□:<3□>=<3□> clusters are FBBs of yet-unknown crystal structures, as they do not contain non-planar borate triangles or short B–B separations. It is very unlikely that any of the 4Δ:<3Δ>=<3Δ>, 3Δ□:<2Δ□>=<2Δ□>, 3Δ□:<2Δ□>=<3Δ>, 2Δ2□: <2Δ□>=<2Δ□>, 2Δ2□:<Δ2□>=<2Δ□> or 3Δ□:<Δ2□>=<Δ2□> clusters will occur as the FBB of a crystal structure.

CONCLUSIONS

(1) Borate structures based on FBBs with four polyhedra contain either the 4□:<4□> cluster (one example) or the 2Δ2□:<Δ2□>=<Δ2□> cluster (seventeen examples), although there are twenty-one chemically feasible borate clusters that contain four polyhedra.

(2) Molecular-orbital calculations for the 2Δ2□: <Δ2□>=<Δ2□> cluster have given a predicted equilibrium-geometry that is in good agreement with the average geometry of the FBBs of crystal structures.

(3) Molecular-orbital calculations have provided equilibrium geometries for each of the nine clusters of the form 4B:<3B>=<3B>; of these, the calculations indicate that the 2Δ2□:<Δ2□>=<Δ2□> cluster is likely to be the most stable.

(4) The 2Δ2□:<Δ2□>=<Δ2□> cluster is the only cluster of the form 4B:<3B>=<3B> that is utilized as a FBB of structures because of local bonding considerations, which make the cluster more stable than the alternatives.

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