

## Bond analyses of borates from the Inorganic Crystal Structure Database

Daqiu Yu and Dongfeng Xue\*

State Key Laboratory of Fine Chemicals,  
Department of Materials Science and Chemical  
Engineering, School of Chemical Engineering,  
Dalian University of Technology, 158 Zhong-  
shan Road, Dalian 116012, People's Republic  
of ChinaCorrespondence e-mail:  
dfxue@chem.dlut.edu.cnReceived 13 January 2006  
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Various fundamental building blocks (FBBs) are observed in the crystallographic structures of oxoborates available in the Inorganic Crystal Structure Database, Version 1.3.3 (2004); the occurrence of borate groups with low complexity is dominant. Bond-valence parameters  $d_0$  of B—O bonds in 758 oxoborates with various FBBs have been calculated using the bond-valence sum model. Some discrepancies in the  $d_0$  values obviously occur if the detailed configurations of FBBs in borate crystals are considered;  $d_0$  is sensitive to the chemical bonding structure of B atoms in the crystallographic framework. Moreover,  $d_0$  values are affected by the existence of interstitial atoms and the substitution of other anionic groups. In addition, the  $d_0$  parameters for B—N, B—S, B—P and B—F bonds are also calculated statistically. Some suitable  $d_0$  data for various borate FBBs are recommended according to their particular configurations, especially for those with low complexity. On the basis of the proposed linear relationship between calculated nonlinear optical (NLO) coefficients of borates and the current  $d_0$  values for various FBBs, it is found that the  $d_0$  values may be regarded as a useful parameter for pre-investigating the NLO properties of borates, leading to an efficient structural evaluation and design of novel borates.

## 1. Introduction

In recent years, much of the work on the synthesis, characterization and physical studies of the ultraviolet (UV) nonlinear optical (NLO) crystals has been focused on borate compounds (see *e.g.* Becker, 1998; Sasaki *et al.*, 2000), owing to their high UV transmittance, large second-harmonic conversion efficiency and high optical damage threshold at shorter wavelengths. Various kinds of borates, including  $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4]\cdot 2\text{H}_2\text{O}$ ,  $\beta\text{-BaB}_2\text{O}_4$ ,  $\text{LiB}_3\text{O}_5$  and  $\text{Sr}_2\text{B}_2\text{Be}_2\text{O}_7$  (Dewey *et al.*, 1975; Chen *et al.*, 1985, 1989, 1995), have been found and used as promising NLO crystals.

In oxoborates (henceforth, oxoborates will be simply called borates) the B atom usually coordinates with either three or four O atoms to form  $[\text{BO}_3]$  or  $[\text{BO}_4]$  groups. Accordingly, the atomic orbitals are hybridized to a planar  $sp^2$  or three-dimensional  $sp^3$  structure. Further, such structure units can comprise several different typical  $\text{B}_x\text{O}_y$  groups by various combinations (Xue, Betzler, Hesse & Lammers 2000), which is considered to be a dominant factor for the versatile physical properties, particularly for the attractive NLO properties of borates. Therefore, a comprehensive study of the structural chemistry concerning borate crystals is of great significance for a profound understanding of the relationship between crystal structures and their physical properties.

The bond-valence sum (BVS) model (Brown & Altermatt, 1985; Xue & Ratajczak, 2005) is a powerful tool for the analysis and evaluation of crystal structures. The bond-valence parameter  $d_0$  can be viewed as the bond length of unit valence, which relates the bond valence to bond length. Once obtained, it is very useful in a great number of ways. The most obvious applications in crystallography are the prediction of bond lengths from a given bond valence and the use of bond-valence sums at atoms as a check on the reliability of a determined structure (Palenik, 2003; Roulhac & Palenik, 2003; Trzesowska *et al.*, 2005). Consequently, in this study the microscopic structural characteristics of borates are investigated on the basis of the BVS model, with the aim of guiding the structural design of new types of NLO borates.

Over 1000 borate crystal structures are available in the Inorganic Crystal Structure Database (ICSD), Version 1.3.3 (2004). Becker (2001) analyzed the structural characteristics of different anhydrous borates solved before 2001 [using ICSD (2001) as the source of initial information], and investigated the condensation degree of polyborate anions using the Lewis acid strength of cations and the ratio of cations and B atoms, which is helpful in predicting the stoichiometry of a new compound and its probable structural building units. As a supplement to Becker's results, the crystal structures of 88 anhydrous borates added to the database in the years 2001–2004 were firstly examined on the basis of ICSD (2004). Further, we focused our research on the detailed configurations of the fundamental building blocks (FBBs) of borates, *i.e.* the linking of boron–oxygen (B–O) polyhedra. Cations other than  $B^{3+}$ , halogen anions and  $H_2O$  molecules are all regarded as interstitial atoms when forming the infrastructures of borate polyanions in the crystallographic framework. The bond-valence parameters  $d_0$  of B–O bonds in the 758 investigated borates are calculated on the basis of the BVS model, including 420 anhydrous borates, 129 hydrated borates, 82 borates containing halogen anions and 127 borates with mixed polyanions. Additionally,  $d_0$  values of B–N, B–S, B–P and B–F bonds are also calculated statistically *via* a survey of borates without B–O polyanions. All crystal structures included in the final calculation of parameters  $d_0$  are those with crystallographic  $R$  factors of less than 0.1. Herein, the recommended  $d_0$  data for all investigated FBBs can be employed to predict NLO properties and structurally design novel borates by considering the microscopic configurations of borate FBBs.

## 2. Theoretical basis

The BVS model (Brown & Altermatt, 1985; Xue & Ratajczak, 2005) provides a useful way of understanding various physico-chemical properties of solids from the chemical bond viewpoint. In the BVS model the bond valence  $s_{ij}$  between atoms  $i$  and  $j$  may be related to the bond length  $d_{ij}$  by an inverse exponential form,

$$s_{ij} = \exp[(d_0 - d_{ij})/B], \quad (1)$$

where the parameters  $d_0$  and  $B$  are constants fitted empirically.  $B$  varies very little from one atom pair to another. Brown & Altermatt (1985) found that  $B$  could rarely be determined to be better than 0.05 Å and that a value of 0.37 Å is convenient for most or all bond types. Using the same value of  $B$  for all bond types makes the determination of  $d_0$  simpler, since only one parameter now needs to be fitted (Brown, 2002). In the current study we use a value of  $B$  of 0.37 Å throughout. In terms of the above expression, the sum of the nearest integers to each BVS value for a structure is equal to the total of the atom oxidation states  $V_i$ , *i.e.*

$$V_i = \sum_j s_{ij}. \quad (2)$$

This expression necessarily holds for sums around both the anions and cations.

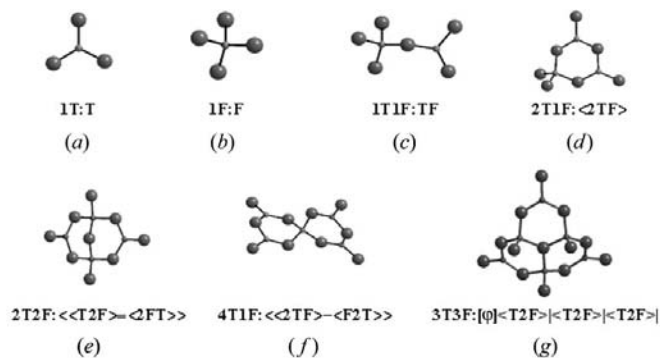
In borate crystal structures, B atoms are generally considered as central atoms bonded to three or four O atoms; therefore the  $d_0$  parameters of B–O bonds in borate polyhedra are calculated using the following equation (Brese & O'Keeffe, 1991; Brown, 2002),

$$d_{0i} = B \ln \left[ V_i / \sum_{j=1}^{CN} \exp(-d_{ij}/B) \right], \quad (3)$$

where the summation is over all bonds in a single coordination sphere  $i$ . The number of ligands, CN, is equal to 3 or 4 for threefold- or fourfold-coordinated B atoms, respectively. Since the bond-length data can be retrieved from ICSD (2004) and the value of  $B$  is fixed at 0.37 Å [that is, all terms on the right-hand side in (3) are known], it is easy to calculate  $d_{0i}$  for trivalent B atoms. The mean  $d_0$  values of various FBBs can be obtained by averaging all calculated parameters  $d_{0i}$ .

## 3. Occurrence of FBBs in the crystallographic structure of anhydrous borates

In order to describe various FBBs and give a clear nomenclature for more and more complicated polyborate anions, Burns *et al.* (1995) developed a type of comprehensive algebraic descriptor based on FBBs, where the triangle and square symbols represent triangular [ $B\varphi_3$ ] and tetrahedral [ $B\varphi_4$ ] ( $\varphi = O^{2-}$ ,  $OH^-$ ), respectively. In this paper the algebraic descriptor is used in a slightly modified form with triangular and square symbols replaced by T and F, and the delimiters  $\langle \rangle$  and  $\langle \langle \rangle \rangle$  are adopted to indicate that the included polyhedra share corners to form single and double rings. The descriptor has the general form  $A:B$  (where  $A$  is the number of borate polyhedra in the FBB, and  $B$  gives information on their connectivity), which conforms to the representations in the work of Burns *et al.* (1995) and Hawthorne *et al.* (1996). Fig. 1 shows several examples of the algebraic descriptors for FBBs in general borates. All details of the structural characteristics of borate FBBs are taken into consideration by such a symbolic algebraic descriptor [for further details, readers can refer to the paper by Burns *et al.* (1995) or Hawthorne *et al.* (1996)].



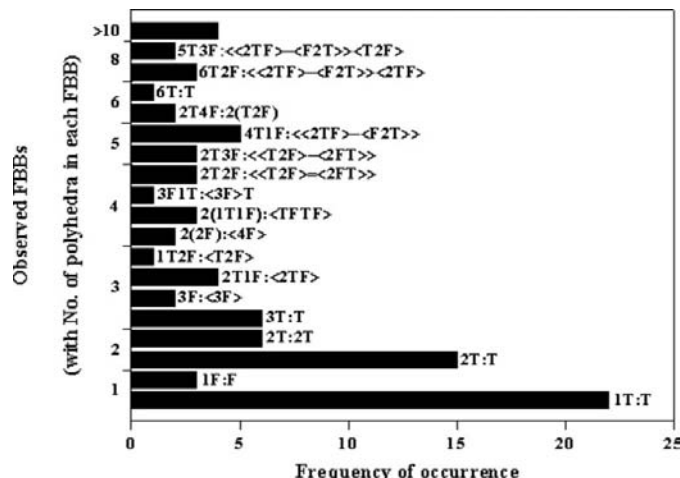
**Figure 1**  
Examples of the algebraic descriptors for FBBs in general borates (T: three-coordinated boron group [B $\phi_3$ ]; F: four-coordinated boron group [B $\phi_4$ ];  $\phi = O^{2-}, OH^-$ ).

With the aid of the above algebraic descriptors of borate FBBs, a statistical analysis of the occurrence of FBBs is made to obtain detailed knowledge of various kinds of FBBs in 88 anhydrous borates from 2001 to 2004 available in the ICSD [while the occurrence of borate FBBs before 2001 has been given in the work of Becker (2001)]. Obviously there are many possible kinds of borate FBBs that have not yet been observed, whereas others are quite common in these crystal structures (Fig. 2). The occurrence of FBBs containing less than six B—O polyhedra is high (86%), which indicates that the formation of borate groups with low complexity is preferred in anhydrous borates. If the detailed configurations of FBBs are considered, approximately 53% of the investigated crystal structures contain FBBs built only from the isolated polyhedra [BO $_3$ ] or [BO $_4$ ]. This distribution of frequency is similar to that reported by Becker (2001), in which the ratios are 90 and 52%, respectively.

## 4. Bond-valence parameters $d_0$ of borates

### 4.1. Crystallographic data retrieval

Crystallographic data for calculating bond-valence parameters  $d_0$  were obtained from the ICSD (2004), which contains information on the crystal structures of 76 480 inorganic compounds. All retrieved structures from over 1000 borates were those with crystallographic  $R$  factors of less than 0.1. The duplicated structures were excluded, having the same chemical formula and cell parameters as other structures solved in the same or related space groups. Since the borate structure was regarded as the construction of the framework of FBBs and interstitial atoms (such as metal cations, halogen anions, H $_2$ O molecules *etc.*), the following categories were investigated comprehensively. Firstly, 420 anhydrous borates were extracted, which were the compounds without halogen anions and other anionic groups like [PO $_4$ ] $^{3-}$ , [CO $_3$ ] $^{2-}$ , [SiO $_4$ ] $^{4-}$  *etc.* In particular, various FBBs built from less than six B—O polyhedra were fully considered in the calculation of  $d_0$  values because of their high occurrence. Secondly, 129 hydrated borates were selected with the same criteria for comparison with anhydrous ones; the configurations of FBBs



**Figure 2**  
Frequency of the occurrence of FBBs observed in anhydrous borate crystal structures from 2001 to 2004, which are available in ICSD (2004).

were analyzed and classified without considering the position of H atoms. Further, 82 borates with interstitial halogen anions (*i.e.* F, Cl, Br or I) were investigated, which include anhydrous and hydrated structures without other anionic groups. Additionally, the simultaneous presence of other anion groups such as [PO $_4$ ] $^{3-}$ , [CO $_3$ ] $^{2-}$  or [SiO $_4$ ] $^{4-}$  in the crystal structure influenced the percentage of [BO $_4$ ] or [BO $_3$ ] units in a polyanion. The competition of boron and central cations of the mentioned groups for oxygen ligands led to the formation of mixed polyanions, where B atoms were substituted by these cations. Therefore, 58 phosphate-, seven carbonate- and 62 silicate-borates were screened from numerous borate structures. Finally, the  $d_0$  parameters of the B—N, B—S, B—P and B—F bonds were also calculated statistically for other types of borates, in which N, S, P or F atoms replace O ligands to coordinate with central B atoms. All statistical data were tabulated with the calculated  $d_0$  values in the last two columns of Tables 1–5.

### 4.2. B—O bond-length distribution

There are a vast number of structures existing in borate crystals due to the different combinations of [B $\phi_3$ ] and [B $\phi_4$ ] polyhedra. Generally, these groups prefer to maintain their configurations in various crystal structures, whereas the individual bond lengths show systematic variations depending on the location of bonds in a group (Filatov & Bubnova, 2000). From Tables 1–4 it can be observed that the range of B—O bond lengths is quite wide, although the averaged lengths are all around 1.37 Å for [B $\phi_3$ ] triangles and around 1.48 Å for [B $\phi_4$ ] tetrahedra regardless of the microscopic structures of borates. In the anhydrous borates investigated, the largest spread of B—O bond lengths in [BO $_3$ ] and [BO $_4$ ] can reach 0.676 and 0.517 Å, respectively. Correspondingly, the length spread of B—O bonds in hydrated borates are 0.198 and 0.405 Å, which are relatively narrow compared with anhydrous cases. A similar distribution of B—O bond lengths also occurs in those structures containing halogen anions, as listed in Table 3.

**Table 1**

Bond-valence parameters  $d_0$  of B—O bonds of 420 anhydrous borates.

Bond-length data of the investigated crystals are available in ICSD (2004).  $N$ : number of the statisticised compounds; CN: coordinated number of central B atoms;  $n$ : number of investigated B—O (or B— $\varphi$ ;  $\varphi = \text{O}^{2-}$ ,  $\text{OH}^-$ ) groups;  $\langle d_{ij} \rangle$ : averaged value of bond lengths  $d_{ij}$  for the involved bonds, with the standard uncertainties  $\text{su}(i) = [\sum(d_{ij} - \langle d_{ij} \rangle)^2/(i-1)]^{1/2}$  and s.u. =  $\text{su}(i)/(i)^{1/2}$  ( $i$ : size of the set used in the calculations) in parentheses;  $\langle d_0 \rangle$ : averaged  $d_0$  value of the included groups, with the standard uncertainties  $\text{su}(i) = [\sum(d_{0i} - \langle d_0 \rangle)^2/(i-1)]^{1/2}$  and s.u. =  $\text{su}(i)/(i)^{1/2}$  ( $i$ : size of the set used in the calculations) in parentheses. The units of  $d_{ij}$  and  $d_0$  are Å.

$N$	FBB	CN	$n$	Range of $d_{ij}$	$\langle d_{ij} \rangle$ [su(i)/s.u.]	Range of $d_0$	$\langle d_0 \rangle$ [su(i)/s.u.]
420†	All types	3	819	1.157–1.833	1.375 [34/1]	1.278–1.541	1.373 [17/1]
		4	246	1.163–1.680	1.477 [38/1]	1.183–1.509	
248	$m\text{T}:\text{T}\ddagger$	3	398	1.157–1.833	1.378 [32/1]	1.278–1.525	1.378 [18/1]
		4	10	1.435–1.586	1.488 [33/5]	1.363–1.414	1.380 [15/5]
10	1F:F	4	10	1.435–1.586	1.488 [33/5]	1.363–1.414	1.380 [15/5]
30	2T:2T	3	76	1.240–1.817	1.378 [52/3]	1.317–1.541	1.376 [28/3]
10	3T:(3T)	3	33	1.280–1.433	1.376 [46/5]	1.365–1.378	1.373 [4/1]
12	2T1F:(2TF)	3	24	1.308–1.454	1.368 [27/3]	1.341–1.385	1.367 [11/2]
		4	12	1.337–1.607	1.477 [41/6]	1.346–1.412	
4	3F:(3F)	4	12	1.446–1.515	1.479 [19/3]	1.361–1.381	1.372 [8/2]
9	2T2F:(T2F)=(2FT))	3	18	1.321–1.444	1.370 [21/3]	1.361–1.380	1.366 [7/1]
		4	18	1.417–1.549	1.471 [34/4]	1.343–1.371	
7	4T1F:(T2F)-(F2T))	3	28	1.285–1.495	1.371 [35/4]	1.350–1.469	1.369 [18/3]
		4	7	1.437–1.504	1.473 [15/3]	1.361–1.371	
4	3T2F:(T2F)-(F2T))	3	12	1.253–1.443	1.368 [32/5]	1.336–1.379	1.366 [10/2]
		4	8	1.300–1.590	1.477 [58/10]	1.352–1.379	
13	2T3F:(T2F)-(2FT))	3	26	1.312–1.434	1.370 [21/2]	1.355–1.380	1.371 [7/1]
		4	39	1.431–1.539	1.479 [20/2]	1.360–1.384	

† 73 compounds not listed here are those containing more than six B—O polyhedra in FBBs or without the listed FBBs. ‡  $m$  is the number of isolated  $[\text{BO}_3]$  or  $[\text{BO}_4]$  groups in each FBB.

The bond length usually depends on the sizes of the two bonded atoms, bond order and the nature of the two atoms. However, if polymerization occurs in  $[\text{BO}_3]$  and  $[\text{BO}_4]$  polyhedra, the discrepancies of individual B—O bond lengths may also be attributed to the variation of bond valences of the  $[\text{BO}_3]$  triangle and  $[\text{BO}_4]$  tetrahedron, which can be interpreted by the BVS model (Pauling, 1929; Brown & Altermatt, 1985). Ideally, the formal bond valence of one B—O bond is equal to 1 valence unit (v.u.) for a  $[\text{BO}_3]$  triangle and 0.75 v.u. for a  $[\text{BO}_4]$  tetrahedron. When a triangle is linked to a tetrahedron by sharing one O atom, the B—O bond formed by the shared O atom in the  $[\text{BO}_3]$  group will be stronger than that in the  $[\text{BO}_4]$  group, so the bond valence increases in the  $[\text{BO}_3]$  triangle and decreases in the  $[\text{BO}_4]$  tetrahedron simultaneously. Therefore, according to the BVS model, the considered bond length decreases in the triangle and increases in the tetrahedron. In each polyhedron, in order to satisfy the oxidation state of the B atom, bond lengths should be changed and matched correspondingly. While referring to the whole B—O six-membered ring, the variation of bond lengths and valences will be remarkably complicated. Furthermore, in the crystal the molecules are frequently distorted to some extent by the adjacent molecules and ions, which should also be taken into account when analyzing the lengths of B—O bonds in borates.

### 4.3. Bond-valence parameters $d_0$

Brown & Altermatt (1985) determined the parameter  $d_0$  of B—O bonds by statistical analysis of the compounds obtained from ICSD (1983); they assigned a value of 1.371 Å, which has been applied universally over the past decades. In borate crystals the distortion and variety of the local environments of

constituent bonds, which are induced by the polymerization of  $[\text{B}\varphi_3]$  and  $[\text{B}\varphi_4]$  polyhedra, may result in the discrepancy of  $d_0$  values of B—O bonds. From the last two columns in Tables 1–4 it can be observed that the wide range of calculated  $d_0$  values deserves to be noted, even though the  $\langle d_0 \rangle$  value of the B—O bonds in all 758 investigated oxoborates is equal to 1.372 Å, which is similar to the value given by Brown & Altermatt (1985). Therefore, particular consideration should be paid to the discrepancy of the  $d_0$  values with respect to the detailed configurations of various borate FBBs.

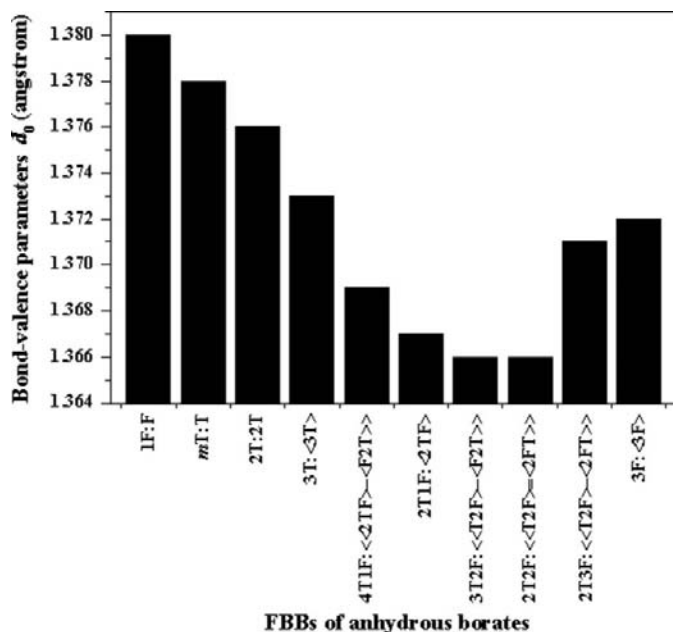
The foregoing statistical analysis of the occurrence of FBBs in anhydrous borates taken from the ICSD (2004) has indicated that the formation of borate groups with low complexity is preferred in anhydrous borates (approximately 90%); furthermore, relatively complicated FBBs are easily formed when existing more than six B—O polyhedra. Therefore, the study of anhydrous borates is mainly focused on ten kinds of FBBs built from less than six B—O polyhedra (see Table 1), which can provide some information on the influence of the polymerization degree on  $d_0$  values. As shown in Fig. 3, a simple trend occurs with the formation of B—O six-membered rings and the change of  $[\text{BO}_3]/[\text{BO}_4]$  ratios in the ring. The maximum  $\langle d_0 \rangle$  value of 1.380 Å occurs for FBBs consisting of isolated  $[\text{BO}_4]$  tetrahedra; 1.378 Å is the next highest value for FBBs built from isolated  $[\text{BO}_3]$  triangles (Fig. 3). The  $\langle d_0 \rangle$  value evidently decreases with the polymerization of the  $[\text{BO}_3]$  and  $[\text{BO}_4]$  groups, especially when the  $[\text{BO}_3]$  and  $[\text{BO}_4]$  groups are polymerized into single or double B—O six-membered rings. The occurrence of the  $[\text{BO}_4]$  groups in rings leads to a corresponding decrease in the proportion of  $[\text{BO}_3]$  groups; the  $\langle d_0 \rangle$  value reduces to 1.366 Å in the double six-membered ring notated as 3T2F:(T2F)-(F2T)) or 2T2F:(T2F)=(2FT)).

**Table 2**

Bond-valence parameters  $d_0$  of B—O bonds of 129 hydrated borates.

<i>N</i>	FBB	CN	<i>n</i>	Range of $d_{ij}$	$\langle d_{ij} \rangle$ [su( <i>i</i> )/s.u.]	Range of $d_0$	$\langle d_0 \rangle$ [su( <i>i</i> )/s.u.]
129†	All types	3	274	1.273–1.471	1.368 [21/1]	1.273–1.415	1.368 [11/0]
		4	294	1.339–1.744	1.476 [32/1]	1.294–1.442	
12	<i>m</i> T:T‡	3	17	1.273–1.439	1.372 [36/5]	1.273–1.415	1.371 [31/8]
16	<i>m</i> F:F‡	4	25	1.356–1.656	1.481 [43/4]	1.338–1.442	1.373 [21/4]
4	2T1F:(2TF)	3	8	1.317–1.432	1.371 [27/6]	1.363–1.379	1.370 [5/2]
		4	4	1.444–1.506	1.476 [19/5]	1.363–1.372	
15	1T2F:(T2F)	3	16	1.297–1.422	1.368 [20/3]	1.349–1.373	1.369 [7/1]
		4	32	1.381–1.576	1.478 [28/2]	1.348–1.391	
15	2T2F:(T2F)=(F2T)	3	38	1.312–1.401	1.369 [12/1]	1.359–1.376	1.369 [7/1]
		4	38	1.416–1.678	1.477 [29/2]	1.362–1.418	
13	2T3F:(T2F)–(F2T)	3	26	1.325–1.452	1.369 [19/2]	1.358–1.395	1.369 [7/1]
		4	39	1.424–1.543	1.476 [25/2]	1.349–1.393	
6	3T2F:(T2F)–(F2T)	3	21	1.306–1.415	1.367 [21/3]	1.358–1.377	1.368 [5/1]
		4	14	1.421–1.514	1.476 [22/3]	1.361–1.376	
9	4T1F:(T2F)–(F2T)	3	36	1.307–1.415	1.364 [20/2]	1.335–1.386	1.364 [9/1]
		4	9	1.433–1.510	1.474 [18/3]	1.362–1.377	
9	3T3F:[ $\varphi$ ](T2F) (T2F) (T2F)	3	33	1.341–1.398	1.365 [11/1]	1.359–1.372	1.364 [3/0]
		4	33	1.425–1.538	1.471 [29/3]	1.348–1.368	

† 30 compounds not listed here are those containing more than six B– $\varphi$  ( $\varphi = \text{O}^{2-}, \text{OH}^-$ ) polyhedra in FBBs or without the listed FBBs. ‡ *m* is the number of isolated  $[\text{B}\varphi_3]$  or  $[\text{B}\varphi_4]$  groups in each FBB.

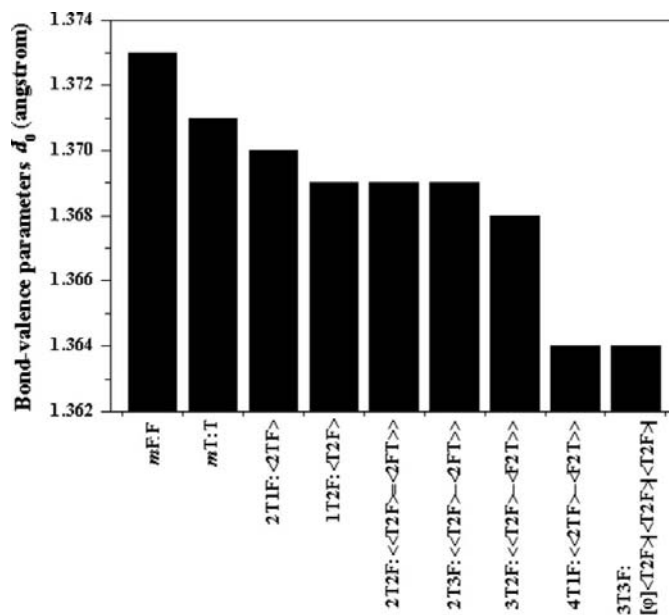


**Figure 3**

Bond-valence parameters  $d_0$  of B—O bonds of anhydrous borates of various FBBs, which are built from the isolated  $[\text{BO}_3]$ ,  $[\text{BO}_4]$  or  $[\text{B}_2\text{O}_5]$  groups and single or double B—O six-membered rings, respectively.

The  $d_0$  parameters of B—O bonds in hydrated borates without halogen anions and other anionic groups are calculated in Table 2. The  $\langle d_0 \rangle$  value of B—O bonds in all included 129 hydrated borates is 1.368 Å, which is slightly smaller than that for anhydrous cases (1.373 Å). The evolution of  $d_0$  values with the configuration of FBBs is clearly different from that of the anhydrous case, and the spread is also relatively small, which may be attributed to the modulation of hydrogen bonds (the corresponding histogram of  $d_0$  values is provided in Fig. 4).

If halogen anions (*i.e.*  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$ ) are regarded as the interstitial atoms in the borate crystallographic frame-



**Figure 4**

Bond-valence parameters  $d_0$  of B—O bonds of hydrated borates with various FBBs, which are built from the isolated  $[\text{B}\varphi_3]$  or  $[\text{B}\varphi_4]$  groups and single, double or treble B– $\varphi$  six-membered rings, respectively ( $\varphi = \text{O}^{2-}, \text{OH}^-$ ).

work, these anions compete with O atoms to coordinate to metal cations. Additionally, with respect to hydrated borates, they can also replace O atoms as the proton acceptors of hydrogen bonds. 82 borates with halogen anions are used in the calculation of  $d_0$  values (see Table 3). It is interesting to note that there are no hydrated borates containing Br or I anions; furthermore, anhydrous borates containing F anions are only built from three-coordinated borate groups. The  $\langle d_0 \rangle$  value of anhydrous borates with Br anions is the minimum (1.364 Å). However, the large range of individual  $d_0$  values should be noted here.

**Table 3**  
Bond-valence parameters  $d_0$  of B—O bonds of 82 borates containing halogen anions.

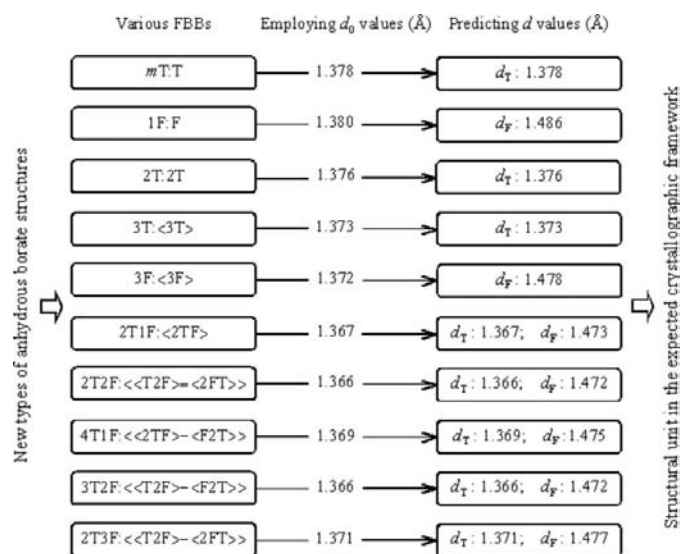
Halogen anion	$N$	CN	$n$	Range of $d_{ij}$	$\langle d_{ij} \rangle$ [su( $i$ )/s.u.]	Range of $d_0$	$\langle d_0 \rangle$ [su( $i$ )/s.u.]
Anhydrous borates							
F	14	3	22	1.276–1.496	1.383 [36/4]	1.361–1.471	1.382 [25/5]
Cl	23	3	32	1.187–1.767	1.377 [51/5]	1.359–1.387	1.372 [21/2]
		4	51	1.237–1.912	1.484 [79/6]	1.317–1.482	
Br	10	3	11	1.174–1.572	1.365 [61/11]	1.307–1.377	1.364 [14/2]
		4	33	1.304–1.736	1.476 [64/6]	1.330–1.384	
I	9	3	4	0.980–1.737	1.400 [186/54]	1.196–1.528	1.372 [48/9]
		4	27	1.298–1.791	1.485 [75/7]	1.302–1.439	
Hydrated borates							
F	7	3	7	1.371–1.401	1.376 [7/2]	1.373–1.389	1.374 [6/2]
		4	2	1.445–1.557	1.477 [40/14]	1.366–1.371	
Cl	19	3	75	1.135–1.589	1.369 [36/2]	1.310–1.426	1.367 [15/1]
		4	86	1.342–1.695	1.475 [38/2]	1.329–1.405	

**Table 4**  
Bond-valence parameters  $d_0$  of B—O bonds of 127 borates containing mixed polyanions ( $d_0$  values of P—O, C—O and Si—O bonds are also calculated in this table).

Anionic group†	$N$	CN	$n$	Range of $d_{ij}$	$\langle d_{ij} \rangle$ [su( $i$ )/s.u.]	Range of $d_0$	$\langle d_0 \rangle$ [su( $i$ )/s.u.]
$[\text{P}\phi_4]^{3-}$	58	3	9	1.281–1.411	1.365 [36/7]	1.281–1.411	1.367 [17/2]
		4	61	1.410–1.601	1.474 [26/2]	1.343–1.417	
		4(P)‡	96	1.348–1.760	1.534 [33/2]	1.548–1.678	1.615 [12/1]
$[\text{C}\phi_3]^{2-}$	7	3	4	1.250–1.428	1.371 [45/13]	1.319–1.394	1.371 [23/8]
		4	4	1.397–1.520	1.480 [29/7]	1.363–1.377	
		3(C)‡	6	1.250–1.389	1.302 [45/11]	1.373–1.478	1.407 [39/16]
$[\text{Si}\phi_4]^{4-}$	62	3	32	1.324–1.475	1.373 [19/2]	1.360–1.385	1.374 [11/1]
		4	49	1.233–1.821	1.484 [51/4]	1.330–1.405	
		4(Si)‡	103	1.398–1.685	1.622 [28/1]	1.531–1.657	1.622 [15/1]

Subsequently, the influence of other anionic groups on the  $d_0$  parameters of B—O bonds is examined *via* a survey of crystallographic data of 58 phosphate-, seven carbonate- and 62 silicate-borates, as shown in Table 4. The formation of these structures can be described as a substitution process, in which the original four-coordinated or three-coordinated B atoms are replaced by four-coordinated P/Si or three-coordinated C atoms. The  $\langle d_0 \rangle$  values of B—O bonds in phosphate- and silicate-borates are 1.367 and 1.374 Å, respectively, whereas the value of 1.371 Å in carbonate-borates is almost identical to that given by Brown & Altermatt (1985). However, the large range of individual  $d_0$  values should also be noted here. Meanwhile, the bond-valence parameters of P—O, C—O and Si—O bonds for borate compounds containing mixed polyanions are also calculated in Table 4, and are 1.615, 1.407 and 1.622 Å, respectively.

From the above statistical calculation, the conclusion can be reached that the discrepancy in the  $d_0$  parameters of B—O bonds is a result of a combination of many factors, including the detailed configurations of borate anions, anhydrous or hydrous, the interstitial halogen anions, and the substitution of other anionic groups like  $[\text{PO}_4]^{3-}$ ,  $[\text{CO}_3]^{2-}$  or  $[\text{SiO}_4]^{4-}$ . As  $d_0$  is related to  $V_i$  of a given atom by equations (1) and (2), a slight difference in  $d_0$  may lead to a large change in  $V_i$  owing to the exponential relation involved. Consequently, these recommended  $d_0$  data are useful, not only for the structural verification of the available crystallographic data concerning



**Figure 5**  
Employing the current  $d_0$  values of B—O bonds to design new types of anhydrous borate structures ( $d$ : the predicted or designed bond length of B—O bonds; subscripts T: three-coordinated boron group  $[\text{BO}_3]$ ; subscripts F: four-coordinated boron group  $[\text{BO}_4]$ ).

the detailed microscopic configurations, but also for the structural design of new types of borates by employing the current  $d_0$  values in the expected crystallographic framework

on the basis of the BVS model (the normal procedure in this case is provided in Fig. 5).

From the chemical bond viewpoint, a complex crystal is regarded as a combination of all constituent chemical bonds (Xue & Zhang, 1998). As important tools for understanding the relationship between the crystal structure and properties, the BVS model and chemical bond method of complex crystals both effectively reflect the bonding behaviors of constituent bonds in a crystal depending on their bond lengths. The chemical bond method of complex crystals has been successfully applied to the studies of NLO responses of different borate crystals (Xue & Zhang, 1996, 1998; Xue, Betzler & Hesse, 2000, 2002; Xue, Betzler, Hesse & Lammers, 2000). In Fig. 6 the absolute values of the calculated largest NLO tensor coefficients  $d_{ij}^{\max}$  by the chemical bond method are plotted against the recommended bond-valence parameters  $d_0$  for the corresponding FBB configurations (tabulated data have been deposited<sup>1</sup>). A linear relationship can be observed with a correlation coefficient of 0.82, which shows that the relative magnitude of  $d_0$  values reflects well the NLO susceptibilities of borate crystals, although some deviations exist ( $d_{ij}$  tensors are calculated at different wavelength ranges). The borates built from the isolated  $[\text{BO}_3]$  groups exhibit larger NLO coefficients, corresponding to  $d_0 = 1.378 \text{ \AA}$ ; however, hydrated borates with FBB notated as  $4\text{T}1\text{F}:\langle 2\text{Tf}\rangle - \langle \text{F}2\text{T}\rangle$  or those containing Br ions have relatively smaller NLO coefficients, with  $d_0 = 1.364 \text{ \AA}$ . Therefore,  $d_0$  values for the unique configuration of FBBs may serve as a useful parameter for pre-investigating novel NLO borates.

In addition, boron as a central atom can also bond to other anions (such as N, S, P or F) besides O atoms to form polyanion groups in the borate crystallographic framework. Similarly, the  $d_0$  parameters of B–N, B–S, B–P and B–F bonds are statistically calculated using equation (3) via a survey of the borate compounds with only boron ions surrounded by one kind of ligand (*i.e.* N, S, P or F ligands), and are 1.482, 1.815, 1.920 and 1.289 Å, respectively (the detailed data are shown in Table 5). The current data agree well with the corresponding values of 1.47, 1.82, 1.88 and 1.31 Å provided by the extrapolation of Brese & O’Keeffe (1991).

## 5. Conclusions

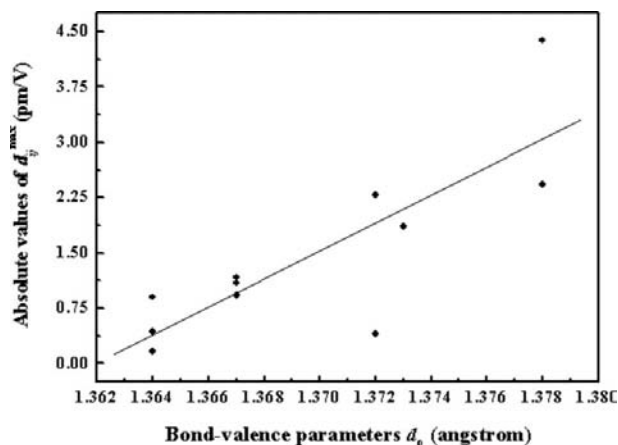
Taking ICSD (2004) as the data source, our present study calculates the  $d_0$  values of B–O bonds in the 758 investigated borates with crystallographic  $R$  factors of less than 0.1. The structural statistics of anhydrous borates show that borate polyanions with low complexity, particularly with less than six B–O polyhedra, exist dominantly in the crystal structure.

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5028). Services for accessing these data are described at the back of the journal.

**Table 5**

Bond-valence parameters  $d_0$  of B– $R$  ( $R = \text{N, S, P, F}$ ) bonds, where  $R$  anions replace O atoms to coordinate with B atoms.

Bond type	$N$	CN	$n$	Range of $d_{ij}$	$\langle d_{ij} \rangle$ [su(i)/s.u.]	Range of $d_0$	$\langle d_0 \rangle$ [su(i)/s.u.]
B–N	29	2	32	1.287–1.383	1.339 [17/2]	1.467–1.516	1.482 [14/2]
		3	19	1.402–1.545	1.471 [27/4]	1.448–1.490	
B–S	36	3	30	1.742–1.860	1.815 [26/3]	1.786–1.841	1.815 [12/1]
		4	61	1.829–2.005	1.922 [28/2]	1.795–1.838	
B–P	5	2	6	1.768–1.773	1.770 [2/1]	1.917–1.923	1.920 [2/1]
B–F	18	4	24	1.242–1.529	1.396 [51/5]	1.212–1.384	1.289 [46/9]



**Figure 6**

Absolute values of the calculated largest NLO tensor coefficients  $d_{ij}^{\max}$  of the selected borate crystals are plotted against the recommended bond-valence parameters  $d_0$  for the corresponding configuration of borate FBBs (tabulated data have been deposited<sup>1</sup>).

Except for isolated borate polyhedra, B–O six-membered rings prefer to form if there are three or more crystallographically independent B atoms existing in borate crystals. The discrepancy of the  $d_0$  values should not be ignored when investigating the microscopic structures of borate crystals, which reflects the chemical bonding behaviors of central cations. By considering the factors that influence the  $d_0$  parameters, including the detailed configurations of borate FBBs (such as the formation of rings, the ratio of  $[\text{BO}_3]$  and  $[\text{BO}_4]$  groups in the ring, and the number of borate polyhedra shared by two rings), anhydrous or hydrous, the interstitial halogen anions and the substitution of borate anions, we find more precise  $d_0$  data for various kinds of FBBs. Owing to the fact that NLO properties of borates are strongly related to the structural characteristics of borate polyanions, the linear relationship between the  $d_0$  parameter of various FBBs and the largest NLO tensor coefficient of different borates (calculated by the chemical bond method) clearly shows that  $d_0$  values for the unique configuration of FBBs may serve as a useful parameter for pre-investigating the NLO properties of borates. Therefore, the current research is useful for structurally designing novel borates with good NLO responses on the basis of the BVS model. In order to achieve large optical susceptibilities, it would be advantageous to concentrate on crystallographic frameworks containing  $[\text{BO}_3]$  infrastructures with the parameter  $d_0$  around 1.378 Å in highly asymmetric unit cells.

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