

Crystal chemical information to be obtained from the bond-number equality concept

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Based on the bond-number equality concept an equation is derived for anion complexes of normal valence compounds with triangularly and/or tetrahedrally coordinated central atoms and anions having one, two, three and four bonds to central atoms: $\% \Delta = 4 - (n/m') \times [2 - \%A^{[1]} + \%A^{[3]} + 2 \times \%A^{[4]}]$. $\% \Delta$ is the ratio of the number of central atoms with triangular anion coordination to the sum of all central atoms in the anion complex. n/m' is the ratio of the number of all A anions to the number of all central atoms C' in the anion complex. $\%A^{[1]}$ is the ratio of the number of anions with **one** bond to a central atom to the sum of all anions in the anion complex. $\%A^{[3]}$ and $\%A^{[4]}$ are defined accordingly. The equation can be used to formulate the possible crystal chemical formulae, which are characterized by partitions of central atoms and anions according to their bond numbers. Nitridosilicates and selected oxoborates are treated as examples of applications of the equation.

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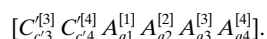
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1. Bond-number equality concept

The number of bonds which originate from all atoms of one kind and are directed towards the atoms of one other kind must be equal to the number of bonds which originate from all atoms of the one other kind and are directed towards the atoms of the first kind. This concept appears so trivial that only very few people have considered whether useful results could possibly be obtained from it.

We consider the general case of a normal valence compound $C_m C_{m'} A_n$ having an (charged) anion complex $[C_{m'} A_n]$, which consists of triangularly and tetrahedrally coordinated central atoms C' and of anions A with one, two, three and four bonds to central atoms.

An application of a crystal chemical formula is particularly apt for our case. The crystal chemical formula of the anion complex $[C_{m'} A_n]$ (with central atoms and anions partitioned according to their bond numbers) can be written as



The terminology and its expression as a formula adhere to the recommendations in a report of an IUCr Subcommittee on the Nomenclature of Inorganic Structure Types (Lima-de-Faria *et al.*, 1990).

The ratio of the number of anions to the number of central atoms n/m' is given by (1).

$$n/m' = [(a1) + (a2) + (a3) + (a4)] / [(c'3) + (c'4)]. \quad (1)$$

The number of bonds originating from central atoms C' must be equal to the number of bonds originating from anions A . Thus,

$$3 \times (c'3) + 4 \times (c'4) = 1 \times (a1) + 2 \times (a2) + 3 \times (a3) + 4 \times (a4). \quad (2)$$

We replace $(c'4)$ with $m' - (c'3)$ and further divide (2) by $m' = (c'3) + (c'4)$. The ratio of the number of triangles to the total number of triangles and tetrahedra in the anion complex $(c'3)/[(c'3) + (c'4)]$ will be denoted by the symbol $\% \Delta$ and in this text we use as a short label 'the fraction of triangularly coordinated central atoms'.

$$4 - \% \Delta = (1/m') \times [1 \times (a1) + 2 \times (a2) + 3 \times (a3) + 4 \times (a4)]. \quad (3)$$

We multiply the denominator and numerator on the right-hand side by $n = (a1) + (a2) + (a3) + (a4)$. The ratio $(a1)/[(a1) + (a2) + (a3) + (a4)]$ is the ratio of the number of anions with **one** bond to a central atom to the sum of all anions in the anion complex, which will be denoted by the symbol $\%A^{[1]}$. In this text we use as a short label 'the fraction of anions with one bond to a central atom'. The meaning of the symbols and

n/m'		$[\text{Si}^{[4]}_3\text{N}^{[3]}_4]^{\pm 0}$	$\%N^{[1]}$	$\%N^{[2]}$	$\%N^{[3]}$	$\%N^{[4]}$
1.333	- Si_3N_4	alpha & beta ICSD 79797 & 79798			1	
1.429	$\text{BaSi}_7\text{N}_{10}$	$[\text{Si}^{[4]}_7\text{N}^{[2]}_2\text{N}^{[3]}_8]^{2-}$ ICSD 405772		2/10	8/10	
1.5	LiSi_2N_3	$[\text{Si}^{[4]}_2\text{N}^{[2]}_2\text{N}^{[3]}_1]^{1-}$ ICSD 89524		1/3	2/3	
1.6	$\text{Ca}_2\text{Si}_5\text{N}_8$	$[\text{Si}^{[4]}_5\text{N}^{[2]}_4\text{N}^{[3]}_4]^{4-}$ ICSD 79070		4/8	4/8	
1.667	$\text{Ce}^{3+}\text{Si}_3\text{N}_5$	$[\text{Si}^{[4]}_3\text{N}^{[2]}_3\text{N}^{[3]}_2]^{3-}$ ICSD 402910		3/5	2/5	
1.75	$\text{SrYb}^{3+}\text{Si}_4\text{N}_7$	$[\text{Si}^{[4]}_4\text{N}^{[2]}_6\text{N}^{[4]}_1]^{5-}$ ICSD 405625		6/7		1/7
1.833	$\text{Pr}_3\text{Si}_6\text{N}_{11}$	$[\text{Si}^{[4]}_6\text{N}^{[2]}_9\text{N}^{[3]}_2]^{9-}$ ICSD 402178		9/11	2/11	
2	BeSiN_2	$[\text{Si}^{[4]}_1\text{N}^{[2]}_2]^{2-}$ ICSD 44112		1		
2.091	$\text{Ba}_2\text{Nd}_7\text{Si}_{11}\text{N}_{23}$	$[\text{Si}^{[4]}_{11}\text{N}^{[1]}_2\text{N}^{[2]}_{21}]^{25-}$ ICSD 407202	2/23	21/23		
3	$\text{Ba}_5\text{Si}_2\text{N}_6$	$[\text{Si}^{[4]}_2\text{N}^{[1]}_4\text{N}^{[2]}_2]^{10-}$ ICSD 81570	4/6	2/6		

Figure 1
Examples of nitridosilicates with $\% \Delta = 0$, their different N anion fractions and crystal chemical formulae of the anion complexes.

short labels for the other anions are analogous to those for $\%A^{[1]}$.

$$4 - \% \Delta = (n/m') \times [1 \times \%A^{[1]} + 2 \times \%A^{[2]} + 3 \times \%A^{[3]} + 4 \times \%A^{[4]}]. \quad (4)$$

Observing that $\%A^{[2]} = 1 - (\%A^{[1]} + \%A^{[3]} + \%A^{[4]})$, $\%A^{[2]}$ can be eliminated and (5) obtained where all five parameters are ratios of integers

$$\% \Delta = 4 - (n/m') \times [2 - \%A^{[1]} + \%A^{[3]} + 2 \times \%A^{[4]}], \quad (5)$$

$\% \Delta$: Ratio of the number of central atoms with triangular coordination to the sum of all central atoms.

n/m' : ratio of the number of all anions A to the number of all central atoms C' in the anion complex.

$\%A^{[1]}$ ($\%A^{[3]}$, $\%A^{[4]}$): ratio of the number of anions with one bond to a central atom (three or four bonds to central atoms, respectively) to the sum of all anions in the anion complex.

2. Application to nitridosilicates

In nitridosilicates the Si atoms are always tetrahedrally coordinated. This means that $\% \Delta = 0$. The equation to be used here is (6). Note that $\%N^{[1]} + \%N^{[2]} + \%N^{[3]} + \%N^{[4]} = 1$.

$$4 = (n/m') \times [2 - \%N^{[1]} + \%N^{[3]} + 2 \times \%N^{[4]}]. \quad (6)$$

Fig. 1 lists 11 examples of different nitridosilicates, which have been studied mostly by Schnick & Huppertz (1997). These authors presented a formula for nitridosilicates to calculate the ratios of differently bonded N anions, however, only $N^{[2]}$ and $N^{[3]}$ anions were taken into consideration, which is not sufficient for all nitridosilicates. Equation (6) applies to all kinds of nitridosilicates. The two Si_3N_4 modifications can be regarded as the binary basis of the nitridosilicates without cations. The crystal chemical formulae of the anion complexes in Fig. 1 correspond – with one exception – to the most uniform solutions of (6). This means that either only one kind of N anion occurs or, if there are two kinds, then the numerals within the superscripted square brackets of the two N anion fractions differ by not more than one. An exception occurs with $\text{SrYb}^{3+}\text{Si}_4\text{N}_7$. Instead of the simple crystal chemical formula $[\text{Si}_4^{[4]}\text{N}_5^{[2]}\text{N}_2^{[3]}]^{5-}$ with $\%N^{[3]} = 2/7$ and $\%N^{[4]} = 0$, one observes here an anion complex with the formula $[\text{Si}_4^{[4]}\text{N}_6^{[2]}\text{N}^{[4]}]^{5-}$ where $\%N^{[3]} = 0$ and $\%N^{[4]} = 1/7$ [which is also in agreement with (6), but does not represent an uniform solution]. Other exceptions, also in agreement with (6), occur with oxonitridosilicates or oxonitridoalumosilicates, such as $\text{Er}_6(\text{Si}_{11}\text{N}_{20})\text{O}$ (Woike & Jeitschko, 1997) or

$\text{Nd}_7(\text{Si}_8\text{Al}_3\text{N}_{20})\text{O}$ (Köllisch *et al.*, 2001), where all four kinds, *i.e.* $N^{[1]}$, $N^{[2]}$, $N^{[3]}$ and $N^{[4]}$ anions, are found in the anion complexes.

The ICSD (Inorganic Crystal Structure Database, Version 1.3.3) collection codes in Figs. 1 and 2 serve to quickly find the complete literature references, the complete crystal structure data and, depending on the database, a list of all the interatomic distances. The latter is needed to verify the statements made in Fig. 1 regarding the different N anion fractions and in Fig. 2 regarding the ratio of triangles-to-tetrahedra in the oxoborates.

3. Application to oxoborates

In the case of oxoborate structures the B atoms can be triangularly and/or tetrahedrally coordinated by O atoms, thus $\% \Delta$ can vary from 0 (tetrahedra only) to 1 (triangles only). For convenience, one divides the $\%O^{[1]}$ fraction into two parts, *i.e.* the fraction of endstanding (terminal) $\%O^T$ anions and the fraction $\%OH$, which corresponds to O atoms which form part of an OH group bound to one B atom. The parameter $\%OH$ can in general be read directly from the chemical formula of the borate. The equation to be used for borates is (7), which has recently been derived by a completely different route without any relation to the bond-number equality concept (Parthé, 2005).

$$\% \Delta = 4 - (n/m') \times [2 - \%O^T - \%OH + \%O^{[3]} + 2 \times \%O^{[4]}] \quad (7)$$

For borate structures the ratio of triangles to tetrahedra $[= \% \Delta / (1 - \% \Delta)]$ is generally used as the first classification parameter. Since the borates (and also borophosphates) have recently been treated in detail in this way (Parthé, 2002, 2004, 2005) we restrict ourselves to the presentation of two examples:

(i) Determination of the triangle-to-tetrahedron ratio of anhydrous borates with $1.5 \leq n/m' \leq 2$, where all O atoms are shared by two B atoms, thus $\%O^{[2]} = 1$.

For these oxoborates, where $\%O^T$, $\%OH$, $\%O^{[3]}$ and $\%O^{[4]}$ all have the value zero, (7) takes on the special form of (8).

$$\% \Delta = 4 - 2 \times (n/m') \quad (8)$$

The fraction of triangles in the anion complex is determined alone by the anion-to-central atom ratio n/m' . Fig. 2, which is an updated version of a previously published table (Parthé, 2005), presents 14 anhydrous borate structures with different n/m' values

n/m'	$\% \Delta$		n/m'	$\% \Delta$	
1.5	1	- B_2O_3 trigonal $[B^{[3]}_2O^{[2]}_3]^{\pm 0}$ ICSD 51575	1.7	$3/5$	$K_2Cs_2B_{10}O_{17}$ $[B^{[3]}_6B^{[4]}_4O^{[2]}_{17}]^{4-}$ ICSD 81478
1.556	$8/9$	CsB_9O_{14} $[B^{[3]}_8B^{[4]}O^{[2]}_{14}]^{1-}$ ICSD 97512	1.714	$4/7$	$Li_3B_7O_{12}$ $[B^{[3]}_4B^{[4]}_3O^{[2]}_{12}]^{3-}$ ICSD 68475
1.6	$4/5$	CsB_5O_8 $[B^{[3]}_4B^{[4]}O^{[2]}_8]^{1-}$ ICSD 93837	1.731	$7/13$	$Na_{12}B_{26}O_{45}$ $[B^{[3]}_{14}B^{[4]}_{12}O^{[2]}_{45}]^{12-}$ Penin <i>et al.</i> , 2005
1.615	$10/13$	$Cs_3B_{13}O_{21}$ $[B^{[3]}_{10}B^{[4]}_3O^{[2]}_{21}]^{3-}$ ICSD 95728	1.75	$1/2$	$K_2B_4O_7$ $[B^{[3]}_2B^{[4]}_2O^{[2]}_7]^{2-}$ ICSD 2833
1.625	$3/4$	$Na_2B_8O_{13}$ $[B^{[3]}_6B^{[4]}_2O^{[2]}_{13}]^{2-}$ ICSD 14355	1.8	$2/5$	$Ca_2BrB_5O_9$ $[B^{[3]}_2B^{[4]}_3O^{[2]}_9]^{3-}$ ICSD 18001
1.632	$14/19$	$K_5B_{19}O_{31}$ $[B^{[3]}_{14}B^{[4]}_5O^{[2]}_{31}]^{5-}$ ICSD 2131	1.833	$1/3$	$Ca_2B_6O_{11}$ $[B^{[3]}_2B^{[4]}_4O^{[2]}_{11}]^{4-}$ ICSD 23032
1.667	$2/3$	CsB_3O_5 $[B^{[3]}_2B^{[4]}O^{[2]}_5]^{1-}$ ICSD 93837	2	0	$Pd^{2+}B_2O_4$ $[B^{[4]}_2O^{[2]}_4]^{2-}$ ICSD 32539

Figure 2

Different examples of anhydrous borates, where all O atoms are $O^{[2]}$ atoms, the calculated $\% \Delta$ values and the observed crystal chemical formulae of the anion complexes.

where the numerical values of the observed fractions of triangularly coordinated B atoms can be calculated correctly with (8). For the rare exceptions where O^T or $O^{[3]}$ anions occur and where (7) must be applied, see Parthé (2005).

(ii) Determination of a possible crystal chemical formula for $Pb_6B_{11}O_{18}(OH)_9$.

From the $Pb_6B_{11}O_{18}(OH)_9$ formula given the numerical values of two parameters can be derived directly: $n/m' = 27/11$ and $\%OH = 9/27$. Of the borates synthesized under ambient pressure conditions, only a small number is known where the anion complex contains $O^{[3]}$ and/or $O^{[4]}$ anions [e.g. SrB_4O_7 ; Perloff & Block, 1966; or $Tb(BO_2)_3$; Nikelski & Schleid, 2003]. Based on the assumption that $O^{[3]}$ and $O^{[4]}$ anions do not occur in $Pb_6B_{11}O_{18}(OH)_9$, two possible limiting crystal chemical formulae can be derived, *i.e.* one where the anion complex is constructed of linked BO_3 triangles only ($\% \Delta = 1$) and the second where the anion complex is constructed of linked BO_4 tetrahedra only ($\% \Delta = 0$).

For $\% \Delta = 1$, from (7), $\%O^T = 12/27$. Thus, $[B^{[3]}_{11}O^{[2]}_6O^{[2]}_{12}(OH)_9]^{12-}$.

For $\% \Delta = 0$, from (7), $\%O^T = 1/27$. Thus, $[B^{[4]}_{11}O^{[2]}_{17}O^T(OH)_9]^{12-}$.

In the IR spectrum of $Pb_6B_{11}O_{18}(OH)_9$, reported by Yu *et al.* (2002), one finds a BO_3 peak and a BO_4 peak. Thus, the real value of $\%O^T$ must be between $1/27$ and $12/27$. Since the BO_3 peak is less than half as large as the BO_4 peak, a good assumption is that of the 11 B atoms in one formula unit, three are triangularly and eight tetrahedrally coordinated. With $\% \Delta = 3/11$, it follows from (7) that $\%O^T = 4/27$. We conclude that a possible crystal chemical formula of the anion complex might be $[B^{[3]}_3B^{[4]}_8O^{[2]}_{14}O^T_4(OH)_9]^{12-}$, which agrees with the results of the single-crystal structure determination of $Pb_6B_{11}O_{18}(OH)_9$ by the same Chinese authors (Yu *et al.*, 2002). However, the crystal chemical formula is merely a general template for a set a potential structures of which the observed one is just one. Such structures might differ both in the connectivity of the groups making up the anion complex, as well as in its overall dimensionality. This is a limitation of the method.

In conclusion, the equation, which was derived from the bond-number equality concept, is easy to apply. It can be of help to formulate the possible crystal chemical formulae for the anion complexes of new compounds.

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