Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Accurate bond-valence parameters for the Bi^{3+}/Br^- ion pair

Vasyl Sidey

Department of Chemistry and Research Institute for Physics and Chemistry of Solids, Uzhgorod National University, Pidgirna Street 46, Uzhgorod 88000, Ukraine

Correspondence e-mail: vasylsidey@yahoo.com

Received 28 February 2006
Accepted 30 May 2006

Using a new calculation scheme, reliable and physically meaningful values of the bond-valence parameters (r_0 = 2.567 Å and b = 0.421 Å) have been deduced for the Bi^{3+}/Br^- ion pair from the molecular geometry and from the crystal structure of $BiBr_3$.

The bond-valence model (BVM) has recently found wide use in mineralogy and structural inorganic chemistry as a valuable tool for detecting errors in crystal structure determination and for predicting interatomic distances in crystal structures of known chemical composition and presupposed topology (Brown, 2002).

Bond valence (BV), s, is defined as the classical valence shared with each bond. According to the bond-valence sum rule, the oxidation state V_i can be calculated from the sum of the individual bond valences s_{ij}

$$V_i = \sum_j s_{ij}, \tag{1}$$

where i denotes an atom bonded to j. Atom i is usually chosen as an electropositive atom (cation) and atom j as an electronegative atom (anion).

Individual bond valences s_{ij} (in 'valence units', v.u.) can be calculated from the observed bond lengths r_{ij} using the Brown–Altermatt formula

$$s_{ij} = \exp\left[\left(r_0 - r_{ij}\right)/b\right], \tag{2}$$

where r_0 and b are empirically determined parameters (Brown & Altermatt, 1985).

The b parameter is commonly taken to be the 'universal constant', equal to 0.37 Å, and the r_0 parameters have been directly calculated (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) or extrapolated (Brese & O'Keeffe, 1991) for a large number of ion (atom) pairs, assuming b = 0.37 Å.

Current research interests of the author required highly accurate BV parameters for the Bi^{3+}/Br^- ion pair. However, the directly calculated BV parameters were not reported for these ions, and the accuracy of the extrapolated BV parameters r_0 = 2.62 Å and b = 0.37 Å (Brese & O'Keeffe, 1991) has been found to be rather poor. Taking all the aforementioned facts into account, the author decided to derive improved BV parameters for the Bi^{3+}/Br^- ion pair.

The traditional procedure of determining the empirical BV parameters from the structural data (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) includes the following steps:

(i) Collecting the structural data of interest from the literature and/or from the crystal structure databases (molecular structures are not usually considered).

(ii) Selecting the most reliable dataset of bond lengths for a given ion pair.

(iii) Solving the equation $V_i = \sum_j s_{ij}$ using the formula

$$r_0 = b \ln\left[V_i / \sum_j \exp\left(-r_{ij}/b\right)\right] \tag{3}$$

(where b is a constant) for every selected coordination sphere of a given ion pair.

doi:10.1107/S0108768106020295

Table 1
Reliability of the BV parameters obtained for the Bi^{3+}/Br^- ion pair by different procedures.

		Bond-valence sum (v.u.)†		
Compound‡	Polyhedron	B/O'K	*S*1	*S*2
$BiBr_3$ (molecule)	$BiBr_3$	3.46 (+15%)	3.253 (+8%)	3.000
$K_4(Bi_2Br_{10})(H_2O)_4$	$[BiBr_6]$	3.17 (+6%)	2.984 (−1%)	3.014 (+0%)
$Cs_3Bi_2Br_9$	$[BiBr_6]$	3.49 (+16%)	3.261 (+9%)	3.253 (+8%)
Rb_3BiBr_6	$[BiBr_6]$	3.20 (+7%)	3.016 (+1%)	3.052 (+2%)
	$[BiBr_6]'$	3.29 (+10%)	3.078 (+3%)	3.107 (+4%)
$Na_7(BiBr_6)(Bi_2Br_{10})(H_2O)_{18}$	$[BiBr_6]$	3.17 (+6%)	2.981 (−1%)	3.021 (+1%)
	$[BiBr_6]'$	3.18 (+6%)	2.998 (−0%)	3.016 (+1%)
$[Sr(H_2O)_8]_2(Bi_2Br_{10})$	$[BiBr_6]$	3.24 (+8%)	3.054 (+2%)	3.067 (+2%)
$[Hg_7(HgBr)_2As_4](Bi_2Br_{10})$	$[BiBr_6]$	3.27 (+9%)	3.062 (+2%)	3.059 (+2%)
	$[BiBr_6]'$	3.07 (+2%)	2.884 (−4%)	2.932 (−2%)
$(NH_4)_6(BiBr_6)Br(HF_2)_2$	$[BiBr_6]$	3.14 (+5%)	2.924 (−3%)	2.970 (−1%)
$Te_4(Bi_2Br_8)$	$[BiBr_6]$	3.30 (+10%)	3.104 (+3%)	3.093 (+3%)
$(Hg_6Sb_4)(BiBr_6)Br$	$[BiBr_6]$	3.14 (+5%)	2.940 (−2%)	2.984 (−1%)
$(Bi_2Br_4)(AlBr_4)_2$	$[BiBr_7]$	3.13 (+4%)	2.927 (−2%)	2.930 (−2%)
α-$BiBr_3$	$[BiBr_8]$	3.20 (+7%)	3.022 (+1%)	3.000
$(BiBr_2)(AuBr_4)$	$[BiBr_8]$	3.17 (+6%)	2.966 (−1%)	3.050 (+2%)
	$[BiBr_8]'$	3.00 (−0%)	2.810 (−6%)	2.946 (−2%)

† B/O'K: $r_0 = 2.62$ Å and $b = 0.37$ Å, extrapolated by Brese & O'Keeffe (1991). *S*1: $r_0 = 2.597$ Å and $b = 0.37$ Å, directly calculated in accordance with the traditional procedure (this work). *S*2: $r_0 = 2.567$ Å and $b = 0.421$ Å, deduced from the molecular and crystal structure of the $BiBr_3$ compound (this work). The precision of the interatomic distances used for calculations of the BVSs was ±0.001 Å for *S*1 and *S*2, and ±0.01 Å for B/O'K. Calculations of the BVSs were performed using the program *VALENCE* (Brown, 1996). ‡ The references for the compounds are: $BiBr_3$ (molecule), Schultz *et al.* (1999); $K_4(Bi_2Br_{10})(H_2O)_4$, Lazarini (1977*a*); $Cs_3Bi_2Br_9$, Lazarini (1977*b*); Rb_3BiBr_6, Lazarini (1978); $Na_7(BiBr_6)(Bi_2Br_{10})(H_2O)_{18}$, Lazarini (1980); $[Sr(H_2O)_8]_2(Bi_2Br_{10})$, Lazarini & Leban (1980); $[Hg_7(HgBr)_2As_4](Bi_2Br_{10})$, Puff *et al.* (1984); $(NH_4)_6(BiBr_6)Br(HF_2)_2$, Gerasimenko *et al.* (1991); $Te_4(Bi_2Br_8)$, Beck *et al.* (1997); $(Hg_6Sb_4)(BiBr_6)Br$, Beck *et al.* (2000); $(Bi_2Br_4)(AlBr_4)_2$, Beck *et al.* (2005); α-$BiBr_3$, von Benda (1980); $(BiBr_2)(AuBr_4)$, Beck & Wagner (1997).

(iv) Averaging the r_0 values calculated for a given ion pair.

In accordance with the above procedure, and taking into account the limitations of the BVM (Brown, 2002), 12 well determined ($R \leq 10\%$) crystal structures (with 16 independent $[BiBr_n]$ coordination spheres) investigated under ambient conditions were selected for the calculations. The references for all these crystal structures are collected in Table 1. The crystal structures with disorder, with partial occupancy, and with strong steric effects caused by the presence of large complex 'pseudoatoms' [such as CH_3NH_3, $C(NH_2)_3$ *etc.*] were not considered. All the $[BiBr_n]$ coordination spheres were analyzed by means of the program *PLATON* (Spek, 2004).

Taking the 'universal constant', $b = 0.37$ Å, an average value of $r_0 = 2.597$ Å (with $\sigma = 0.012$ Å) has been obtained by the author. However, analysis of the above traditional procedure of direct determining the BV parameters revealed at least *two* serious deficiencies: ignoring the physical meaning of the r_0 parameter and considering the V_i value in (3) as a constant.

By definition, the r_0 parameter is equal to the length of a bond of unit valence. The *exact* (actually, close to exact) r_0 values can be directly observed in high-symmetry simple covalent molecules, or can be deduced from the correctly determined 'bond length *versus* bond valence' curves. In all cases, however, the r_0 value is an absolutely *independent* parameter for a given ion pair: if $r_{ij} = r_0$, then $s_{ij} = 1$ for *any* non-zero value of the b parameter. Nevertheless, critical dependence of the r_0 value on the preset b value is clear from (3) and was indirectly confirmed in the article of Brown & Altermatt (1985). Hence, if the b parameter is set incorrectly for a given ion pair, the obtained r_0 parameter loses its physical meaning and becomes purely artificial.

Furthermore, most crystal structures are influenced by steric and/or electronic constraints so that the bond-valence sums (BVSs) calculated from the observed interatomic distances are not exactly equal to the oxidation state of the central ions. For a given coordination sphere, however, (3) can be derived from a series of equations (2) only with the assumption that V_i = BVS. Hence, the correct r_0 value can be obtained from (3) only if the b value is set correctly *and* if V_i = BVS.

For determining the BV parameters, deviation of the BVSs from V_i seems to be less significant than incorrect setting of the b value because averaging can compensate for deviations of the BVSs in the particular structures. If, however, the number of crystal structures reported for a given ion pair is rather small (as for the Bi^{3+}/Br^- ion pair), poor and biased results caused by this deviation can be obtained even for the correct b parameter. In this case the use of alternate calculation schemes for determining the BV parameters should be considered.

The particular problem of determining reliable and physically meaningful BV parameters for the Bi^{3+}/Br^- ion pair has been solved using only two basic assumptions: (i) the term 'bond valence'/'bond order' is strictly considered as the *exact* fraction/number of Lewis electron pair(s) contributing to the bond; and (ii) for $BiBr_3$ the bond-valence sum rule (Brown, 2002) is fulfilled *exactly* (V_i = BVS = 3).

Based on the chemistry of halogens, it can easily be assumed that in the $BiBr_3$ molecule the *exact* number of Lewis electron pairs associated with each Bi—Br bond is 1; and, therefore, the Bi—Br bond length of 2.567 Å reported for this molecule by Schultz *et al.* (1999) is equal to the *correct* (actually, to the best available) value of the r_0 parameter for the Bi^{3+}/Br^- ion pair. The same assumption can also be made from the Gillespie–Nyholm theory (Gillespie & Nyholm, 1957): the pyramidal shape of the $BiBr_3$ molecule clearly indicates that the $6s^2$ lone pair of the Bi atom is located *separately* and not involved in the chemical bonding.

On the other hand, in the crystal structure of α-$BiBr_3$ (Benda, 1980) all the valence electrons are shared exclusively between the Bi^{3+} and Br^- ions and are not influenced by the additional ('third party') ions. Since α-$BiBr_3$ is stoichiometric, it can be concluded that the *exact* number of Lewis electron pairs used by the Bi^{3+} ion for bonding in this structure (in other words, BVS) is 3. The crystal structure of β-$BiBr_3$ was determined poorly (Benda, 1980) and cannot be regarded as the reference structure.

Taking $r_0 = 2.567$ Å, the b parameter has been adjusted to give BVS = 3 for the Bi^{3+} ions in the crystal structure of α-$BiBr_3$. The value of the b parameter determined in this way for the Bi^{3+}/Br^- ion pair is 0.421 Å.

The reliability of the BV parameters obtained for the Bi^{3+}/Br^- ion pair by different procedures is illustrated in Table 1. The BV parameters deduced from the molecular and crystal structure of $BiBr_3$ (*S*2) demonstrate the highest reliability: the BVSs calculated for the $BiBr_3$ molecule and for the crystal structures are equal or close to 3. The BV parameters calculated in this work by using the traditional procedure (*S*1) show reasonable performance for the crystal structures, but erroneously indicate significant 'overbonding' for the $BiBr_3$ molecule. Use of the BV parameters extrapolated by Brese & O'Keeffe (1991) for the Bi^{3+}/Br^- ion pair (B/O'K) should definitely be avoided.

Both sets of BV parameters determined in this work ($S1$ and $S2$) can be recommended for routine BVS calculations. However, in theoretical BVM studies, use of the $S2$ parameters should be preferred because these parameters are based on the physically measured r_0 value.

It is important to note that the $S2$ parameters show good results for the *whole* range of the coordination numbers observed for the Bi^{3+}/Br^{-} ion pair (see Table 1) and, therefore, give the best approximation of the *real* 'bond length *versus* bond valence' curve for these ions. Nevertheless, the author believes that the $S2$ parameters can still be improved using structural data of better accuracy.

The calculation scheme as well as assumptions used in the present work for determining the BV parameters for the Bi^{3+}/Br^{-} ion pair cannot be regarded as universal, but use of this scheme in BVM studies should always be attempted if the traditional BV parameters supposedly fail.

References

Beck, J., Hedderich, S. & Neisel, U. (2000). *J. Solid State Chem.* **154**, 350–355.

Beck, J., Hengstmann, M. & Schlüter, S. (2005). *Z. Kristallogr.* **220**, 147–151.

Beck, J., Kasper, M. & Stankowski, A. (1997). *Chem. Ber./Recueil*, **130**, 1189–1192.

Beck, J. & Wagner, S. (1997). *Z. Anorg. Allg. Chem.* **623**, 1810–1814.

Benda, H. von (1980). *Z. Kristallogr.* **151**, 271–285.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.

Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model.* IUCr Monograph on Crystallography 12. Oxford University Press.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Gerasimenko, A. V., Bukvetskii, B. V., Udovenko, A. A. & Davidovich, R. L. (1991). *Koord. Khim.* **17**, 322–324.

Gillespie, R. J. & Nyholm, R. S. (1957). *Q. Rev. Chem. Soc.* **11**, 339–380.

Lazarini, F. (1977*a*). *Acta Cryst.* B**33**, 1954–1956.

Lazarini, F. (1977*b*). *Acta Cryst.* B**33**, 2961–2964.

Lazarini, F. (1978). *Acta Cryst.* B**34**, 2288–2290.

Lazarini, F. (1980). *Acta Cryst.* B**36**, 2748–2750.

Lazarini, F. & Leban, I. (1980). *Acta Cryst.* B**36**, 2745–2747.

Puff, H., Grönke, M., Kilger, B. & Möltgen, P. (1984). *Z. Anorg. Allg. Chem.* **518**, 120–128.

Schultz, G., Kolonits, M. & Hargittai, M. (1999). *Struct. Chem.* **10**, 321–325.

Spek, A. L. (2004). *PLATON, A Multipurpose Crystallographic Tool.* Utrecht University, The Netherlands.