The Contribution To Bond Valences By Lone Electron Pairs

Xiqu Wang*
Department of Chemistry, University of Houston, Houston, TX 77204-5003, U.S.A.
Friedrich Liebau
Institut für Geowissenschaften, Universität zu Kiel, D-24106 Kiel, Germany.

ABSTRACT

Bond valence sums (BVS) calculated for lone-pair cations are found increasingly higher than their formal valences as the retraction of the lone electron pair (LEP) from the nucleus is more pronounced. The increase in BVS is interpreted as a continuous increase of an effective valence of an atom that is a measure of its actual ability to bind other atoms without changing its formal valence. How the LEP of a lone-pair cation affects the effective valence of other atoms in a structure is studied by bond valence calculations for specific structures. For structures rich in alkali cations, it is found that the high effective valence of the lone-pair cations tends to be balanced by low effective valence of alkali cations. The LEP transfers bonding power or effective valence from the alkali cations to the lone-pair cations by joining the coordination sphere of the alkali cations.

INTRODUCTION

The bond valence model that has a root in Pauling's electrostatic valence rule [1] is an empirical method widely and successfully used to describe and interpret crystal structures. The model was thoroughly reviewed in a recent monograph by Brown [2]. According to the bond valence model, an inorganic structure is considered an arrangement of atoms linked by bonds between atoms with opposite signs of valences. A bond valence is assigned to each bond so that the bond valence sum for all bonds around an atom equals the absolute value of the valence of the atom. By setting the atomic valence equal to the oxidation number or formal valence ${}^{for}V$, the following empirical relationship between bond valence and bond length is widely used:

$$S_{ij} = \exp\,[(r_0 - D_{ij}) / b] \qquad (1)$$

where D_{ij} is the length of the bond between atoms i and j, S_{ij} is the bond valence, and r_0 and b are empirical parameters derived from well-refined structures. b is taken as a constant equal to 0.37Å and normally independent of bond types, whereas r_0 is tabulated for every bond type (cation - anion pair). The tabulated r_0 value for an A–X bond type is derived by averaging individual r_{0i} values calculated for every available [AX_n] polyhedron according to

$$r_{0i} = b\ \{[\ \ln\,({}^{for}V\ /\ [\Sigma_j \exp\,(-\,D_{ij})\ /\ b)]\} \qquad (2)$$

where b = 0.37 Å [2-4]. For the majority of inorganic structures, bond valence sums (BVS) calculated by using equation (1) are satisfactorily close to the formal valences ${}^{for}V$ of the corresponding atoms. Large deviations can usually be attributed to chemical or steric reasons [2]. For example, if the hydrogen atom of a hydroxyl group OH^- in a structure is not located the calculated BVS for the O atom will be remarkably lower than the formal valence 2 v.u. If the ignored hydrogen atom is involved in an O-H…X hydrogen bond the calculated BVS for the X atom will also be lower than the formal valence. Systematic deviations of BVS from ${}^{for}V$ have been found previously for cations with non-bonding pairs of valence-shell electrons or, as popularly called, lone-pair cations [5,6]. Here we will discuss the influence of the lone electron pair (LEP) of lone-pair cations on other ions and how it may be interpreted in a comparable way as the above case of hydrogen bond.

PROCEDURE

Lone-pair cations such as Tl^{I}, Sn^{II}, Sb^{III} (the Roman numberals indicate the oxidation numbers) often show characteristically irregular coordination environments due to the stereoactivity of the LEP [7]. In order to measure the stereochemical influence of LEP, we defined, in a previous work [6], a vector

$$\boldsymbol{\Phi}_i = -\Sigma_j \phi_{ij} \qquad (3)$$

where ϕ_{ij} is directed from the lone-pair cation L_i to a ligand X_j and has a length $|\phi_{ij}| = \exp(-D_{ij}/g)$ with $g = 0.2$ Å (figure 1). The length of $\boldsymbol{\Phi}_i$ is considered a measure of the deviation of the spatial distribution of the LEP from spherical symmetry.

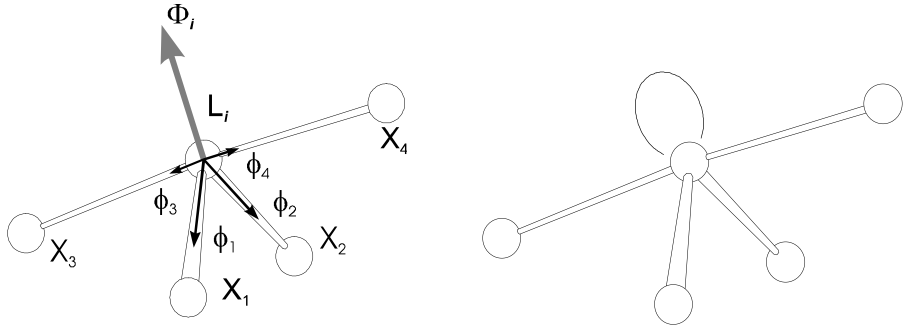

Figure 1. Schematic diagram showing the vector $\boldsymbol{\Phi}_i$ as a measure of the deviation of the LEP from spherical symmetry.

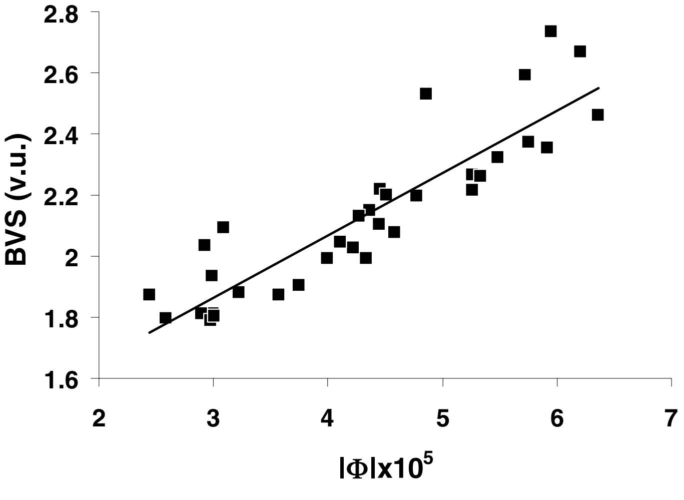

Figure 2. Correlation between $|\Phi|$ and BVS calculated for $[Sn^{II}O_n]$ polyhedra.

Structural data were analyzed for Sn^{II}-O bonds as an example. The data were taken from the 2004/1 release of the Inorganic Crystal Structure Database (ICSD) [8] with the criteria: 1) all Sn atoms are stoichiometrically divalent, 2) all anions are oxygen, 3) all atoms are ordered and all sites are fully occupied, 4) $R(F)$ value is less than 5.51%, 5) no warning comments indicating that atomic coordinates are incorrect, 6) the structure was determined from data measured under ambient temperature and pressure conditions. These criteria result in 20 structures with 34 $[SnO_n]$ coordination polyhedra in total. For each polyhedron the BVS and $|\Phi|$ values were calculated from the Sn-O bonds with bond lengths up to 3.0 Å by using the tabulated $r_0 = 1.984$ Å for Sn^{II}-O bonds [4]. As shown in figure 2, the calculated BVS values are strongly correlated with $|\Phi|$ (linear correlation coefficient $R^2 = 80.1\%$). Similar correlations are also observed for other bond types involving lone-pair cations [6], which will be discussed in a separate paper.

DISCUSSION

Figure 2 shows that the BVS values continuously increase as the retraction of the LEP from the nucleus is more pronounced which is indicated by increasingly higher $|\Phi|$ values. The increase in BVS is interpreted as a continuous increase of an effective valence of an atom that is a measure of its actual ability to bind other atoms without changing its formal valence. Therefore, different crystallographic sites of the same ion in a structure may have different effective valences that can be approximated by the BVS values. Despite the strong correlation, the majority of the polyhedra in figure 2 have BVS values within the range of 2 ± 0.3 v.u. or less than 15% deviation from the formal valence ${}^{for}V$ of Sn^{II}. However, the polyhedra with large $|\Phi_i|$ values have BVS values remarkably higher than ${}^{for}V$. These polyhedra belong to structures dominated by stannites rich in alkali cations. Inspection of the data for other lone-pair cations reveals similar situations. Table I lists representative oxosalt examples for such structures together with BVS values calculated using tabulated r_0 values [4].

Table I. Example structures with large deviations of BVS from ${}^{for}V$.

Structure	Cations	BVS (v.u.)	BVS– ${}^{for}V$ (v.u.)	(BVS– ${}^{for}V$)/ ${}^{for}V$	ICSD Code	Ref.
Na_3TlO_2	Tl(1)	1.98	0.98	98 %	202028	9
Na_4SnO_3	Sn(1)	2.73	0.73	37 %	49624	10
K_4SnO_3	Sn(1)	2.53	0.53	27 %	79101	11
Cs_4SnO_3	Sn(1) Sn(2)	2.62 2.59	0.62 0.59	31 % 30 %	408389	12
K_4PbO_3	Pb(1)	2.59	0.59	30 %	74874	13
K_2PbO_2	Pb(1) Pb(2)	2.56 2.56	0.56 0.56	28 % 28 %	2266	14
Na_3SbO_3	Sb(1)	3.72	0.72	24 %	23346	15
K_3SbO_3	Sb(1)	3.43	0.43	14 %	279579	16
Cs_3SbO_3	Sb(1)	3.39	0.39	13 %	279580	16
Na_3BiO_3	Bi(1)	3.31	0.31	10 %	23347	15
K_3BiO_3	Bi(1)	3.23	0.23	8 %	407293	17
Rb_3BiO_3	Bi(1)	3.32	0.32	11 %	407294	17
Cs_3BiO_3	Bi(1)	3.47	0.47	16 %	406563	18
K_2TeO_3	Te(1)	4.60	0.60	15 %	65640	19

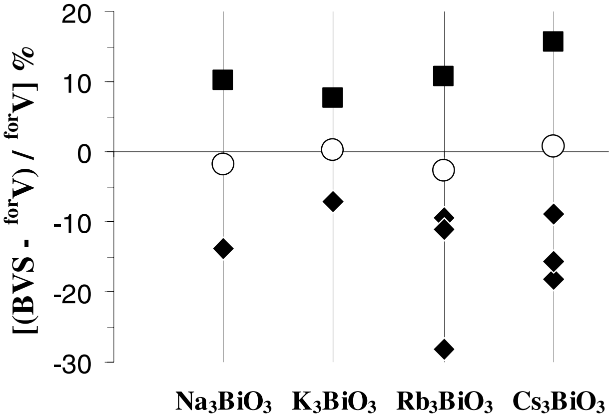

Figure 3. Deviations of BVS from ^{for}V in the A_3BiO_3 structures [15, 17-18]. Squares, circles and diamonds represent data for the Bi, O and alkali metal atoms, respectively.

Since the sum of BVS for all cations in a structure equals the sum of BVS for all the anions, deviations of the BVS from the formal valence of lone-pair cations must be compensated by corresponding deviations in other ions of the structure. Analysis of specific structures that are rich in large low-valent cations such as those listed in Table I (figure 3), shows that the positive deviations for lone-pair cations are mainly compensated by negative deviations in other cations. The lone-pair cations in these structures are almost exclusively coordinated by three anions to form a trigonal pyramid that is traditionally described as intermediate between a sp^3 hybrid with one LEP and three bonding electron pairs and a sp^3d^2 hybrid with three LEPs and three bonding electron pairs occupying the hybrid orbitals. The highly asymmetric distribution of the LEP withdraws negative charge from the nucleus and leaves more positive charge of the nucleus exposed to the bonding anions, and therefore leads to enhanced bonding capability or effective valence for the lone-pair cation. This interpretation is consistent with the electric dipole description of the lone-pair cations where the dipole moment depends on the degree of sp^3 hybridization [2]. The steroactive LEP with a negative charge may participate in the coordination sphere of other cations such as alkali cations. This is particularly apparent in structures such as those listed in Table I. The large alkali cations require high coordination numbers, however, there are not enough anions in these structures to meet the requirement. Therefore, the LEP joins the coordination sphere acting like an extra anion. Figure 4 shows the structure of Na_4SnO_3 as an example. In this structure [10], BVS values calculated for the Sn, Na and O atoms are 2.73, 0.53-0.86 and 1.86-1.99 v.u., respectively. In particular, the Na(1) atom is coordinated by only two oxygen atoms and has a BVS value as low as 0.53 v.u. Two LEPs from two Sn atoms complement the $Na(1)O_2$ coordination environment in a highly distorted tetrahedral configuration. The positive charge of the Na^+ cation is partially balanced by the negative charge of the LEP, which lowers the bonding capability or effective valence of the Na^+ cation. Therefore, the LEPs transfer bonding power or effective valence from the alkali cations to the surrounding lone-pair cations. Although the LEP cannot be located like an atom, its effect is reflected in the calculated BVS for the involved cations. This is similar to the case of O-H…X hydrogen bonds when the H atom is not located, as mentioned in the Introduction.

An alternative treatment for structures such as Na_4SnO_3 is to assume a cation-cation bond with a bond valence that must be counted negative for the lone-pair cation but positive for the alkali cation so that the BVS for both cations will agree with the formal valences. Such treatment has been proposed for coordination complexes such as $[Cu(NO_2)_6]^{4-}$ where the Cu atom is octahedrally coordinated by six N atoms [2].

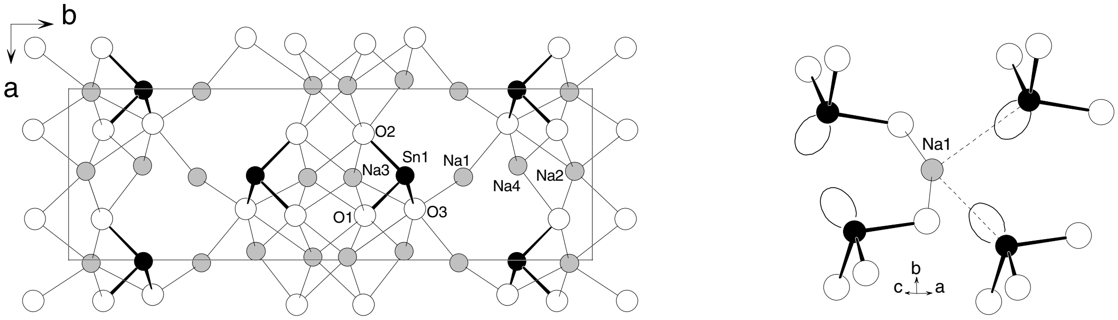

Figure 4. The structure of Na_4SnO_3. The coordination environment of the Na(1) atom is shown on the right side. Black, grey and white circles represent Sn, Na and O atoms respectively. The LEP of the Sn atom is drawn schematically.

As first found for thioantimonites and selenoantimonites [5], the valence of the L-X bond between lone-pair cation L and ligand X in a $[LX_3]$ pyramid tends to approach $({}^{for}V + 2)/4$ v.u. for a full sp^3 hybridization, where ${}^{for}V$ is the formal valence of L. Consequently, the effective valence of L will be between approximately ${}^{for}V$ and $3({}^{for}V + 2)/4$ v.u. In other words, the contribution of the LEP to the effective valence of L tends to be in the range between zero and $3({}^{for}V + 2)/4 - {}^{for}V = (6 - {}^{for}V)/4$ v.u. Therefore, low valent L cations tend to have higher deviations of BVS from ${}^{for}V$ as can be seen from Table I.

If the effective valence of an L cation in a $[LX_n]$ polyhedron is substantially higher than its formal valence, the r_{0i} value calculated with equation (2) will be lower than the value expected for an effective valence of L to be equal to ${}^{for}V$. Including such polyhedra in the process of averaging r_{0i} will lower the r_0 value. This probably explains the fact that some of the polyhedra with low $|\Phi|$ values in figure 2 have BVS values considerably lower than ${}^{for}V$. Such polyhedra mainly belong to structures containing small high-valent cations such as S^{VI} and P^{V} in tin sulfates and phosphates. The strong bonds between the high-valent cations and oxygen atoms and the low cation/anion ratio in such structures favor weak Sn-O bonds and high coordination numbers for Sn^{II}, and thus favor more symmetrical $[SnO_n]$ polyhedra with the steroactivity of the LEP of Sn^{II} largely suppressed.

Because of the frequent occurrence of large deviations of BVS from ${}^{for}V$ for lone-pair cations, the accuracy of the tabulated bond valence parameters for bonds with lone-pair cations have been questioned. In particular, the parameter b in equation (1) has been adjusted to values other than 0.37Å [20, 21]. These approaches may successfully improve the agreement between ${}^{for}V$ and BVS of lone-pair cations but would likely enhance the deviation of other ions from their ${}^{for}V$ values in the same structure. Take the structures in figure 3 as an example, eliminating the deviation of BVS from ${}^{for}V$ for the Bi^{III} cations by changing the bond valence parameters for Bi^{III}-O bonds will simply shift the deviation to oxygen anions. The result will of course make the influence of the LEP of Bi on bonding capabilities of the atoms in the structure more difficult to be seen.

Many inorganic materials containing cations with lone pair electrons have interesting physical properties such as ferroelectricity, semiconductivity and superconductivity. The effect of LEPs on these properties remains a fundamental open question in materials science. The effective valence of the lone-pair cations can be related to material properties as shown for the conduction paths in the semiconducting cetineite-type phases [22]. The effects of LEP in the majority of the materials are expected to be much more complicated than the extreme cases discussed as examples here. Extended studies of the subject should improve the applicability of the bond valence model and our understanding of the involved structural chemistry.

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