

On the valences of bonds in the oxycomplexes of Sn^{2+}

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The differences between Wang and Liebau's [Wang & Liebau (2007). *Acta Cryst. B* **63**, 216–228] stoichiometric valence (atomic valence) and structural valence (bond-valence sum) observed in Sn^{2+} and other lone-pair cation oxycomplexes arises from their use of the Brese & O'Keeffe bond-valence parameters which are based on the assumption that the bond-valence parameter $b = 0.37 \text{ \AA}$ applies to all bond types. According to the theory of the bond-valence model, the bond-valence sum is necessarily equal to the ionic charge, implying that in the Wang and Liebau model the ionic charges are equal to the structural valence. If charges are chosen equal to the stoichiometric valence, the bond-valence parameters for $\text{Sn}^{2+}-\text{O}$ bonds are $R_0 = 1.859 \text{ \AA}$, $b = 0.55 \text{ \AA}$. While both models are theoretically valid, only the standard model relates bond valences to the concept of atomic valence. Wang and Liebau's suggestion that cation–lone-pair bonds make a significant contribution to the valence sums is confirmed, but such bonds cannot account for the full difference between the stoichiometric and structural valences because they are present in only a few compounds.

1. Introduction

In a recent series of papers Wang and Liebau (Liebau & Wang, 2005; Wang & Liebau, 1996, 2005, 2007, 2009; Liebau *et al.*, 2009) have pointed out that the bond-valence sum calculated around a lone-pair cation increases as the cation's environment becomes more distorted, *i.e.* as the lone pair becomes more stereoactive (Fig. 1). They distinguish between the traditional valence of an atom, which they call the *stoichiometric valence*, and the sum of the experimental bond valences, which they call the *structural valence* (Liebau & Wang, 2005). In the present paper the terms 'experimental bond-valence sums' and 'structural valence' are used interchangeably according to context. Liebau & Wang (2005) propose that while the stoichiometric valence measures the number of valence electrons formally involved in bonding, the structural valence measures the actual number of electrons physically associated with the bonds formed by the atom, a number which, in general, is larger. Consequently, they infer that cations with stereoactive lone pairs use more electrons in bonding than those in which the lone pair is inactive. They suggest (Wang & Liebau, 2007, 2009) that as the environment of the cation becomes less symmetric, the non-bonding lone pair of electrons is increasingly involved in the cohesion of the structure. They give a number of qualitative examples that support their hypothesis but they do not provide numerical evidence that the value of the structural valences they measure reproduces the number of additional electrons quantitatively, possibly because of the difficulty of finding

alternative experimental or theoretical methods for determining what this number should be.

In this paper Wang and Liebau's hypothesis is examined in some detail, because it contradicts the basic assumption of the bond-valence model, namely that the bond-valence sum is by definition equal to the (stoichiometric) atomic valence (the *valence-sum rule*). This definition is the basis of a number of rigorous theorems, which are linked to experiment by the empirical correlation between bond valence and the observed bond length. This correlation is usually approximated by (2) below with two fitted *bond-valence parameters*, R_0 and b , as described in §2.

In practice, bond-valence sums determined from observed bond lengths using this correlation may deviate slightly as a result of experimental uncertainty, and may deviate systematically in cases where steric constraints cause the bonds to be stretched or compressed, but such deviations are well understood and do not indicate the involvement of more or fewer electrons in the bonds (Brown, 2002).

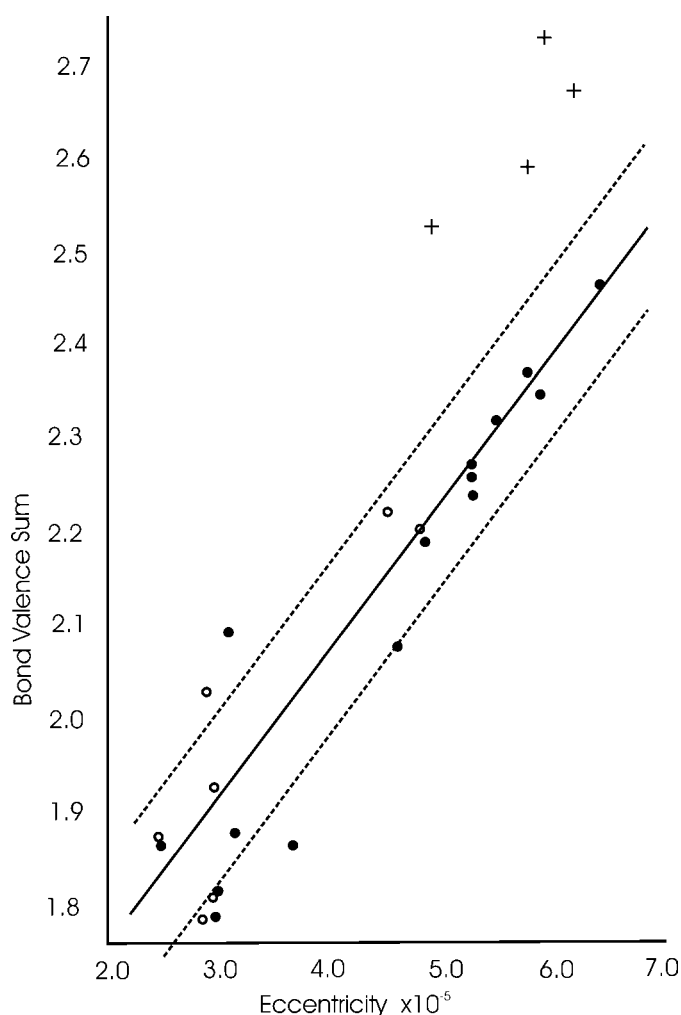


Figure 1
Bond-valence sum (structural valence) versus eccentricity for the Wang and Liebau model. Open circles are structures published before 1980, filled circles structures published after 1980. Crosses are the structures with $G > 0.2$. Broken lines represent the range of ± 0.09 v.u.

Wang and Liebau's hypothesis, and the arguments used to support it, challenge the basis on which the bond-valence model has been developed. For this reason, in §2 the bond-valence theory is derived to show that the bond-valence parameters must be chosen to ensure that the valence-sum rule is obeyed by bond valences calculated from bond lengths. The *Wang and Liebau model* is distinguished from the *standard model*. In the standard bond-valence model the ionic charges are chosen to be equal to the atomic valences and the bond-valence parameters are then chosen to ensure that the valence sum rule is obeyed. If this rule fails, at least some aspects of the model also fail and it is essential to understand the scope of this failure. Following the suggestion by Sidey (2008) that the difference between the models arises from Wang and Liebau's adoption of bond-valence parameters in which b is fixed at 0.37 \AA , §3 describes my analysis of a representative selection of well determined structures (*the training set*) from the Sn^{2+} compounds studied by Wang and Liebau. Using bond-valence parameters derived with a procedure recently proposed by Sidey (2009b), all the compounds in the training set are found to obey the valence-sum rule within the limits of experimental uncertainty, meaning that when the bond valence is determined using the procedures of the standard model, there is no significant difference between the stoichiometric and structural valence.

Wang & Liebau (2009) suggest that the effect they observe may be the result of ignoring the unconventional bonds formed between the counter-cations and the lone pairs. Therefore, in §4 the four structures in the training set that contain such bonds are examined and they show that while they contribute to the bond-valence sum, these bonds are unable to account for the full differences between the structural and stoichiometric valences observed by Wang & Liebau (2007).

In §5 the Wang and Liebau model is compared with the standard model and while both are mathematically valid approaches, they suggest different chemical interpretations. The large value of the bond-valence parameter b in the standard model implies that the stereoactive behaviour is associated with the lone-pair polarizability. The chemical significance of the Wang and Liebau model is much less clear and the interpretations they advance have a number of serious problems.

2. Theory of the bond-valence model

This section provides a theoretical rationale for the bond-valence model starting with the ionic model. It is noted that the ionic model allows many choices of ionic charges; however, in the *standard bond-valence model* the charges are chosen to be equal to the traditional (stoichiometric) atomic valences since these serve to link the bond-valence model to the Lewis electron-pair model and thence to traditional chemical concepts.

The ionic model, introduced early in the twentieth century, was originally proposed as a description of chemical bonding, *i.e.* one that leads to a successful explanation of inorganic

structure, but the subsequent development of quantum mechanics revealed the deficiencies of the ionic model as a picture of chemical bonding since it takes no account of the physical distribution of electron density that is responsible for the cohesion between the atoms. However, the model has proved to be remarkably successful in reproducing observed chemical structures, since it is able to accurately predict the arrangement of atoms in condensed phases. In the form of the two-body potential model it is routinely used for simulating the structures of complex crystalline and non-crystalline materials. Why does such a model succeed in describing the structure when it is based on such an implausible picture of chemical bonding? Its success lies in the repulsive potential that, for a given set of ionic charges, is chosen to ensure that the ions in the ionic model adopt the same positions as the atoms in the solid. These potentials are largely transferable between the same ion pairs in different compounds, so once the potentials are known, the geometries of new chemical compounds can be predicted with confidence. Further, there is nothing special about the charges used in the model; any set of ionic charges can be assigned provided the appropriate empirical repulsive potential is used. Setting the charges of the standard model to be equal to the atomic valences is an arbitrary choice which, however, links the model to traditional chemical concepts.

While the traditional goal of the ionic model is to find the arrangement of ions that minimizes the potential energy, the bond-valence model focuses instead on the electrostatic field. Ions carrying an electric charge arrange themselves with cations surrounded by anions and *vice versa* according to the principle of local charge neutrality (Pauling, 1929). It is an elementary exercise to show that such an arrangement results in Faraday field lines that link each cation with its first neighbour anion shell, and *vice versa*. In this model a bond is defined as existing between a cation and an anion if they are linked by lines of field, *i.e.* by electrostatic flux, and the strength of the bond is given by the corresponding number of lines of field, *i.e.* by the magnitude of the electrostatic flux. According to Gauss' electrostatic theorem, the total electrostatic flux incident at an ion is equal to its charge. Therefore, by setting the ionic charges equal to the atomic valence, the fluxes represent the amount of valence carried by each bond, hence they are called bond valences. The bond valences are also the same as the number of resonant electron pairs assigned to the bond in the Lewis model (*cf.* Boisen *et al.*, 1988). The sum of the bond valences around any ion is therefore, by Gauss' theorem, equal to the atomic valence, a law known as the *valence sum rule*. This is the first and most important of the various bond valence rules that are derived from the electrostatic model. These rules can be used, for example, to predict ideal bond valences if the topology of the bond network is known (Brown, 2002).

In non-standard versions of the model, such as that proposed by Wang and Liebau, the ionic charges are no longer equal to the atomic valences, but they are still equal to the sum of the bond fluxes, and if the fluxes (valences) are calculated from the bond lengths, the ionic charges of the model are

equal to the bond-valence sum, *i.e.* the structural valence. The significance of these charges depends on the way they are chosen.

It is not surprising that when two ions are brought closer together, the electrostatic flux between them, *i.e.* the valence of the bond that links them, will increase. The correlation between the bond valence, S , and the bond length, R , has been well studied and is typically approximated using (1) or (2), each with two empirically fitted *bond-valence parameters*, R_0 and n , or R_0 and b . However, these equations are only approximations and there are cases, *e.g.* H–O bonds, where they are only valid over limited ranges (Brown, 2002).

$$S = (R/R_0)^{-n} \quad (1)$$

$$S = \exp((R_0 - R)/b) \quad (2)$$

This correlation plays the same role in the bond-valence model that the repulsive potential does in the traditional ionic model. Like the repulsive potential it must be determined empirically by comparing ideal bond valences with observed bond lengths. The bond-valence parameters determined in this way have proved robustly transferable between bonds of the same type in different compounds. Naturally the bond-valence parameters depend on the choice of ionic charges. For the standard model a standard set of bond-valence parameters has been determined by ensuring that bond valences determined from bond lengths obey the valence-sum rule. Assigning ionic charges that are not equal to the atomic valences requires a different set of bond-valence parameters. Conversely, using a different set of bond-valence parameters implies the adoption of a different set of ionic charges.

Although it has been customary to determine b by trial and error, and then fit R_0 to ensure the valence-sum rule is obeyed in a set of training structures, Sidey (2009*b*) has proposed a more powerful method of determining both R_0 and b simultaneously. He notes that (2) can be rewritten as (3).

$$R_S = R_0 - b \ln(S), \quad (3)$$

where R_S is a measured bond distance and is therefore known. The bond valence S corresponding to this distance is usually not known *a priori*, but in the special case of a cation environment where all the bonds have the same length, S should equal V/N , where V is the ionic charge and N is the coordination number. A plot of R_S against $\ln(V/N)$ should, if (3) is valid, result in a straight line of slope $-b$ and intercept R_0 . In the case where the bond lengths are not all the same, the average value of S is still V/N , but according to the distortion theorem (Urusov, 2003), the value of the distance R_S corresponding to a valence of V/N is related to the average bond length, $\langle R \rangle$, by

$$R_S = \langle R \rangle - \delta_2/2b + \delta_3/3b^2. \quad (4)$$

Here δ_2 is the mean-square deviation and δ_3 is the mean-cube deviation, of the individual bond lengths from $\langle R \rangle$, both of which can be obtained from the observed bond lengths. Equation (4) requires a knowledge of b , but even though this

is not known *a priori*, it only appears in the two small correction terms and an approximate value is sufficient.

There have been many determinations of the bond-valence parameters for the standard model by traditional methods, some of them systematic such as that by Brown & Wu (1976) who determined R_0 and n for 86 different bond types using (1), and Brown & Altermatt (1985) and Brese & O'Keeffe (1991) who did the same for R_0 and b in (2). In most cases b (or n), which determines the slope of the correlation curve, is difficult to determine accurately, particularly if the observed bond lengths cover only a small range. As b did not appear to vary significantly between one bond type and another in their training set, Brown & Altermatt (1985) simplified the calculation by using the single value, 0.37 Å, for all bond types. Brese & O'Keeffe (1991) assumed, without testing, that this value would apply to all other bond types and therefore refined only R_0 when preparing their more extensive list of bond-valence parameters. This list contains the only parameters for Sn^{2+} -O bonds that have been published, $R_0 = 1.984$, $b = 0.37$ Å. The value of b has therefore been assumed but never refined against a training set of Sn^{2+} -O bonds and there is no guarantee that its value is correct.

Experimental uncertainties cause the valence sums obtained from observed bond lengths to deviate typically by around 0.1 v.u. (valence units) for most well determined structures. However, if an ion resides in a cavity that is constrained to be too large or too small; the valence sums obtained from the bond lengths will be significantly smaller or larger than the ionic charge. A measure of the failure of the valence-sum rule under these circumstances is the global instability index, G , the r.m.s. difference between the atomic valence and the bond-valence sums defined in

$$G = [\sum_i (\sum_j S_{ij} - V_i)^2 / M]^{1/2}. \quad (5)$$

The inner sum is over all the bonds ij around atom i and the outer sum is taken over the M atoms, i , in the formula unit. Steric strain, where bonds are compressed or stretched from their ideal bond length, tends to destabilize the structure and leads to larger values of G . Correctly determined structures are rarely found with G greater than 0.2 v.u. (Brown, 2002). If a larger value is found it can usually be attributed to the use of inappropriate bond-valence parameters or an incorrect crystal structure determination. In examining the causes for the apparent failure of the valence-sum rule reported by Wang and Liebau, it is important to eliminate these two possibilities before claiming that the effect arises from a real but hitherto unnoticed chemical cause.

3. Experimental procedure

This section reviews the work of Wang and Liebau and shows that the bond-valence sums around Sn^{2+} are, as expected, all equal to 2.0 v.u. within the limits of experimental uncertainty when using bond-valence parameters fitted according to the procedures of the standard model.

Wang & Liebau (2007) examined a large number of cation environments of the form XY_N , where X is a main group element with a single lone pair, and Y is O^{2-} , S^{2-} or Se^{2-} . In each case all the ligands, Y , surrounding a given cation, X , were the same chemical species. Wang and Liebau measured the stereoactivity of the lone pair using an *eccentricity parameter*, Φ , which is the negative of the sum of vectors with a magnitude of $\exp(-5R)$ directed along each bond. The eccentricity function is zero if the cation is at the centre of its coordination sphere, and it increases the further the cation is displaced from this centre, *i.e.* the more the lone pair is expressed. In Figs. 5–7 in their paper Wang & Liebau (2007) show that for essentially all the 22 bond types they studied, the bond-valence sums calculated with the bond-valence parameters of Brese & O'Keeffe (1991) increased linearly with eccentricity.

Professors Wang and Liebau have been kind enough to send me details of their training set of Sn^{2+} -O environments. I chose these bonds for a detailed study because they show a particularly good correlation between the bond-valence sum and the degree of distortion around the central ion. In assembling this list of 52 Sn^{2+} -O environments, Wang & Liebau (2007) carefully screened each structure, rejecting all structures with crystallographic agreement indices (R factors) greater than 0.075 or which failed to meet a number of other criteria. This list still contained some problem structure determinations so I further filtered it by looking at the value of G [see (5)] calculated with the Brese & O'Keeffe (1991) bond-valence parameters used by Wang and Liebau. The purpose of this filter was to draw attention to any problem structure determinations, specifically those with $G > 0.2$ v.u. Since the positions of all atoms must be known in order to calculate G , 19 compounds with missing H-atom coordinates had to be dropped from the list. Six of the remaining structures had G greater than 0.20 v.u. and in all these cases G was greater than 0.30 v.u. suggesting an error in the structure determination or in its interpretation. Two of these structures (SnSO_4 ; Donaldson & Puxley, 1972, and an early determination of $\text{K}_2\text{Sn}_2\text{O}_3$; Braun, 1978) were clearly poor or problematic and were removed from the list. The other four had plausible structures with large eccentricity parameters, and therefore large deviations between the structural and stoichiometric valences around Sn^{2+} which might possibly account for the large value of G . However, there were two other structures with equally large eccentricity parameters but with $G < 0.2$ v.u., showing that a large difference between the stoichiometric valence and bond-valence sum around Sn^{2+} is not in itself sufficient to prevent the structure passing the G filter.

These four structures were included in the study, but together with two other structures with large eccentricity factors, they were subject to a detailed analysis, reported in §4, showing that the large value of G arises from the neglect of bonds between a counter-cation and the lone pair. The remaining 13 structures listed in Table 1 all passed the G filter. They include 23 Sn^{2+} environments with eccentricity parameters lying between 2.5 and 6.4×10^{-5} . In the figures these compounds are shown as circles, while the four compounds

Table 1

Summary of calculations on the training set.

Φ = eccentricity $\times 10^5$; CN = coordination number, S = bond-valence sum around Sn, G = global instability index, WL = Wang & Liebau model, SM = standard model, ICSD = Inorganic Crystal Structure Database number.

	Φ	CN	S (WL)	S (SM)	G (WL)	G (SM)	ICSD
Na ₂ Sn(C ₂ O ₄)	2.5	6	1.88	2.10	0.15	0.14	388
Sn ₂ (S ₂ O ₄) ₂	2.5	4	1.87	1.91	0.14	0.13	32684
SnWO ₄	2.9	6	2.03	2.21	0.02	0.11	2147
SnHPO ₄	2.9	5	1.79	1.94	0.13	0.11	658
β -SnWO ₄	3.0	6	1.93	2.10	0.17	0.15	2840
Sn ₃ (PO ₄) ₂	4.5	5	2.08	2.13	0.11	0.07	966
	4.8	3	2.20	1.94			966
	3.0	6	1.74	1.99			966
SnO	3.1	4	2.09	2.06	0.09	0.06	16481
Sn ₂ OSO ₄	3.0	5	1.79	1.93	0.14	0.09	35101
	3.2	5	1.88	1.98			35101
Sn ₄ (PO ₄) ₂ (C ₂ O ₄)	4.6	4	2.01	1.95	0.19	0.15	50969
	3.6	5	1.87	1.98			50969
SnNb ₂ O ₆	3.0	4	1.80	1.84	0.11	0.10	202827
NH ₄ Sn ₄ P ₂ O ₁₂	†	4	2.25	2.07	0.13	0.09	90843
	4.9	3	2.19	1.93			90843
Na ₄ Sn ₄ O(OH) ₁₀	6.4	3	2.46	2.09	0.20	0.11	35420
	5.3	3	2.26	1.98			35420
	5.8	3	2.37	2.04			35420
	†	3	2.38	2.04			35420
Na ₂ Sn ₂ O(OH) ₄	5.9	3	2.35	2.03	0.17	0.10	35421
	5.3	3	2.26	1.97			35421
	5.3	3	2.22	1.95			35421
	5.5	3	2.32	2.01			35421
K ₂ Sn ₂ O ₃	6.2	3	2.67	2.11	0.20‡	0.28	15511
Rb ₂ Sn ₂ O ₃	5.7	3	2.59	2.11	0.21‡	0.20	24816
Na ₄ SnO ₃	5.9	3	2.73	1.98	0.10‡	0.15	49624
K ₄ SnO ₃	4.9	3	2.53	2.01	0.15‡	0.30	79101

ICSD codes: 388: Donaldson *et al.* (1976); 658: Schroeder & Prince (1976); 966: Mathew *et al.* (1977); 2147: Jeitschko & Sleight (1974); 2840: Jeitschko & Sleight (1972); 15511: Braun & Hoppe (1981); 16481: Pannetier & Denes (1980); 24816: Braun & Hoppe (1982); 32684: Magnusson & Johansson (1982); 35101: Lundren *et al.* (1982); 35420, 35421: von Schnering *et al.* (1983); 49624: Nowitzki & Hoppe (1984); 50969: Natarajan (1998); 79101: Röhr (1995); 90843: Ayyappan *et al.* (2000); 202827: Ercit & Cerny (1988). † Not available ‡ After correction for the cation–lone-pair bonds. Before correction these values are 0.33, 0.38, 0.32 and 0.31 v.u.

discussed in §4 that did not pass the G filter are shown as crosses.

Fig. 1 plots the structural valence (*i.e.* the bond-valence sums) calculated around the Sn²⁺ ions with the Brese & O’Keeffe (1991) parameters as a function of the eccentricity parameter. It reproduces Wang and Liebau’s results and confirms their assertion that the valence sum calculated in this way increases significantly with eccentricity. Fig. 1 rules out the possibility that this correlation is a consequence of the inclusion of a number of poorly determined structures in the original sample, but it is significant that the four structures shown by crosses all have structural valences around Sn²⁺ that lie well above the correlation line that goes through the other points.

Having shown that Wang and Liebau’s observations cannot be explained by incorrect structure determinations, the next step was to examine the bond-valence parameters they used. The only values published for Sn²⁺–O bonds are those of Brese & O’Keeffe (1991) which are based on the assumption that the bond-valence parameter, b , is universally equal to 0.37 Å. R_0 and b are not chosen with any particular physical model in mind, and the only criterion for assigning their value

is that the ideal and experimental bond valences should be the same. There is no theoretical reason for believing either parameter should be the same for all bond types, and the notion that a single fixed value for b can be used for all bond types within the standard model has been challenged. Adams (2001) pointed out that b depends on how many bonds are included in the bond-valence sum, with b increasing as the distances to the second coordination sphere are added. He also showed that b is related to the difference in the softness of the terminal ions, being close to 0.37 Å for bonds between ions of similar softness, but rising to 0.50 Å and higher for bonds whose terminal ions differ in softness. Others have confirmed this observation, particularly for bonds formed by ions with lone pairs, *e.g.* Krivovichev & Brown (2001) found $b = 0.49$ Å for Pb²⁺–O bonds, and Locock & Burns (2004) found $b = 0.50$ Å for Tl⁺–O bonds. Sidey (2009*a*) calculated values of b between 0.44 and 0.50 Å for bonds between O²⁻ and Sn²⁺, Sb³⁺, Te⁴⁺ and I⁵⁺ from the values of n given by Brown & Wu (1976). In particular, the parameters he gives for Sn²⁺–O bonds are $R_0 = 1.849$; $b = 0.50$ Å. According to Adams’ (2001) observations, these larger values of b are consistent with the lone-pair cation being relatively soft or polarizable. In other words lone-pair cations have a number of states with closely spaced energies each of which can be stabilized by a different environment. The presence of strongly bonding ligands results in stronger, and therefore fewer, bonds, leaving space in the coordination shell for a stereoactive lone pair. The presence of weakly bonding ligands results in a larger number of weaker bonds which forces the lone pair into the center of the ion.

Fig. 2 shows a Sidey plot [see (3)] of R_S against $\ln(V/N)$ for the Sn²⁺–O bonds in the training set with the values of R_S corrected according to (4). In many cases, particularly for the three-coordinate atoms, the corrections are negligible, but in other cases corrections up to 0.15 Å had to be applied to the

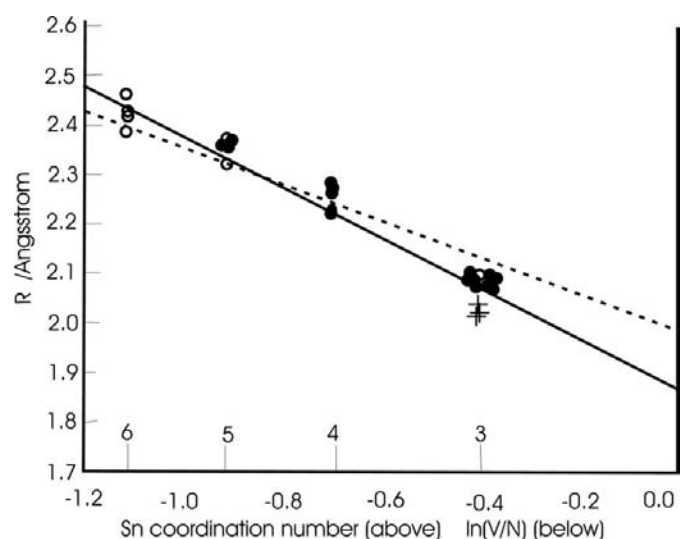


Figure 2 Sidey plot of Sn²⁺–O bonds showing the corrected average bond length R_S versus $\ln(V/N)$. The value of the coordination number, N , is also shown above the horizontal axis. The solid line is a fit with slope 0.55 Å, the broken line represents the bond-valence parameters of Brese & O’Keeffe (1991) with slope 0.37 Å. Conventions otherwise as in Fig. 1.

average bond length. The best-fit line shown on the graph has a slope of $b = 0.55 \text{ \AA}$ and an intercept of $R_0 = 1.859 \text{ \AA}$, values close to those quoted above by Sidey (2009a). For comparison the line corresponding to the Brese and O'Keeffe parameters is shown as a dotted line. The bond-valence parameters can also be determined analytically from differences in the average values of R_S for different coordination numbers. The four compounds that failed the G test, shown with crosses, were not used to determine the bond-valence parameters since their valence sums need to be adjusted for the bonds formed by the lone pair, as discussed in §4.

Fig. 3 shows the bond-valence sums calculated using the bond-valence parameters determined from the Sidey plot (Fig. 2). The filled points represent the structures determined since 1980 when the introduction of X-ray diffractometers and computers resulted in improved accuracy. Most of these points lie within 0.06 v.u. of the expected value of 2.0 v.u. (broken lines). Those that lie outside these limits include the four structures discussed in §4 below (crosses) and many of the structures determined before in 1980 (open circles). For these early determinations the estimated standard deviation of the difference between the stoichiometric valence and the valence sums around Sn^{2+} is 0.11 v.u., which can be compared with a value of 0.06 v.u. for the post-1980 structures. The corresponding average values of G are 0.11 and 0.09 v.u. The valence sums around Sn^{2+} in the Wang and Liebau and the standard models, as well as the values of G for all the compounds in the training set, are listed in Table 1.

The outliers in Figs. 1 and 3 were examined for indications of steric strain, but none of the structures shown by circles displayed the characteristic strain signature in which some cations have valence sums that are too large (compression), while others have valence sums that are too small (tension). The structures indicated with crosses do show this signature, but for a different reason as explained in the next section.

4. Alkali-rich compounds

This section examines in more detail the four structures that failed the G test (shown by crosses in the figures) and show that the discrepancy is the result of ignoring bonds between the alkali metal cations and the lone pairs.

In recent papers Wang & Liebau (2007, 2009) suggest that lone pairs might be directly involved in the bonding, thus accounting for at least some of the increase in the structural valence relative to the stoichiometric valence in cases where the lone pair is stereoactive. They examined eight alkali-rich salts of lone-pair cations, one of which, Na_4SnO_3 , contains Sn^{2+} . These structures all have stereoactive lone pairs (*i.e.* high eccentricity parameters) and lone-pair cations with structural valences that are considerably larger than their stoichiometric valence. Wang and Liebau illustrate Na_4SnO_3 , showing that it contains short distances between the lone pair and nearby Na^+ cations, the lone pair acting in this case as an anion. They propose that a short Na^+ –lone-pair distance should be considered an acid–base bond, *i.e.* that although the stoichiometric valence around Sn^{2+} is 2.0, the structural valence is

larger because some of the electrons of the lone pair become involved in bonding.

Wang and Liebau point out that the bond-valence model already has a mechanism for interpreting cation–lone-pair bonds. This mechanism can be described in two different but equivalent ways. In the first description, that used by Wang and Liebau, the lone pair is treated as a divalent anion, conveniently labelled Lp^{2-} , with the remainder of the Sn ion assigned a valence of +4. If the fictitious Lp^{2-} anion is not involved in external bonding, it forms a bond of 2.0 v.u. with the Sn^{4+} ion. The presence of an Na^+ – Lp^{2-} bond of, say, 0.1 v.u. would reduce the valence of the Sn^{4+} – Lp^{2-} bond to 1.9 v.u. requiring that the sum of the Sn^{4+} – O^{2-} bond valences compensate by increasing from 2.0 to 2.1 v.u. This would explain why, if one ignores the contributions of the Na^+ – Lp^{2-} bonds, the structural valence of Sn^{2+} appears to be too large and that of Na^+ too low.

The alternative description is to regard Sn as part cation with a valence of $2+x$ and part anion with a valence of $-x$, giving a net valence (charge) of +2. The valence of any bonds formed by the anion component, *i.e.* the lone pair, would be subtracted from the bond-valence sum calculated for the bonds formed by the cation component, *i.e.* Sn^{2+} . The two descriptions are equivalent, and in either case the sum of the valences of the cation–Lp bonds must be equal to both the deficit in the valence sums at the cations (*e.g.* Na^+) and the excess of the valence sums at Sn^{2+} . The following shows that

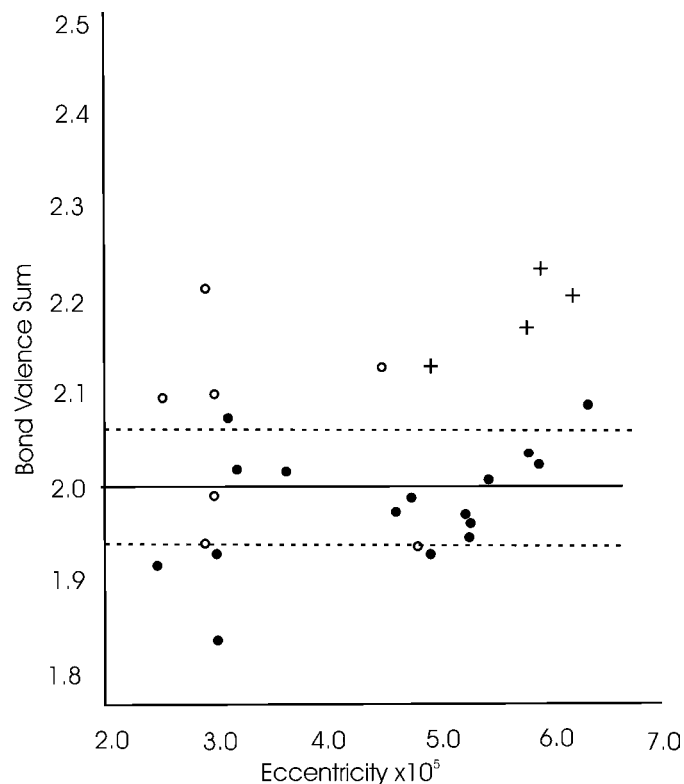


Figure 3
Bond-valence sum *versus* eccentricity for the standard model. Conventions the same as Fig. 1. The broken lines represent the range of ± 0.06 v.u.

Table 2

Number of lone-pair electrons involved in bonding and the global instability index, *G*, after correcting for cation–Lp bonds according to the Wang and Liebau and standard models.

Column 2: Na:Sn ratio; column 3: eccentricity factor, Φ ($\times 10^5$); column 4: total cation–Lp bond valence for the Wang and Liebau model; column 5: total cation–Lp bond valence for the standard model; column 6: *G* for the Wang and Liebau model; column 7: *G* for the standard model; column 8: ICSD references (see Table 1).

	Na:Sn	Φ	Lone pair		<i>G</i>		ICSD
			WL	Standard	WL	Standard	
Na ₄ SnO ₃	4.0	5.9	0.62	0.26	0.10	0.15	49624
K ₄ SnO ₃	4.0	4.9	0.53	0.12	0.17	0.30	79101
K ₂ Sn ₂ O ₃	1.0	6.2	0.55	0.10	0.20	0.15	15511
Rb ₂ Sn ₂ O ₃	1.0	5.7	0.44	0.06	0.21	0.13	24816
Na ₄ Sn ₄ O(OH) ₁₀	1.0	5.3–6.4	0.00†	0.00†	0.20	0.11	35420
Na ₂ Sn ₂ O(OH) ₄	1.0	5.3–5.9	0.00†	0.00†	0.17	0.10	35421

† No Na–Lp bonds occur in these compounds.

Table 3

Bond-valence sums for Na₄SnO₃.

All values in v.u.; bond-valence parameters in Å. The values in parentheses are the sums of all the Na–Lp bond valences.

	WL model		Standard model		Including Na–Lp bonds	
	R ₀	<i>b</i>	R ₀	<i>b</i>	WL model	Standard model
Sn–O	1.984	0.37	1.859	0.55		
Na–O	1.803	0.37	1.803	0.37		
Sn	2.73		2.24		2.11 (0.62)	1.98 (0.26)
Na1	0.53		0.54		1.00	0.73
Na2	0.85†		0.78†		0.85	0.78
Na3	0.86		0.87		0.86	0.87
Na4	0.85		0.86		1.00	0.94
O1	1.98		1.84		1.98	1.84
O2	1.86		1.70		1.86	1.70
O3	1.99		1.74		1.99	1.74
<i>G</i>	0.32		0.26		0.10	0.15

† The values in column 2 were taken from Wang & Liebau's (2009) paper, the values in column 3 were recalculated for this paper which accounts for the differences in the sums around Na⁺ which should be the same.

while cation–Lp bonds are real and need to be included in the calculation of the bond-valence sums in order to account for the excess valence shown by the crosses in Fig. 3, there are problems in expecting it to account for the much larger difference between the structural and stoichiometric valences shown for all the structures in Fig. 1.

In order to take the Na⁺–Lp²⁻ bonds into account, it is first necessary to assign bond valences to them, but no procedure for this has yet been published, and the assignment depends on whether one is trying to account for the large excess valence of the Wang and Liebau model or the much smaller excess of the standard model. There are only six structures in the training set that have eccentricity factors greater than 4.9×10^{-5} and these are all alkali-metal-rich as indicated by the ratios given in column 2 of Table 2. The large Na:Sn ratio in these compounds results in the presence of a lower anion-to-cation ratio, leading to low cation coordination numbers. By forming bonds to the lone pair the cations can increase

their coordination numbers, and this in turn tends to increase the lone-pair stereoactivity.

A full analysis of the structures of Na₄SnO₃ has been included in Table 3 and K₄SnO₃ in Table 4. The second column in these tables shows the bond-valence sums calculated using the Brese and O'Keeffe parameters, confirming the observations of Wang and Liebau that the structural valence around Sn²⁺ is larger than the stoichiometric valence, while the opposite is true around the alkali metals. The bond-valence sums around O²⁻ are close to the stoichiometric valence. The third column gives the bond-valence sums calculated using the standard model Sn²⁺–O²⁻ parameters determined in §3. In this model the valence sums around Sn²⁺ are smaller, although still larger than expected, and consequently the sums around O²⁻ are now too small. The *G* factors are not noticeably improved and in both compounds *G* is larger than the normal stability limit of 0.2 v.u.

The valence of cation–lone-pair bonds will contribute to increasing the bond-valence sum around the alkali metal and decreasing it around Sn²⁺, but in order to estimate this contribution, it is first necessary to estimate their length which requires first estimating the position of the lone pair, and then assigning a bond valence. However, without any guidelines to work from, the best that can be done is to find a consistent set of bond valences that correlates with the notional bond lengths and at the same time accounts for the excess bond valence at Sn²⁺ and deficit at Na⁺ and K⁺.

The hypothetical Sn–Lp bond is expected to have a length of around 1 Å (Galy *et al.*, 1975), so any Sn–Na distance pointing directly along the Sn–Lp axis should be reduced by this amount in order to estimate its contribution to the bond-valence sum. Columns A, D and E in Table 5 show the distances between the Sn²⁺ nucleus and the nearest alkali metals in all four of the alkali-rich crystals that failed the *G* test. In all these compounds, there are several alkali metals at distances between 3.3 and 4.0 Å from Sn²⁺, but only those in column A are near the lone pair. For these the cation–Lp distances (shown in parentheses) have been approximated by subtracting 0.7 Å from the cation–Sn distances, recognizing that these bonds do not, in general, point directly down the lone-pair axis.

In Na₄SnO₃, Na1⁺ forms two bonds to O²⁻ anions and two to Lp²⁻ pseudo-anions, the four bonds pointing to the corners of a tetrahedron. Similarly Na4⁺ is bonded to three O²⁻ neighbours and one Lp²⁻, again at the corners of a tetrahedron. These are shown in column A of Table 5. In addition to the three Sn–Na distances that are correctly oriented to form bonds with the lone pair, there are a further nine Na⁺ contacts lying at distances between 3.1 and 3.6 Å, six in the plane perpendicular to the pseudo-threefold axis that runs through Sn and the lone pair (Table 5, column D) with the

Table 4Bond-valence sums for K_4SnO_3 .

All values in v.u.; bond-valence parameters in Å. The values in parentheses are the sums of all the K–Lp bond valences.

	WL model		Standard model		Including K–Lp bonds	
	R_0	b	R_0	b	WL model	Standard model
Sn–O	1.984	0.37	1.859	0.55		
K–O	2.132	0.37	2.132	0.37		
Sn	2.53		2.13		2.00 (0.53)	2.01 (0.12)
K1	0.53		0.53		0.80	0.59
K2	0.84		0.84		0.84	0.84
K3	0.84		0.76		0.84	0.76
K4	0.71		0.71		0.91	0.79
O1	1.71		1.49		1.71	1.49
O2	1.94		1.80		1.94	1.80
O3	1.80		1.67		1.80	1.67
G	0.29		0.32		0.17	0.30

remaining three lying between the three O^{2-} ligands on the opposite side to the lone pair (Table 5, column E). The cations with distances marked with a dagger are linked to Sn^{2+} through two O^{2-} anions which accounts for their proximity to Sn^{2+} . Although these nine Na^+ ions are as close to Sn^{2+} as the three Lp-bonded Na^+ ions, they are further from the lone pair and so cannot be considered as bonding within the hypothesis being tested. The situation in all four compounds is similar.

If the cation–Lp bonds are to account for the whole difference between Wang and Liebau's structural and stoichiometric valences, the Na^+ – Lp^{2-} bonds must be assigned the valences shown in column B of Table 5. These have been chosen to reflect the relative lengths of the cation–Lp bonds and to ensure that after the correction has been applied the cation and Sn^{2+} bond valences are approximately equal to their stoichiometric valence. Column C of Table 5 shows the much smaller corrections needed in the standard model.

These corrections are only able to improve the valence sums around $Na1^+$ and $Na4^+$ in Table 3 and $K1^+$ and $K4^+$ in Table 4; they cannot change the bond-valence sums around $Na2^+$ and $Na3^+$ (or $K2^+$ and $K3^+$) since these cations do not form bonds to the lone pair. In Tables 3 and 4, the second column shows the bond-valence sums calculated with the Brese and O'Keeffe parameters (Wang and Liebau's structural valence). The third column shows the bond valences calculated using the standard model. The fourth column shows the Wang and Liebau model with a cation–Lp correction designed to remove the difference between the structural and stoichiometric valence, while the fifth column shows the similar correction for the standard model. The values in parentheses represent the total contribution of the cation–Lp bonds.

These compounds are unusually rich in alkali metal cations. As such they are highly moisture sensitive and require special handling (Nowitzki & Hoppe, 1984). It is therefore hardly surprising that their structures show unusual features. If the three O^{2-} ions each form six bonds, this still leaves fewer than

Table 5Alkali metal– Sn^{2+} distances (Å) in alkali-rich crystals together with estimated bond valences using the present model and Wang and Liebau's model (these values are used in Tables 3 and 4).

A: cation–Sn distances in the direction of the lone pair (approximate cation–Lp distance); B: estimated bond valence to match the Wang and Liebau model; C: estimated bond valence to match the standard model; D: equatorial cation–Sn distances; E: distances opposite to the direction of the lone pair. For ICSD references see Table 1.

	A (Å)	B (v.u.)	C (v.u.)	D (Å)	E (Å)	ICSD
Na_4SnO_3						
Na1	3.32 (2.6)	0.27	0.12	3.42	3.32†	49624
Na1	3.43 (2.7)	0.20	0.09	3.43	3.11†	
Na4	3.63 (2.9)	0.15	0.05	3.52	3.25†	
				3.53		
				3.58		
				3.38		
K_4SnO_3						
K1	3.77 (3.1)	0.27	0.06	3.51	3.69†	79101
K4	3.85 (3.2)	0.20	0.07	3.62	3.49†	
				3.56	3.52†	
				3.39		
				3.37		
$K_2Sn_2O_3$						
K1	3.72 (3.0)	0.53	0.10	3.62x3†	3.44	15511
$Rb_2Sn_2O_3$						
Rb1	4.00 (3.3)	0.44	0.06	3.66x3†	3.55	24816

† Bridges to Sn^{2+} through two O ions.

four bonds available for each Na^+ ion, a situation which encourages the formation of cation–lone-pair bonds. Even after correction for these unconventional bonds, the bond-valence sums around O^{2-} and Na^+ are still too low, possibly because, with so few O^{2-} ions, the alkali metal cations are in sufficiently close contact that their mutual repulsion becomes significant.

The results of making corrections for the cation–Lp bonds in all the six high-eccentricity compounds of the training set are summarized in Table 2. The last two compounds in this table, with a total of eight Sn^{2+} ions between them, contain no cation–lone-pair bonds. All six compounds shown in Table 2 are alkali-rich (column 2) and have large eccentricities (column 3). The sums of the valences of the cation–Lp bonds applied in this correction are shown in columns 4 and 5 for the Wang and Liebau, and standard models, while columns 6 and 7 show the corresponding G indices after the corrections have been made. With the exception of K_4SnO_3 , these have values that one might expect for compounds that are highly moisture-sensitive and hence near the limit of stability.

This examination shows that the alkali-metal–lone-pair bonds do make an important contribution to the bond-valence sum and could, where they occur, account for the difference between the stoichiometric and structural valences. However, in order to do this the alkali-metal–lone-pair bonds would have to be stronger than most other bonds formed by the alkali metal, and this mechanism cannot account for the differences found in the majority of compounds, those that have no such bonds. The smaller corrections of the standard model appear to give a better description of the valence of these unconventional bonds.

5. Discussion

Both Wang and Liebau's model, and the standard model agree that cations with lone pairs require a different treatment from most other cations, but they differ in the way in which this is expressed. The standard model assigns ionic charges equal to the traditional atomic valence and requires that the parameters that express the bond-valence–bond-length correlation be chosen to ensure that the experimental bond-valence sums are equal to the traditional, *i.e.* stoichiometric, atomic valence within the limits of experimental uncertainty. The consequence of this is that, while the bond valence parameter b for many bond types is equal to 0.37 Å, there is growing evidence that larger values are needed for cations with lone-electron pairs, specifically 0.55 Å for Sn²⁺–O bonds.

On the other hand, by choosing to use the bond-valence parameters of Brese & O'Keeffe (1991), Wang and Liebau implicitly assume that the value of b is equal to 0.37 Å for all the bond types studied, regardless of the fact that this value has never been refined against observed Sn²⁺–O bond lengths. For many bond types the stoichiometric and structural valences are the same when calculated with b equal to 0.37 Å, but for cations with lone-electron pairs they are not. According to the theory developed in §2, the charges on the ions are equal to the bond-valence sums, *i.e.* the ionic charges in the Wang and Liebau model are equal to the structural valence rather than the stoichiometric valences assumed in the standard model. For lone-pair cations therefore the Wang and Liebau model implicitly assumes ionic charges that are not related to the traditional atomic valences. The question then is how is one to interpret these two models in chemical terms.

In the standard model the ionic charges are fixed *a priori* to the number of valence electrons that the atom has available for bonding, thus tying the model to traditional chemical concepts. The bond valence itself can be identified with the Lewis bond order. While the value of the bond-valence parameter b , like that of R_0 , must then be fitted, it is found to be transferable between all bonds of the same type (bonds having the same terminal ions) in stable compounds regardless of where the bonds are found or how distorted the environment. (For less stable compounds, such as those discussed in §4 and reported in Tables 3 and 4, the strains responsible for the instability can lead to significant deviations which are beyond the scope of this paper.) The value of b is associated with the softness or polarizability of the ion, large values of b indicating that one of the ions forming the bond is deformable, in this case the cation with the lone-electron pair.

The meaning of the Wang and Liebau model is less clear. According to the analysis given in §2 above, the ionic charges implicitly adopted in this model are equal to the structural valence, but they cannot be assigned *a priori* because they depend on the eccentricity of the Sn²⁺ environment. They can only be used for *e.g.* structure prediction if the eccentricity, which depends on the other atoms in the compound, can also be predicted *a priori*.

Liebau *et al.* (2009) have recently published a paper to give some context to the concept of structural valence. An

apparent simplifying feature of their model is the use of the Brese & O'Keeffe (1991) bond-valence parameters which are based on the assumption that b can be set to 0.37 Å for all bonds, so that only R_0 needs to be determined. However, fitting R_0 is not as simple in this model as it is in the standard model. Liebau *et al.* (2009) point out that the value of R_0 , as well as the structural valence, depends on the eccentricity [see (4), (5) and (6) in their paper]. However, the variation of the structural valence with eccentricity can only be determined if the value of R_0 is held fixed, or alternatively, the variation of R_0 with eccentricity can only be determined if the structural valence is held fixed. One must first decide which of these two quantities to fix, otherwise there is no unique solution to the way the other quantity varies with eccentricity. Assuming that one decides to fix R_0 , a new problem arises. The role of R_0 is to scale the bond valence which requires that the value of the structural valence be arbitrarily chosen for some particular value of the eccentricity. There are various possibilities. Wang & Liebau (2005) suggest that one should set the structural valence equal to the stoichiometric valence when the eccentricity is zero, that is when the coordination polyhedron is undistorted. This choice makes sense if one assumes that the structural valence measures the excess electrons involved in bonding as a result of the stereoactivity of the lone pair. However, in their calculations Wang and Liebau have consistently used the Brese and O'Keeffe value of R_0 in which the stoichiometric and structural valences are implicitly chosen to be equal in the middle of the observed eccentricity range (3.5×10^{-5}). This latter choice means that for the more regular Sn²⁺ coordination spheres the structural valence is less than 2.0, implying that in these cases some of the stoichiometric valence electrons are not involved in bonding. The choice of R_0 is not trivial. In the present study the two choices described above lead to structural valence scales that differ by almost 0.5 v.u. leading to very different estimates of the number of electrons that each atom uses in bonding.

Liebau *et al.* (2009) also point out that stoichiometric valences are integers, while structural valences in general are not. They draw attention to many other examples of non-integral valences determined by a variety of experimental and theoretical methods, but they do not discuss how these valences are defined, nor do they show that any of these other scales reproduce their own structural valences, leaving open to question the meaning and usefulness of the concept.

In the same paper they suggest that the stereoactivity of the lone pair can be thought of as related to the process of oxidation in which the lone pair is gradually removed from the Sn²⁺ ion to yield Sn⁴⁺ together with two electrons which can be used to convert molecular oxygen to O²⁻, but even the most strongly distorted Sn²⁺ complexes show no indications of oxidation.

The large Sn–O valences enhance the structural valence of the O²⁻ anions as well as the Sn²⁺ cations but the extra bonding electrons that this implies cannot come from the lone pair which becomes further removed from either the anions or the Sn–O bonds as the eccentricity increases.

These contradictions need to be resolved before a clear interpretation of the Wang and Liebau model is possible. The role of the extra electrons in bonding needs to be delineated so that a numerical comparison can be made between the structural valence and alternative methods of calculating or measuring the same quantity. If this can be done, it will be possible to determine the correct value of R_0 and provide the model with a more secure interpretation.

Wang & Liebau (2009) have identified the existence of unconventional bonds between the cations and the lone electron pairs of Sn^{2+} cations, and the present analysis provides quantitative evidence that the valences of such bonds should be included in the bond-valence sums. As these bonds are only found in a small number of relatively unstable compounds, they are likely to be weak. However their contribution is important even though it is not large enough to account for most of the difference between the structural and stoichiometric valences.

According to the standard model, the property that characterizes the stereochemistry of the lone-pair ions is their polarizability. If this is the correct physical explanation, the structural valence of the Wang and Liebau model could be understood as a measure of the polarization of the electrons in the lone pair, the wide range of structural valences reflecting the wide range of observed polarizations.

Different models of the same phenomenon can coexist if they provide complementary insights; for example, structure simulations using density-functional theory and simulations using the ionic model lead to the same structures but interpret them differently. The choice of which of two competing but equally successful models to use is largely a personal preference. The same is true of the two models discussed here, but whichever model one chooses to use in a particular application, it is important to understand the assumptions and concepts that underlie both models as well as their internal and external contradictions, so as to avoid misunderstandings that can lead to unnecessary confusion.

It is a pleasure to acknowledge the honour done to me by Professors Wang and Liebau for dedicating their 2007 paper in part to me, and also to thank them for kindly providing me with the details of their calculations for Sn^{2+} –O bonds. Subsequent discussions have done much to stimulate the development of the ideas presented in this paper.

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