

Novel Approach to the Concept of Bond-Valence Vectors

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Received June 16, 2007

A new approach to the old idea of deriving a bond-valence vector from the well-known bond-valence concept has been proposed. The foundation of the proposal is the previous electrostatic model in which bond valences are interpreted as electric fluxes. The outcome of this approach is actual vectorial quantities whose magnitudes are strictly but nonlinearly related to the scalar bond valences and are directed along the bond lines. It has been proved that the sum of all these bond-valence vectors drawn from a coordination center to its ligating atoms will be close to zero for the complete coordination sphere. Therefore, unlike the scalar bond valences, the obtained vectors provide information about the spatial arrangement of ligands. The geometrical consequences of the proposed bond-valence vector (BVV) model are analyzed for the geometries of the carbonates, phosphates, and five-coordinated organoaluminum compounds with CO_3 , PO_4 , and AlCO_4 skeletons, respectively, retrieved from the Cambridge Structural Database. For acyclic carbonates this BVV model allows one to predict the O–C–O angles with a mean absolute error of 1.0° using the empirical C–O distances only. Furthermore, this BVV model is able to quantitatively describe the strains in cyclic carbonates. The preliminary studies for NO_2E , PO_3E , and SO_3E systems with a strongly stereoactive lone electron pair (E) show that the model may serve as a quantitative description of the lone electron pair effect on the coordination sphere. A great advantage of the presented BVV approach is that the derived relation between a bond-valence vector, bond valence, and bond length is given by an uncomplicated equation allowing quick and simple computations, thus providing a new analytical tool for describing the geometry of a coordination sphere that may be applied for structure validation.

Introduction

Since the introduction of the bond number concept by Pauling¹ there has been continuous interest in the bond-valence (BV) model and its application for interpretation and prediction of bond lengths in various chemical systems in the solid state.² The well-established BV model operates with bond valence as a scalar quantity, and the bond valences of all bonds from a given atom sum to the valence of that atom. However, the scalar bond valences do not provide information about the spatial arrangement of ligands. Since, for both covalent and ionic bonds, a more strongly bonded ligand (greater bond valence) subtends a greater solid angle at the coordination center, it has already been postulated to transform the bond valence into a vector quantity which can be used to characterize the role of a ligand in the coordination

sphere.^{3–5} All existing concepts of a vectorial description of the coordination sphere postulate that (i) vectors drawn from a coordination center to its ligands have magnitudes equal (or proportional) to the corresponding bond valences and (ii) for a complete coordination sphere the bond-valence vector sum is close to zero.^{4,5} Nevertheless, in all models the bond-valence vectors are only arbitrarily derived from the scalar bond valences. In contrast, in this paper it is shown that use of a simple electrostatic model of bond valence gives a foundation to derive an actual vectorial quantity with a magnitude strictly but nonlinearly related (approximately by the quadratic function) to the scalar bond valence. The validity of the proposed bond-valence vector (BVV) model has been proven for a variety of molecules of the main-group elements, and the usefulness of this new approach for analysis of the coordination sphere geometry is presented.

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The correlation between the bond length (d_{ij}) between the i th and j th atoms and the valence of this bond (s_{ij}) is most often presented in an inverse exponential, negative power, or polynomial form. The most widely used empirical expression for calculation of s_{ij} has the form⁶

$$s_{ij} = \exp[(r_{ij} - d_{ij})/b] \quad (1)$$

where d_{ij} is the experimental bond length while r_{ij} and b are empirically determined constants for the given i - j bond. Brown tabulated these parameters for numerous bond types, and they are easily available on the Web.⁷ r_{ij} is equal to the length of a conceptual bond of a unit valence. When no experimental data are present, it is possible to estimate the r_{ij} value from the sum of atomic radii of the i th and j th atoms modified by an electronegativity-related correction term.⁸ The parameter b is generally treated as a 'universal' constant, often taken to be 0.37 Å.^{6,9} Nevertheless, one should be aware of the close correspondence between the b parameter and the bond-specific softness parameter. This justifies use of specific (individual) values of b to a given bond.¹⁰

A valuable physical interpretation of the bond-valence model has been provided by Brown and his colleagues.¹¹ Examination of the electrostatic field generated by ions was performed, starting from the ionic model of the bond. It has been shown that the Coulomb field around each ion could be naturally divided into localized regions (bonds) which are characterized by electric fluxes linking neighboring ions of opposite charge. The hypothesis that the fluxes are the same as the bond valences was proposed and verified. Brown and his colleagues consequently stated that Gauss' law is mathematically equivalent to the bond-valence-sum rule. Moreover, the bond-valence-electric flux equivalence is fulfilled regardless of the bond character, i.e., the degree of ionicity. Nevertheless, it was pointed out that such a simple electrostatic model describes the structure well only if the atoms carry a charge and are spherically symmetric, i.e., if the monopole term of the Coulomb field strongly dominates over the multipole terms. Thus, the model is expected to work well when the central atom is hard by means of Pearson's definition, whereas for soft centers with asymmetries in the distribution of electron density around the central atom the effects of the multipoles should be included in the model for the hypothesis to be fulfilled. This is a case of electronically strained structures represented by compounds with stereoactive lone pairs or transition-metal complexes comprising d^0 and d^1 cations as well as those with octahedral coordination that show Jahn-Teller distortions.

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Results

Bond-Valence Vector Model. Let us now consider the simplest, unstrained structural fragment comprising a coordination center without lone electron pairs (i.e., the atomic core) and surrounded by more electronegative, monodentate donor ligands. The space around the nucleus of the coordination center can then be roughly divided into two parts: the inner-electron part (core electrons) and the valence-electron part. Thus, a closed equipotential surface S embracing most of the inner shell electrons of the central atom can be defined assuming that the net charge enclosed in the surface is equal to the charge of the atomic core. Such a near-spherical surface has a radius close to the ionic radius of the given atomic core. For example, the radii of carbon or phosphorus cores cover the localization region of $1s^2$ and $1s^2 2s^2 2p^6$ closed shells, respectively. Thus, according to Brown's model, the electric flux, Φ_i , out of a closed spherical surface, S , obeys Gauss' law

$$\Phi_i = \oint_S \epsilon_0 \mathbf{E} \cdot d\mathbf{A} = Q_i \quad (2)$$

where Q_i is the charge of the core of the central i th atom, \mathbf{E} is the electric field, $d\mathbf{A}$ is a differential area element with an outward facing surface normal defining its direction, and ϵ_0 is the permittivity of free space. According to the model presented by Brown and his colleagues¹¹ the sphere S can be separated into bond regions S_{ij} characterized by the scalar electrostatic fluxes Φ_{ij} related to the s_{ij} valences of the i - j bonds

$$\Phi_i = \sum_j \Phi_{ij} = Q_i \quad (3)$$

where

$$\Phi_{ij} = \int_{S_{ij}} \epsilon_0 \mathbf{E} \cdot d\mathbf{A} = s_{ij} (3,4) \quad (4)$$

In an idealized case of spherical symmetry the electric field, \mathbf{E} , will be perpendicular to the sphere and almost the same in magnitude in each point, which leads to the equations

$$Q_i = 4\pi R_c^2 \epsilon_0 E_c \quad (5)$$

and

$$s_{ij} = A_{ij} \epsilon_0 E_c = \frac{A_{ij}}{4\pi R_c^2} Q_i \quad (6)$$

where E_c is the field on the sphere embracing the atomic core of radius R_c and A_{ij} is the area of the surface S_{ij} .

To find a vector that has the property of summing to zero I will consider integration of the electric field regardless of the direction of the surface, i.e., when $d\mathbf{A}$ is treated as a scalar. Thus, integration of the new vectorial quantity $d\mathbf{v} = \epsilon_0 \mathbf{E} dA$ over the whole sphere in the case of an idealized spherically symmetric field gives the zero vector

$$\mathbf{v}_i = \oint_S \epsilon_0 \mathbf{E} dA = \mathbf{0} \quad (7)$$

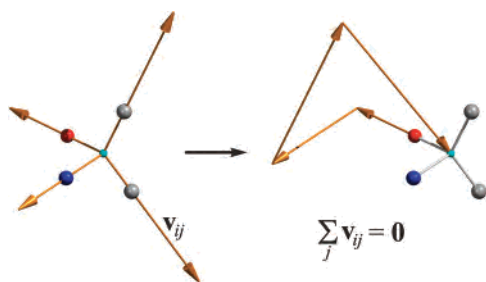


Figure 1. Schematic representation of a coordination center with assigned bond-valence vectors, \mathbf{v}_{ij} , and zeroing of the bond-valence vector sum for the case of tetragonal geometry.

Division of the sphere into the S_{ij} valence regions allows us to define individual bond-valence vectors \mathbf{v}_{ij} in an analogous manner

$$\mathbf{v}_{ij} = \int_{S_{ij}} \epsilon_0 \mathbf{E} \, dA \quad (8)$$

Thus, the resultant zero vector \mathbf{v}_i can be regarded as the sum over all \mathbf{v}_{ij} vectors, which represent bonds between the coordination center, i , and all ligating atoms, j , within the coordination sphere (Figure 1)

$$\mathbf{v}_i = \sum_j \mathbf{v}_{ij} = \mathbf{0} \quad (9)$$

The length of the \mathbf{v}_{ij} vector will be, therefore, directly connected with the bond-valence s_{ij} . However, due to the curvature of the surface S_{ij} the length of the \mathbf{v}_{ij} vector is not equal to the bond-valence s_{ij} . To derive the relation between s_{ij} and \mathbf{v}_{ij} it is reasonable to assume that the surface S_{ij} on the sphere is of a circular spherical cap shape. This is undoubtedly true for the case of linear two-coordinate systems but is only an estimation for higher coordination numbers. In the latter case the bond surface S_{ij} takes the form of a spherical polygon and in general can be asymmetrically arranged around the bond direction. Nevertheless, because of the difficulty in defining (in most cases) both the bond path and the bond surface, the following useful simplification has been introduced. It was assumed that the bond surface S_{ij} takes the form of a circular cap and is cut-out symmetrically around the bond direction on the spherical surface of radius R_c by a cone with the vertex located at the center of the sphere such that the area of the cap is equal to $s_{ij} \cdot 4\pi R_c^2 / Q_i$ (cf. eq 6). If \mathbf{E} is perpendicular to the spherical surface with constant magnitude ($|\mathbf{E}| = E_c$), then the integral in eq 4 can be written as

$$s_{ij} = 2\pi\epsilon_0 E_c R_c^2 (1 - \cos \vartheta_{ij}) = \frac{Q_i}{2} (1 - \cos \vartheta_{ij}) \quad (10)$$

where $2\vartheta_{ij}$ is the opening angle of the cone.

Consequently, according to eq 8 the bond-valence vector \mathbf{v}_{ij} is aligned along the i - j bond line to the negatively charged j th ligand and has a magnitude proportional to the area of the planar base of the cap

$$|\mathbf{v}_{ij}| = \pi\epsilon_0 E_c R_c^2 \sin^2 \vartheta_{ij} = \frac{Q_i}{4} \sin^2 \vartheta_{ij} \quad (11)$$

By eliminating the ϑ_{ij} value from both equations we easily get the final relation

$$|\mathbf{v}_{ij}| = s_{ij} \left(1 - \frac{s_{ij}}{Q_i} \right) \quad (12)$$

Summarizing the above-presented simplified electrostatic model the following theses are proposed. (i) The bond between the coordination center i and the more electronegative ligating atom j of s_{ij} valence can be represented by the bond-valence vector \mathbf{v}_{ij} of the length defined by eq 12 and directed from i to j . (ii) In stable symmetric coordination spheres the vector-sum of all these vectors tends to be zero vector (eq 9).

It should be clearly stated that the bond-valence vectors of the magnitude given by the eq 12 and the direction along the bond line are only an approximation of the actual vectors from eqs 8 and 9. The exact equations for the particular case in which the bond surface S_{ij} takes the form of a regular spherical polygon are presented in the Supporting Information. Examples of calculations performed according to both the exact equation and eq 12 show that the discrepancies between the obtained values are insignificant. Therefore, despite considerable simplifications, the proposed relations are reasonably well obeyed in practice as shown below.

Discussion

To provide a necessary test of the BVV model an analysis of selected molecules using empirical structural data was undertaken. It is obvious that eq 9 cannot hold for the electronically strained structures with asymmetry in the distribution of electron density in the core region when multipole terms are important nor for systems in which the coordination center has at least one lone electron pair in the valence shell. Moreover, one can expect a nonzero bond-valence vector sum for structures in which there are additional constraints introduced by steric factors (e.g., strained ring systems, congested coordination spheres with strong interligand repulsion) causing bond angles to be strained.

Linear AX₂ Molecules. In the particular case of simple two-coordinated unstrained linear molecules X-A-Y the relation presented in eq 9 is always satisfied, although two bond valences can be different. This relationship can easily be obtained by considering the equation

$$|\mathbf{v}_A| = |\mathbf{v}_{AX}| - |\mathbf{v}_{AY}| = s_{AX} \left(\frac{Q_A - s_{AX}}{Q_A} \right) - s_{AY} \left(\frac{Q_A - s_{AY}}{Q_A} \right) \quad (13)$$

The length of the resultant bond valence vector $|\mathbf{v}_A|$ equals zero if $s_{AX} + s_{AY} = Q_A$, that is, if the bond valence sum rule is fulfilled. It should be pointed out that while the bond valence vectors necessarily sum to zero, the same is not true of the traditionally defined valence vectors with magnitudes equal to the bond valence.

Three-Coordinated Molecules. In order to verify the applicability of the bond-valence vector method to three-coordinated centers, 70 structures of carbonate derivatives

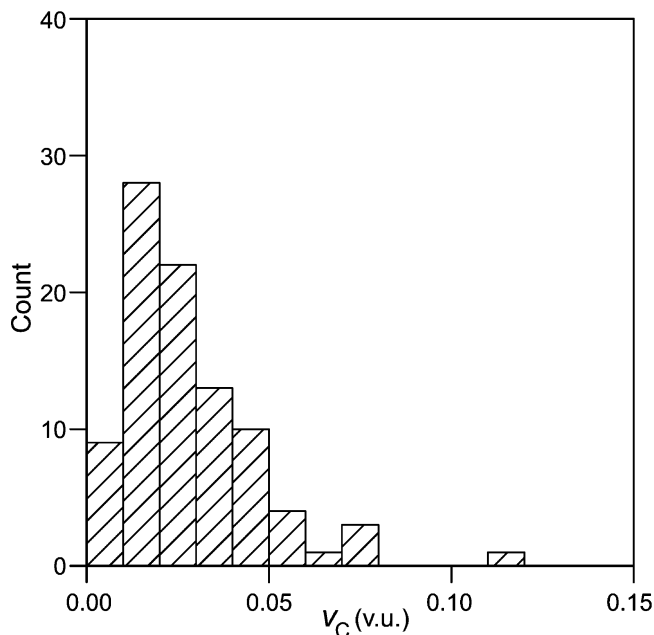


Figure 2. Histogram of the length of the resultant bond-valence vector, v_C , for carbonates.

collected in the CSD^{12,13} have been chosen. The set of crystal data concerning CO_3 skeletons was restricted to fragments without strains introduced by cyclic systems, including H-bridged ring motives. For all C–O bonds the bond valences were calculated using an exponential relation (eq 1) with parameters $r_{\text{C-O}} = 1.390 \text{ \AA}$ and $b = 0.37 \text{ \AA}$.⁶ The analyzed carbonates show diversified C–O bond valences ranging between 1.0 and 1.9 v.u. (valence units). All structural fragments are indeed planar, and the maximum observed deviation of the carbon atom position from the plane defined by the oxygen atoms (d_C) is 0.032 \AA . According to eq 12 the length of the bond-valence vectors v_{CO} and the resultant vector v_C were calculated by setting the carbon core charge $Q_C = 4$.

Figure 2 presents a histogram of the length of the resultant vector v_C whose quantities ought to be zero according to the bond-valence vector sum rule (eq 9). As expected, the majority of $|v_C|$ values (90%) is less than 0.05 and the maximum value 0.116. However, for vectorial quantities it is more informative to show their spatial distribution. For this purpose, the orientation of the resultant v_C vectors relative to the CO_3 skeleton were analyzed using the three-dimensional Cartesian coordinate system. For almost planar CO_3 moieties it was convenient to place the origin on the carbon atom and define three orthogonal axes as follows:

(12) (a) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *B58*, 380–388. (b) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B* **2002**, *B58*, 389–397.

(13) The CSD (version 5.27, Aug 2006) search was restricted to the structures containing the CO_3 skeleton with an acyclic carbon atom. Only structures with a R factor of less than 0.05, the mean $\sigma(\text{C-C}) \leq 0.01 \text{ \AA}$, and those that had no errors and no disorder were considered. The bond-valence-sum rule was checked, and three structures that showed a carbon valence-sum greater than 4.5 or less than 3.5 v.u. were rejected. In addition, crystal structures showing eight-membered hydrogen-bridged ring motives ($\text{CO}_2\text{H}\cdots\text{HO}_2\text{C}$) were manually excluded. The resulting data set comprises 70 entries with 90 CO_3 fragments.

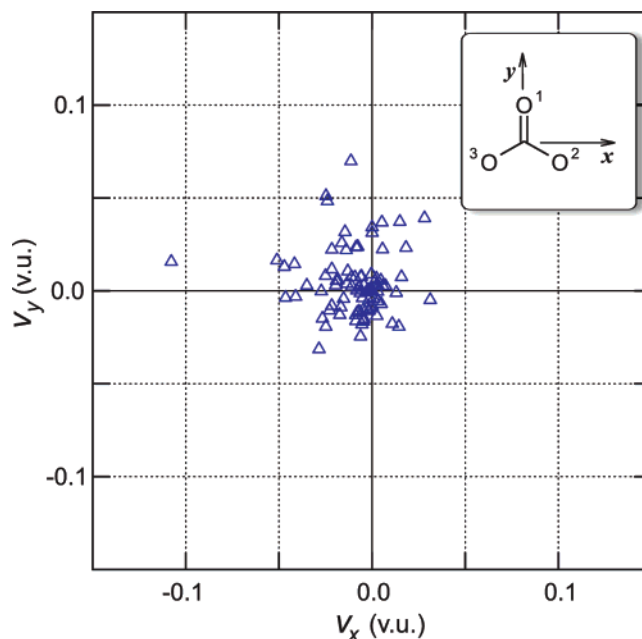


Figure 3. Distribution of the resultant bond-valence vectors, v_C , calculated for carbonates and projected on the CO_3 molecular plane with the y axis directed along the shortest C=O bond.

the y axis along the shortest C–O¹ bond, the x axis in the O¹CO² plane, and the z axis perpendicular to this plane being close to the molecule plane. The scatter plot presented in Figure 3 clearly shows that the resultant vectors v_C projected on the xy plane are distributed close to the origin, i.e., the zero vector.

It is obvious that the z component of resultant v_C vectors (v_{Cz}) correlate well with parameters describing deviation of CO_3 skeleton from planarity. Indeed, the simple linear relation between v_{Cz} and d_C of the form $v_{Cz} = 2.05(3)d_C$ was found ($r^2 = 0.985$, d_C in Å). One should notice that for planar molecular moieties eq 9 allows us to evaluate O–C–O bond angles using a simple trigonometric relation on the basis of bond valences only, that is, if eq 9 is obeyed the three bond-valence vectors must form a closed triangle from which the bond angles can be calculated. A comparison of the observed angles with calculated ones is presented in Figure 4. The obtained relation is linear with a regression coefficient $r^2 = 0.967$. The linear regression parameters, the slope and intercept, are equal to $0.997(11)$ and $0.4(14)^\circ$, respectively. In comparison, applying eq 9 for the bond-valence vectors calculated according to earlier models^{4,5} in which the length of the vector magnitude is equal to the appropriate bond valence also provides a linear relation (crosses in Figure 4), but the slope is much greater than 1 [$2.69(3)$] and the intercept equals $-202(3)^\circ$. It should be emphasized that in the view of the proposed relation 11, the earlier models^{4,5} are valid only if the second term is constant for all bonds, i.e., the bond valences do not differ significantly from one another.

The presented analyses demonstrate that the BVV model accurately describes the molecular geometry of carbonates and predicts the value of the O–C–O angles with a mean absolute error of 1.0° using the empirical C–O distances.

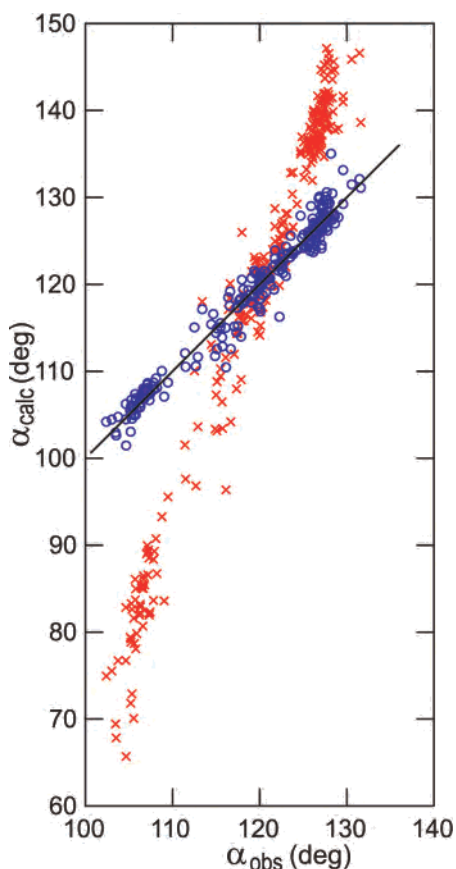


Figure 4. Scatter plots of the calculated (vertical axis) vs observed (horizontal axis) O–C–O angles for carbonates. The magnitude of the C–O bond-valence vector is (i) calculated according to eq 12 (circles) and (ii) equal to the appropriate bond-valence (crosses).

Sterically Strained Carbonates. A detailed analysis of the differences between predicted and observed angles for structures with strains introduced by cyclic systems allows us to divide the data into several subsets containing structures with various types of strains. Accordingly, one may distinguish four groups of molecules: cyclic carbonates comprising five- and six-membered rings, chelate carbonate complexes, and H-bonded dimeric bicarbonate anions (inset in Figure 5).^{12,14}

The scatter plot of the resultant bond-valence vectors \mathbf{v}_C projected on the xy plane (Figure 5) shows systematic deviation of v_{Cy} components (along C=O¹ “double” bonds) from zero for each group. The highest positive deviation of ~ 0.15 v.u. is observed for cyclocarbonates with a six-membered ring, indicating that the large ring strains cause a considerable increase (by an average 12°) in the value of the internal O²–C–O³ angle relative to unstrained acyclic systems. The deviation of v_{Cy} components from zero in five-membered cyclic carbonates and, accordingly, the ring-strain

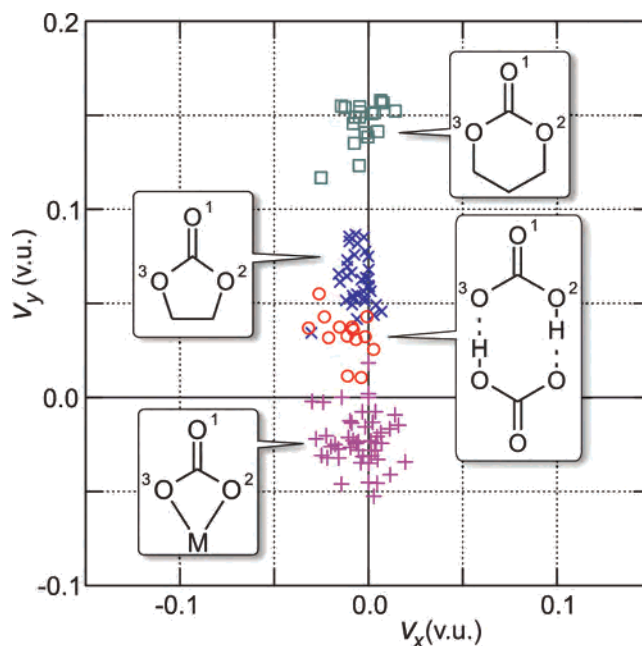


Figure 5. Distribution of the resultant bond-valence vectors, \mathbf{v}_C , projected on the CO₃ molecular plane with the y axis directed along the shortest C=O bond for (i) cyclic carbonates with six-membered ring (squares), (ii) cyclic carbonates with five-membered ring (\times), (iii) H-bonded dimeric bicarbonate anions (circles), and (iv) chelating carbonate groups ($+$).

magnitude are smaller than in the previous group (an average $v_{Cy} = 0.062$ v.u.), which is consistent, for example, with the evaluated ring-strain energy difference between five- and six-membered cyclic carbonates.¹⁵ For the hydrogen-bridged dimeric structures the effect is much less marked but still visible (an average $v_{Cy} = 0.033$ v.u.). This feature may be the result of short repulsive H···H contacts of about 2.2 Å. The significance of such interactions is often overlooked, but as stated by Steiner, they impose serious constraints on the geometry of cyclic H-bonded structures.¹⁶ The opposite propensity is observed in chelating carbonates. The interaction of both oxygen atoms with the metallic coordination center resulted in a slight decrease of internal O²–C–O³ angle, and hence, small negative values of the v_{Cy} components (mean $v_{Cy} = -0.022$) are observed.

Four-Coordinated Molecules. To confirm the validity of the BVV model for four-coordinated molecules the experimental points for the phosphate derivatives with a PO₄ skeleton exhibiting relatively wide spectra of bond valences were selected. As in the case of carbonates, only highly accurate structural data for acyclic phosphates were retrieved from CSD.^{12,17} The bond valences and bond-valence vectors for all P–O bonds were calculated using eqs 1 and 12, respectively, and setting $Q_P = 5$. The appropriate parameters,

(14) Crystal data for cyclic carbonates comprising five- or six-membered ring, chelating carbonate group, and H-bonded dimeric bicarbonate anions with eight-membered ring were retrieved from the CSD (version 5.27, Aug 2006). Structures were included if $R < 0.05$, the mean $\sigma(\text{C–C}) \leq 0.01$ Å, and the coordinate set is error free. The bond-valence-sum rule was checked, and structures that showed a carbon valence-sum greater than 4.5 v.u. were rejected. The resulting four data sets comprise 35(30), 19(19), 14(13), and 46(38) fragments (entries) for five-membered, six-membered, chelated, and H-bonded ring moieties, respectively.

(15) Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 162–168.

(16) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48–76.

(17) Crystallographic coordinates for the phosphate derivatives were retrieved from the CSD (version 5.27, Aug 2006). Structures were only included in this study if $R < 0.05$, the mean $\sigma(\text{C–C}) \leq 0.005$ Å, and the coordinate set is error free. The bond-valence-sum rule was checked, and two structures that showed a phosphorus valence-sum greater than 5.5 v.u. were rejected. In addition, crystal structures showing disorder were excluded. The resulting data set comprises 316 structures and 414 PO₄ fragments.

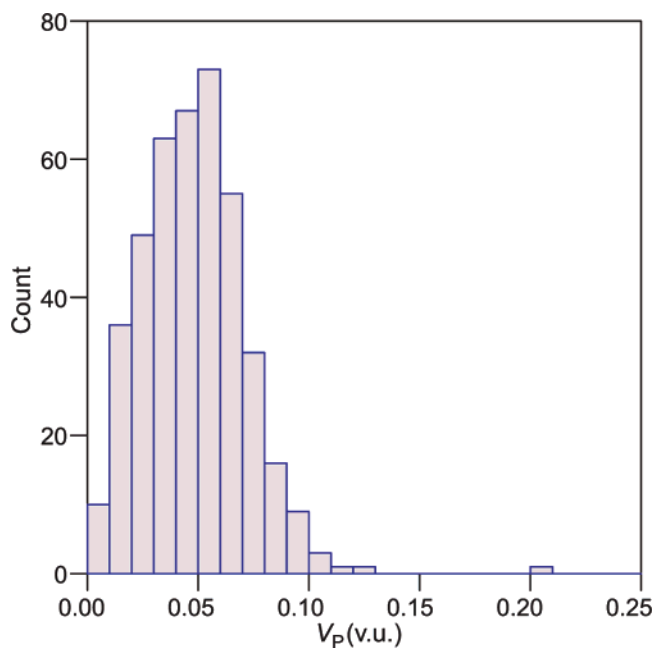


Figure 6. Histogram of the length of the resultant bond-valence vector, \mathbf{v}_P , for phosphates.

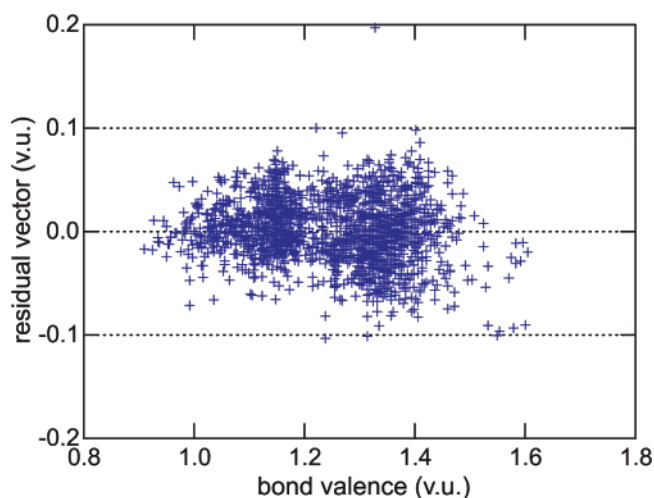


Figure 7. Scatter plot of the residual bond-valence vectors (δv_{Pj}) vs appropriate bond valence (s_{Pj}) for phosphates.

$r_{P-O} = 1.617 \text{ \AA}$ and $b = 0.37 \text{ \AA}$, were taken according to Brown and Altermatt.⁶ The frequency distribution of the calculated lengths of the resultant bond-valence vectors, \mathbf{v}_P , are presented in Figure 6, and almost all of the vectors are shorter than 0.1.

In order to clarify the presentation, the resultant \mathbf{v}_P bond-valence vector for each molecular moiety has been projected on the direction of each of the four P–O bonds. In consequence, for each molecular PO_4 fragment one obtains four residual vectors, δv_{Pj} , showing the magnitude of deviation along bond lines from zero predicted by the model. Figure 7 presents the scatter plot of δv_{Pj} versus the appropriate bond valence, s_{Pj} . In the case of 1656 P–O bonds, for significant variation of s_{Pj} values from 0.9 to 1.5 v.u. the spread of δv_{Pj} values around zero is relatively small and ranges ± 0.1 v.u. (esd = 0.032). Moreover, what is essential is that these two variables do not correlate ($r^2 = 0.01$) and

δv_{Pj} values are spread around zero with a normal distribution. Thus, the condition of zeroing of \mathbf{v}_P may be regarded as fulfilled. It is worth mentioning that the results obtained from the vectorial approach are generally in line with the correlations found by Murray-Rust et al. for deformed tetrahedral molecules of approximate C_{3v} symmetry that map S_N1 reaction pathways.¹⁸

Five-Coordinated Organoaluminum Complexes. In order to show the wide range of applicability of the proposed model, the case of heteroligand systems has also been analyzed. For this purpose, due to my particular interest in organoaluminum compounds, I chose five-coordinate aluminum complexes with CAIO_4 skeletons, i.e., monoalkylaluminum complexes with four ligating oxygen atoms. In such compounds the coordination sphere usually takes the intermediate form between the trigonal bipyramid and square pyramid with the carbon atom in equatorial and apical positions, respectively. Moreover, it is important to realize that such systems cannot be treated as unstrained structures due to the presence of various ring constraints, and thus, deviations from the model are expected. Nevertheless, these structures still serve as a reliable source of information.

Crystal data for 24 complexes served for further analysis.¹⁹ Bond valences were calculated using eq 1 with the following parameters: $r_{\text{Al-O}} = 1.630 \text{ \AA}$, $r_{\text{Al-C}} = 1.914 \text{ \AA}$,²⁰ and a common constant $b = 0.37 \text{ \AA}$. It has been confirmed that the chosen compounds obey the bond valences sum rule, and the sum of experimental bond valences for aluminum ranges from 2.7 to 3.1 v.u. The length of the bond-valence vector was calculated for each aluminum center. Surprisingly, even with the presence of structural strains the lengths of the resultant bond-valence vector \mathbf{v}_{Al} are short and in most cases (22 fragments) less than 0.1 v.u., whereas the maximum equals 0.142 v.u. The residual vectors $\delta v_{\text{Al}j}$ (i.e., the projection of the resultant vector \mathbf{v}_{Al} on the Al– X_j bond direction) for all bonds were calculated in the same manner as in the case of phosphates. The obtained results are presented in Figure 8 as a scatter plot of $\delta v_{\text{Al}j}$ vs $s_{\text{Al}j}$. As in the previous cases and despite the structural strains, $\delta v_{\text{Al}j}$ are close to zero and almost all of them are in the range of ± 0.1 v.u. From the point of view of the BVV model the Al–C bond plays the most important role in the coordination sphere since it has the most covalent character and thus the

(18) Murray-Rust, P.; Bürgi, H.-B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1975**, *97*, 921–922.

(19) Crystallographic coordinates for organoaluminum complexes were retrieved from the CSD (version 5.27, Aug 2006). Structures were included if $R < 0.075$ and the coordinate set is error free. Crystal structures showing disorder were excluded. The resulting data set comprises 24 structures and 25 AlCO_4 fragments.

(20) Owing to discrepancy between values reported for $r_{\text{Al-O}}$ parameter (1.620 and 1.644 \AA in ref 7 and 1.651 \AA in ref 9) and lack of data for the Al–C bond, the appropriate bond-valence parameters were calculated. For that purpose, high-accuracy structural data of Al^{III} complexes comprising AlO_6 , AlO_4 , and AlC_4 central skeletons were retrieved from CSD (version 5.28, Jan 2007, $R \leq 0.05$, $\sigma(\text{C-C}) \leq 0.005 \text{ \AA}$, no errors, no disorder). The resulting data sets comprised 35(27), 23(28), and 34(22) fragments(entries) for AlO_6 , AlO_4 , and AlC_4 moieties, respectively. Then the $r_{\text{Al-O}}$ and $r_{\text{Al-C}}$ values which minimized the sum of the squares of the difference between the expected valence of aluminum (3) and the valence calculated from the bond-valence sum were evaluated. The resulting $r_{\text{Al-O}}$ and $r_{\text{Al-C}}$ bond-valence parameters are equal to 1.630 and 1.614 \AA , respectively.

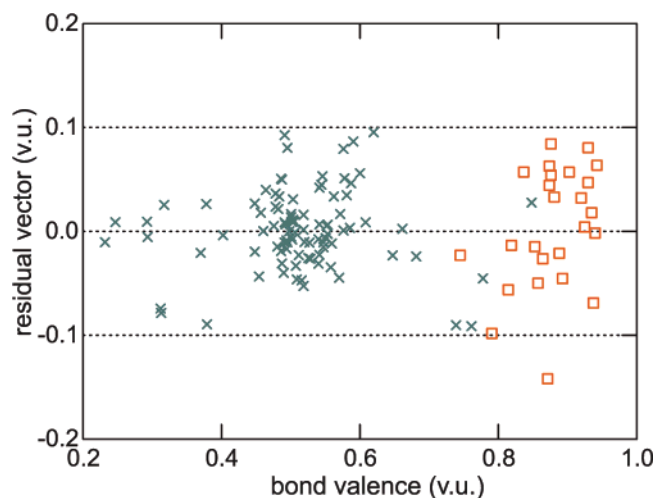


Figure 8. Scatter plot of residual bond-valence vectors (δv_{Aij}) vs appropriate bond-valence (s_{Aij}) for five-coordinated aluminum complexes with $CAIO_4$ skeleton. The squares and crosses correspond to Al–C and Al–O bonds, respectively.

highest bond valence (0.80–0.95 v.u.), although independent of the bond character (and bond valence) the residual vectors are small. Among all 24 studied structures one (MOTCAZ)²¹ exhibits an atypical TBP coordination with the carbon atom and an oxygen atom located in axial positions. In this particular case the resultant \mathbf{v}_{Al} vector is also very short and equals 0.026 v.u., which shows the versatility of this BVV model.

Stereoactive Lone Pairs. An additional comment is required for electronically strained structures, especially for the structures where the coordination center is comprised of a lone electron pair (LEP), which can be treated as a pseudo-ligand. Previously, Brown³ and Wang et al.²² described the stereochemical influence of LEP with the vectorial approach. In order to measure the influence of LEP on the coordination environments an appropriate vector called the eccentricity parameter was defined.²³ By analogy, the proposed BVV model may also deliver a vectorial description of the lone electron pair effect on the coordination sphere.

In order to show the way a lone pair is represented in the BVV model NO_2E , PO_3E , and SO_3E systems have been analyzed. Their selection is due to the fact that in these systems the lone electron pairs are strongly stereoactive. In this work only the preliminary results are presented because the detailed analysis is beyond the scope of this paper and requires a wider discussion. The core charges of nitrogen, phosphorus, and sulfur are taken as $5+$, $5+$, and $6+$, respectively. The resultant bond-valence vectors calculated from bond lengths and angles^{24,25} are plotted against experimental bond-valence sums (Figure 9). In all cases the variation of the resultant bond-valence vectors is rather small (esd is equal to 0.025 for NO_2E , 0.031 for PO_3E , and 0.057 for SO_3E). When the mean values of the resultant vectors (1.15, 1.15, and 1.29) are used to calculate the “lone electron

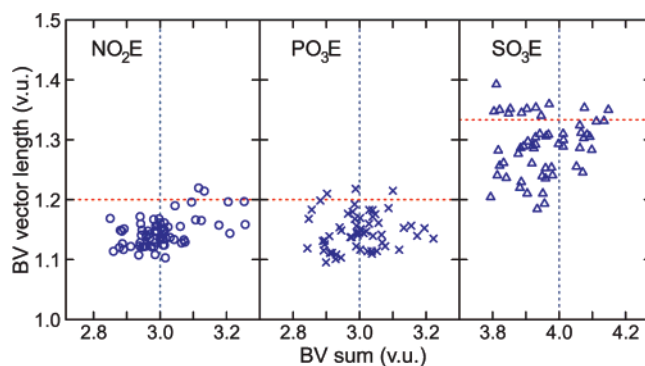


Figure 9. Length of the resultant bond-valence vector plotted against bond-valence-sum for NO_2E , PO_3E , and SO_3E polyhedra. Dashed lines denote the length of bond-valence vectors calculated for bond-valence equal to 2.

pair valences” according to eq 12, the respective values are obtained: 1.78, 1.78, and 1.87. They are close to the value of 2, i.e., the lone electron pair charge. The discrepancies between these values and 2 may be understood in terms of a stronger penetration of the atomic core region by non-bonding electrons than in the case of bonding ones. This conclusion is consistent with the VSEPR proposal that the lone pair is only a partial lone pair with some of its electron density in the valence shell and some in the core.²⁶ Therefore, I propose, similarly as for the bonds, to ascribe the appropriate electric flux to nonbonding electrons. In this sense the lone electron pair may be described by a valence close to 2, as it was proposed a long time ago by Brown,²⁷ and the corresponding lone-pair valence vector. It is noteworthy that the BVV approach may be used to describe the lone electron pair by a vector only when the LEP is strongly stereoactive because in such a case the system lone electron pair–atomic core may be described as a dipole. In other instances, for proper description, the higher multipoles must be taken into account. On this basis the BVV model may serve as a quantitative description of the lone electron pair effect, that

(24) Crystallographic coordinates for PO_3E and SO_3E skeletons were retrieved from the CSD (version 5.28, Jan 2007). Structures were included if $R \leq 0.05$ and the coordinate set was error free. Crystal structures showing disorder were excluded. Bond valences were calculated using eq 1 with the following parameters: $r_{P-O} = 1.630 \text{ \AA}$ (ref 6) and $r_{S-O} = 1.644 \text{ \AA}$ (ref 7). The bond-valence-sum rule was checked, and if the value differed by 0.30 v.u. or more from the expected oxidation states (+3 for P and +4 for S), then those structures were rejected. The resulting data sets comprise 58(31) and 56(47) fragments(entries) for PO_3E and SO_3E , respectively.

(25) Crystallographic coordinates for NO_2E skeletons were retrieved from the CSD (version 5.28, Jan 2007). Structures were included if $R \leq 0.05$, the mean $\sigma(C-C) \leq 0.005 \text{ \AA}$, and the coordinate set was error and disorder free. Since the previously reported bond-valence parameter $r_{N-O} = 1.361 \text{ \AA}$ for $N^{III}-O$ bonds (ref 6) considerably underestimates the bond-valence-sum of nitrogen, the r_{N-O} parameter which minimized the sum of the squares of the difference between the expected valence of nitrogen (3) and the valence calculated from the bond-valence-sum was estimated. Further, for each fragment the bond-valence-sum rule was checked, and if the value differed by 0.30 v.u. or more from the expected oxidation state of 3+, then those structures were rejected, and subsequently, a new r_{N-O} was evaluated. The final r_{N-O} value of 1.397 \AA was calculated using the data set of 54 entries containing 68 NO_2 skeletons.

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is, it can be used as a link between the bond-valence and the VSEPR models.²⁸

The present study does not deal with d- and f-element complexes since the description of d- and f-valence electrons requires special treatment and more sophisticated models. Additionally, a distortion of the core region of these elements from a spherical shape occurs,²⁹ whereas the sphericity of the central core is the main assumption of the BVV model.

Conclusions

A reasonable accuracy of the predicted geometrical relations with the experimental data proves the correctness of the BVV model (at least in the case of the studied systems) and usefulness of the simple electrostatic model of bond valence proposed by Brown and his colleagues.¹¹ The BVV model provides an analytical tool for describing the geometry

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of coordination spheres. It allows us to identify and quantitatively estimate both steric and electronic factors, which cause deformation of the “ideal” structure. In this sense, along with the bond-valence model, the BVV model may be applied for structure validation. A great advantage of this approach is that the relation between a bond length, bond valence, and bond-valence vector is shown by an uncomplicated equation allowing quick and simple computations.

Acknowledgment. This work was supported by the Warsaw University of Technology. The author gratefully thanks one of the reviewers for his constructive and stimulating comments.

Supporting Information Available: Equations for BVV magnitude for the case in which the bond surface takes the form of a regular spherical polygon are presented along with the comment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC7011809