

A new simplifying approach to molecular geometry description: the vectorial bond-valence model

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A method to describe, analyze and even predict the coordination geometries of metal complexes is proposed, based on previous well established concepts such as bond valence and valence-shell electron-pair repulsion (VSEPR). The idea behind the method is the generalization of the scalar bond-valence concept into a vector quantity, the bond-valence vector (BVV), with the innovation that the multidentate ligands are represented by their resultant BVVs. Complex n -ligand coordination spheres (frequently indescribable at the atomic level) reduce to much simpler ones when analyzed in BVV space, with the bonus of a better applicability of the VSEPR predictions. The geometrical implications of the BVV description are analyzed for the cases of $n = 2$ and 3 ($n =$ number of ligands), and the validity of its predictions, checked for a large number of metal complexes.

1. Introduction

In the structural study of coordination compounds, many attempts have been made to find a theory capable of describing (and even predicting) the binding behaviour of different types of ligands around the corresponding metallic centres. Almost all of these endeavours fall into two main categories: those centred in the metal–ligand interaction, with good achievements in the description of bond lengths but with little to say about the spatial distribution of ligands (Brown, 1994); and, on the other side, those which through the study of ligand–ligand (or electron pair) repulsion try to explain their relative disposition around the metal centre, but disregard the relation to the centre itself (Gillespie, 1970; Robinson *et al.*, 1999). Although the latter approach has been the most widely used to describe the metal environments in coordination complexes (probably through the valence-shell electron-pair repulsion model, VSEPR), both points of view have produced meaningful results and have introduced a number of fruitful and familiar concepts in the structural chemist's language: bond valence, coordination sphere *etc.* However, and in spite of their achievements, the theories so far developed encounter some limitations when the ligands involved are not monodentate and the steric limitations introduced by multidentate ligands appear. In these cases the coordination descriptions or predictions begin to deviate considerably from theoretical expectations and attempts to relate real geometries to predicted polyhedra usually become difficult or impossible.

Looking for a phenomenological (but at the same time unified) description which would allow merging of the most important aspects of both approaches we started a systematic study of the coordination geometries of mono- and polydentate ligands, mainly in complexes with group 12 cations (the ones with which we usually deal), but the conclusions

found can be readily extended, with at most minor modifications, to other cations.

Our long-standing experience with group 12 metal complexes containing polydentate ligands had shown us that their adherence to the bond-valence sum rule $\sum_i s_i = V$ (the sum of the bond valences adds up to the metal valence; Brown, 1994) is, at best, fair. The rule is frequently obeyed rather loosely and the coordination polyhedron is hard to describe when polydentate ligands (with their intrinsic restraints imposed by chelation *etc.*) are present.

The so-called ‘Sum Rule’ is a scalar condition, in which knowledge of the particular arrangement of ligands in space is disregarded in principle. However, it is almost intuitive that this spatial information ignored by the model (*viz.* the bunching of donors in a polydentate ligand) ought to be describable through some kind of directional parameter, such as a vector. The idea of vector bond valences is not new: in an early paper Brown (1988) used them as a measure of the distorting influence of lone electron pairs and, more recently, Müller *et al.* (2003) made use of a similar idea. In this paper, however, we apply the concept to the so-far unexplored universe of chelating ligands. The simplifications achievable through this approach in the description of the (very often complex) coordination spheres they give rise to is basically the scope of this paper.

2. The model

On a strictly phenomenological basis, we propose the following.

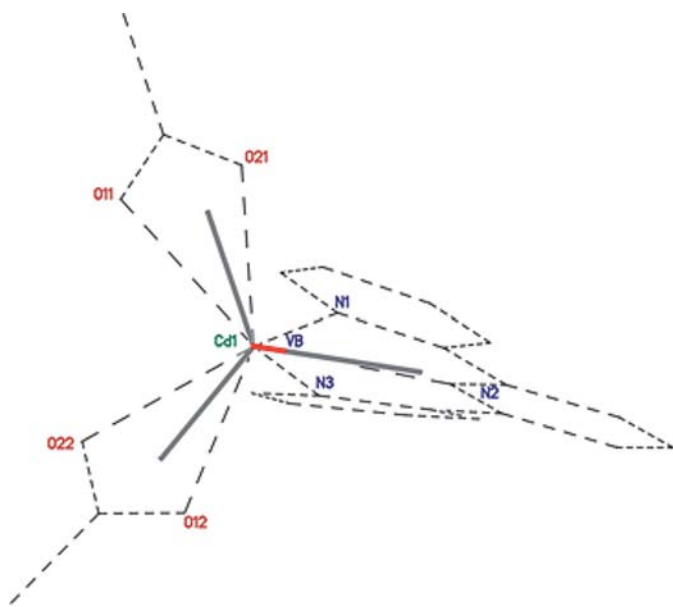


Figure 1
Schematic representation of a three-ligand seven-coordinated complex and its reduction to a simple, planar pseudo-trigonal description using the VBV model.

2.1. Vector bond valence (VBV) or vector sum, postulate

‘Let s_i be a vector directed from the metal to the A_i th coordinated atom, with a length equal to the absolute value of the corresponding ‘bond valence’ s_i , representing the strength of the interaction. Then, in any stable coordination sphere the sum of all these vectors is nearly zero, *i.e.* the condition $\sum s_i \simeq 0$ holds.’

3. Results and analysis

We present some data confirming the validity of this postulate and shall try to show its richness of content, which adds a complementary, and in some sense superseding, condition to the well known charge-balance requirement $\sum_i s_i = V$ imposed by the bond-valence theory.

Before dealing with the quantitative analysis,¹ we discuss in qualitative terms the beautiful simplicity with which this almost naïve vector approach can ‘explain’ many of the findings of other previous ones, such as VSEPR and the recent ‘idealized ionic model’ of Preiser *et al.* (1999) which provides a theoretical foundation for the bond-valence model.

The fact that a strong bond ‘expels’ from its vicinity the neighbouring ones (due to the electron density involved in the bond) is reflected in the vector approach in the fact that in order to compensate for a long vector (= strong interaction = short bond), the remaining shorter vectors (= weaker interaction = longer bond) have to ‘bunch’ trying to oppose it, so as to allow for vectorial cancellation.

The model proposes in quite a natural way a simple treatment of coordination spheres which include multidentate, but ‘directional’, ligands. Here we use the term ‘directional’ as opposed to clathrate, which for the present discussion would operate as an ‘omni-directional’ ligand embracing the cation without a preferred orientation, and which we exclude from our analysis. Inspection of a large number of structures including these ‘directional’ ligands suggests that the way in which they arrange in space might be explained if they behave as ‘fuzzy’ centres, or electron density conglomerates. In trying to find a representative ‘direction of coordination’ for these conglomerates it would be reasonable to choose a vector pointing towards the bulk of the charge distribution, perhaps towards something like its ‘centre of charge’. However, that is precisely what the vectorial sum $\chi = \sum s_i$ of the bond-valence vectors corresponding to the individual bonded atoms represents. As a bonus, by representing the n ligands present in the complex by their resultant vectors χ_j ($j = 1, n$), the frequently indescribable polyatomic coordination sphere reduces to a much simpler one, sometimes adorned with a symmetry which the complexity of the original problem tends to obscure.

¹ The bond valence of a donor atom A_i interacting with a metal atom M is given by the expression $s_i = \exp[(R_o - R_i)/b]$, where s_i : bond valence, R_i : bond length between atoms A_i and M , and R_o and b are experimental parameters, the former being the length of a bond of unit valence. We have used the R_o and b parameters compiled by Orlov & Popov (2002) and originally elaborated by Brown (2002). For those cases not covered therein, the commonly accepted value of 0.37 has been used for b , while R_o was calculated according to O’Keefe & Brese (1991).

Application of this model led us to a surprising simplification of the treatment of the coordination of many compounds studied so far, which had resisted efforts to provide a reasonable description of their geometry. In the following discussion the bold type refers to a vector, normal type to a scalar; indices i run over atoms, and indices j run over ligands.

Fig. 1 illustrates the way in which a three-ligand cadmium complex [Cd(tpy)(Ac)₂·2H₂O] (Harvey *et al.*, 2005) displaying a hepta-coordinated and geometrically hard-to-describe metal centre reduces to a much simpler pseudo-trigonal scheme which fulfills the VSEPR model. The individual χ_j moduli (in grey in Fig. 1) are 0.58, 0.49 and 0.50. The small residual sum vector ($|\Sigma_j \chi_j| = 0.11$, in red in Fig. 1) shows that compliance to the rule is not strict. On the other hand, the planarity of the set of three vectors is almost perfect, as assessed by the sum of the internal angles, 360.0 (1)°

As the original bond-valence model itself might present some limitations in its applicability (for example when electronic distortions are present), we felt it more appropriate to validate our VBV postulate through complexes of group 12 metals (Zn^{II}, Cd^{II}, Hg^{II}), in order to avoid disrupting distortions as well as sterically active free electron-pair effects. As a way to counterbalance any bias introduced by this single group selection, we included Ni^{II} as a fourth probe in the checking procedure.

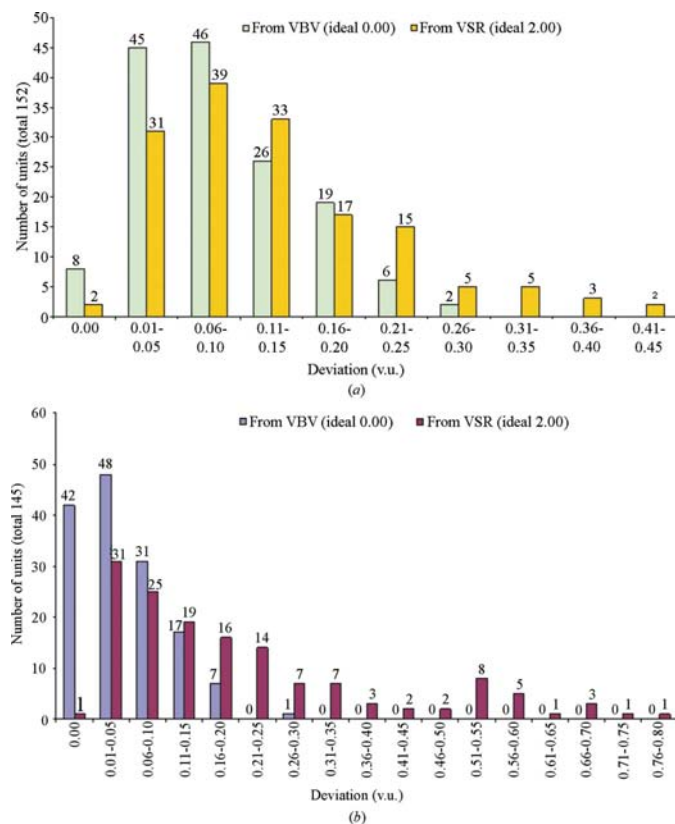


Figure 2 Two-ligands case: deviations from ideal values for the scalar and vectorial bond-valence sum: (a) Group 12 metals; (b) Ni.

Even with this restriction, a thorough confirmation of such a general postulate presents a formidable task. In this first presentation we have limited ourselves to the analysis of a reduced number of donor atoms (N, O and S) and to a small number of ligands ($n = 2$ or 3, although allowing for any possible chelation order). The case examples were single cation monomeric structures taken from the 2004 edition of the Cambridge Structural Database (CSD; Allen, 2002) that had been refined to $R < 0.075$ and had no error flag. There were 152 molecules with $n = 2$ and 98 with $n = 3$ for group 12 metals (Zn^{II}, Cd^{II}, Hg^{II}), and 146 with $n = 2$ and 74 with $n = 3$, for Ni^{II}.

Figs. 2 and 3 present histograms of the quantities $t = \text{abs}(\Sigma_i s_i - V)$ and $r = |\Sigma_j \chi_j|$ for $n = 2$ and $n = 3$, respectively, both of which ought to be zero: t according to the Bond Valence Theory and r based on our vector bond-valence postulate. Even though the quantities represent different (though related) concepts, the condition of the vanishing modulus derived from the latter is better fulfilled.

The most surprising results came from the geometrical implications of this fulfillment, which in both cases would imply very simple and readily verifiable consequences: for $n = 2$, a nil resultant would indicate the presence of collinear, opposite ligands (measurable by an angle between χ_j vectors

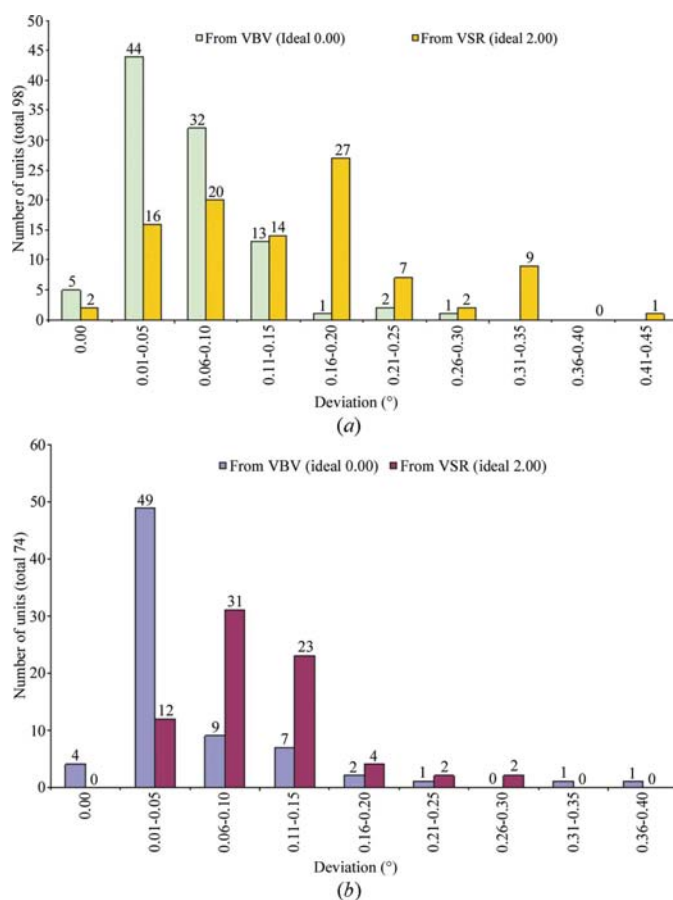


Figure 3 Three-ligands case: deviations from ideal values for the scalar and vectorial bond-valence sum: (a) Group 12 metals; (b) Ni.

of 180°), and for $n = 3$ strictly coplanar ones (as measured by a sum of angles to 360°). Figs. 4 and 5 present histograms of the distribution of the parameters measuring these geometrical characteristics: the deviation from 180° for the angle between ‘opposite’ vectors for $n = 2$ (Fig. 4), and the deviation from 360° for the sum of adjacent angles in the case of $n = 3$ (Fig. 5).

Even though deviations from ideal values in both cases cannot be directly compared, the fact that those for $n = 2$ appear to be larger than those for $n = 3$ seems to be a consequence of the latter case having more degrees of freedom: while the residual $\Sigma_j \chi_j$ vector can in principle be modified by changes in the angles without disturbing the coplanarity and *vice versa*, in the case of $n = 3$, for $n = 2$, there is no way to eliminate any eventual difference between the moduli of the intervening χ_j vectors through the modification of their orientations. Therefore, in the case of group 12 cations, while 98.0% of our $n = 3$ universe (96/98 cases) present a sum of inter χ_j angles in the range $359\text{--}360^\circ$, for $n = 2$ the median is 175° . Similar values can be found for the Ni^{II} complexes: for $n = 3$ all the analyzed cases (74) are in the range $359\text{--}360^\circ$, while for $n = 2$ (146 cases) the median is 177.4° .

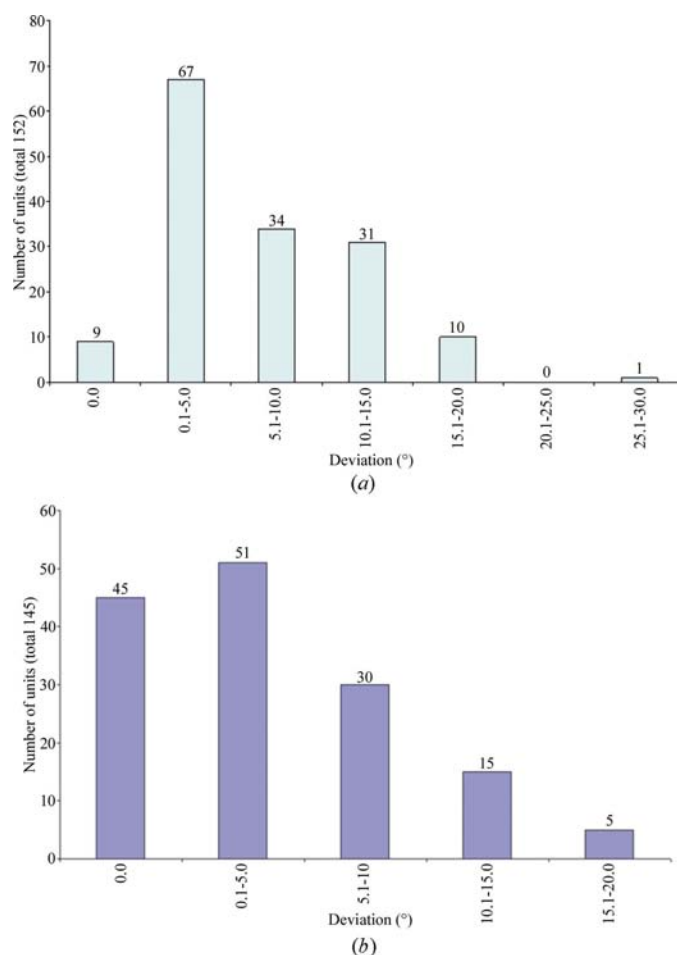


Figure 4
Two-ligands case: deviation from 180° of the inter bond-valence-vector angle: (a) Group 12 metals; (b) Ni.

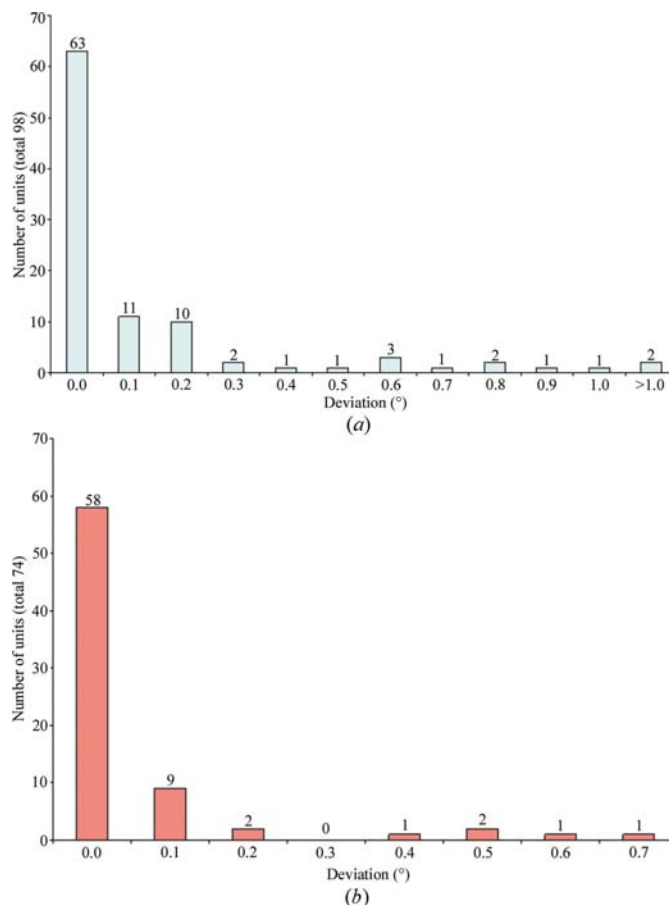


Figure 5
Three-ligands case: deviation from 360° of inter bond-valence-vector angles sum: (a) Group 12 metals; (b) Ni.

4. Conclusions

The present proposal that the ‘bond valence’ could be considered as a vector quantity able to characterize each multidentate ligand in a complex by its resultant vector – a proposal incorporating both the bond-valence and the VSEPR models – presents two main advantages: first it allows an easy geometrical description of the coordination sphere even when complex multidentate ligands are present; second, it furnishes an analytical tool for the analysis of interactions and packing effects, sometimes providing a simple, ‘ideal’ geometry to be used as a reference.

In the present paper the usefulness of the proposal has been proved for a subset of metals for which the principles of the original bond-valence theory was expected to apply (Zn^{II} , Cd^{II} , Hg^{II} , Ni^{II}) and in the simplest cases ($n = 2, 3$), where the computational tools needed could be provided by the authors’ limited expertise.² Extension of the proposal to more complex situations ought to be explored in order to have a more definite view of its real capabilities.

² The very simple programs devised for the calculations are available on request from the authors.

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