

New Bond-Valence Sum Model

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(Received 9 September 1996; accepted 3 June 1997)

Dedicated to Professor H. A. O. Hill on the occasion of his 60th birthday

Abstract

A new expression is devised empirically to accommodate zero and some negative oxidation states in the bond-valence sum approach. The method is worked out in detail for a number of homoleptic copper and nickel complexes of various coordinating atoms in several oxidation states of the metals. An implication of the expression is a linear variation between $1/r_{\text{eq}}$ and $1/r_{\text{ax}}$ in octahedral MX_6 moieties, where r_{eq} and r_{ax} are, respectively, the average equatorial and axial bond lengths. This is verified in $\text{Cu}^{2+}X_6$ chromophores for $X = \text{F}, \text{O}, \text{N}$ and S . The usefulness of the new expression in assessing the compatibility of a coordination sphere with an oxidation state of a metal ion is demonstrated by exemplary applications to some inorganic complexes, azurin and urease.

1. Introduction

A chemical structure can be visualized as a network of stick-like bonds connecting ball-like atoms. A quantum mechanical support for such a 'ball-and-stick' model originates from Bader's theory of atoms in a molecule (Hati & Datta, 1992, and references therein). Such a picture is very helpful to a chemist since from X-ray crystal structure determinations one can learn only about the shape of a molecule in a crystal. The network can be finite as in discrete molecules or infinite as in extended solids. In such networks every atom is assumed to be bonded to its neighbouring atoms. The number of such bonds around a given atom i is its coordination number n . Bond valence v is defined as the oxidation number (or valence) V of an atom per bond. For an atom i the relation between V and v can be written as

$$V_i = \sum_j^n v_{ij}, \quad (1)$$

where j symbolizes an adjacent atom. The quantity V is also known as the bond-valence sum (BVS). The concept of bond valence was originally introduced by Pauling (1929, 1947). Subsequently, it has been developed by several workers (Donnay & Allmann, 1970, and

references therein; Donnay & Donnay, 1973; Brown, 1978, and references therein; O'Keeffe, 1989, and references therein; Brown, 1992, and references therein; Brese & O'Keeffe, 1991).

It has been realized from the beginning that v_{ij} bears an inverse relation with the distance (r) between two atoms i and j – a shorter bond implies higher v_{ij} , while a longer bond indicates lower v_{ij} . However, the exact relation between v_{ij} and r_{ij} is not yet known. Several empirical forms have been suggested over the years (Donnay & Allmann, 1970, and references therein; Donnay & Donnay, 1973; Brown & Shanon, 1973; Brown & Wu, 1976, and references therein; Brown, 1978, and references therein; O'Keeffe, 1989, and references therein; Brown, 1992, and references therein; Brese & O'Keeffe, 1991; Urusov, 1995, and references therein). The currently accepted one is

$$v_{ij} = \exp[(r_o - r_{ij})/b], \quad (2)$$

where r_o is a parameter characteristic of the bond between the i and j atoms under consideration (Altermatt & Brown, 1985; Brown & Altermatt, 1985; O'Keeffe & Brese, 1991; Urusov, 1995) and b an empirical constant. In (2) r_o and r_{ij} are expressed in Å. The value of b is usually taken as 0.37 Å (Urusov, 1995, and references therein). Equation (3)

$$V_i = \sum_j^n \exp[(r_o - r_{ij})/0.37], \quad (3)$$

the combination of (2) and (1) with $b = 0.37$ Å, helps in elucidating the interplay between oxidation state and bonding geometry of a central atom in a sort of quantitative manner.

The bond-valence model based on (3) was originally developed for use in ceramic materials, which are extended ionic solids. However, recently its applicability in discrete metal organic compounds (*i.e.* inorganic complexes) have been examined by several workers (Thorp, 1992; Liu & Thorp, 1993; Pidcock, Collison & Garner, 1993; Scarrow *et al.*, 1994, 1996; Butler & Clague, 1995; Hati & Datta, 1995; Shu *et al.*, 1995;

Garner, Collison & Pidcock, 1996). The method has been transformed into the bond-valence sum (BVS) model focusing on the immediate vicinity of the metal atom only, since there are limitations (*vide infra*) to the applicability of the full bond-valence model to the associated organic fragments. It has been found that the BVS method works well for the organic coordinated metals. These studies have been extended to probe the nature of the metal sites in some metalloproteins and -enzymes by analysing the extended X-ray absorption fine structure (EXAFS) spectroscopic data, where no X-ray crystallographic works are available, with considerable success. Equation (3) can also be utilized to estimate ideal bond lengths for a particular metal ion in a desired coordination geometry (Sironi, 1995) and in some limited situations to resolve any ambiguity involved in the oxidation state of a metal ion with its coordination geometry known from X-ray crystallography (Duan, Tian, Lu & You, 1995). Still, the model, as we have pointed out elsewhere (Hati & Datta, 1995), has several deficiencies. The most significant is that it cannot be applied to metal complexes where the oxidation state of the metal is ≤ 0 . However, at present, a number of inorganic/organometallic compounds are known with zerovalent metals and in many complexes, such as $\text{NaCo}(\text{CO})_4$, $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5(\text{dioxane})$ etc., the oxidation states of the metals involved are considered to be negative (Huheey, 1983a; Elschenbroich & Salzer, 1992). Consequently, a suitable form of (3) is much needed. We have now developed a new relation between V_{ij} and r_{ij} empirically in order to tackle oxidation states ≤ 0 . This we describe here together with its implications and applications.

2. A new expression for BVS

Rather than describing the decrease of v_{ij} with the increase in r_{ij} as an exponential function of r_{ij} , we assume v_{ij} to be a linear function of $(r_{ij})^{-N}$, where N is an adjustable constant. This is not new. Earlier, several workers have considered such a functional form (Pauling, 1929, 1947; Brown & Shannon, 1973; Brown & Wu, 1976). Here we introduce an additional explicit dependence of v_{ij} on the coordination number n of the atom i , the implications of which will be clear later on. We start with a general empirical expression of v_{ij} of the type denoted by

$$v_{ij} = (1 + K'/n)[R_{K,K'}/(r_{ij})^N] - K/n. \quad (4)$$

In (4) $R_{K,K'}$ is the new bond-valence parameter whose value depends on the constants K and K' ; r_{ij} is expressed in Å. From (1) and (4), with a little manipulation, we obtain (5), which can be applied when $V_i > -K$

$$V_i + K = (1 + K'/n) \sum_n R_{K,K'}/(r_{ij})^N. \quad (5)$$

The purpose of employing the constant K in (4) and consequently in (5) is to add a constant shift to the actual oxidation number V on the left-hand side (LHS) so that the LHS becomes a definite positive quantity even when $0 \geq V > -K$. This artificial shift is necessary since the quantity on the right-hand side (RHS) can have only positive values.

At this point, it is imperative to discuss how negative the oxidation state of an atom can be in reality, *i.e.* what value of K will be appropriate to assume here. Very recently we have demonstrated from polarizability (static electric dipole) considerations that a free atom in the gas phase can bear a maximum of only 1.74 units of negative charge (Hati & Datta, 1996). Miller (1990) has shown that molecular polarizability can be expressed as a sum of the polarizabilities of the constituent atoms (the effect of hybridization is included). Thus, our work taken together with that of Miller indicates that V of any individual atom in a discrete molecule can only be ≥ -1.74 . Since it is not customary to discuss in terms of fractional oxidation state, we assume that the oxidation state of an atom in a discrete molecule cannot be less than -2 . Accordingly, we set a value of K to be 4 (which is slightly higher than 2) to have the LHS of (5) sufficiently positive, even when $V_i = -2$. In this context we feel that compounds such as $\text{Na}_3\text{Re}(\text{CO})_4$ or $\text{Na}_4\text{Mo}(\text{CO})_4$, where formally the oxidation states of the metals are implicated to be below -2 , should be viewed with suspicion as far as the assignment of the oxidation state is concerned; it is possible that some amount of negative charge is distributed over the carbonyl moieties. In this article we shall deal with discrete molecules only and not with any extended solids.

With $K = 4$, we have applied (5) to a number of homoleptic copper and nickel complexes in various oxidation states of the metals to optimize the values of K' and N . The criterion for optimizing these quantities has been the minimization of the standard deviation in the $R_{K,K'}$ value for a given atom pair (i and j) derived by the least-squares procedure. Our experience is that as N increases, K' decreases; K' becomes 0 when $N \geq 6$. Thus, for $N = 6$, (5) becomes

$$V_i + 4 = \sum_j^n R_{4,0}/(r_{ij})^6. \quad (6)$$

We have found that for a given combination of N and K' , the standard deviation in the resultant $R_{K,K'}$ value for a particular atom pair decreases as K approaches 0. Thus, (7) gives better results than (6)

$$V_i = \sum_j^n R_{0,0}/(r_{ij})^6. \quad (7)$$

Equation (7) is essentially the same as that recommended by Brown & Wu (1976) for the metal oxides which are extended solids. With $K = 4$, the best reproduction of the known oxidation states of copper and nickel complexes

Table 1. Bond-valence parameter (R) for various bonds

n is the number of structures used for optimizing the corresponding R . Standard deviations are given in parentheses, unless otherwise specified.

Bond	n	R (Å)	V
Cu ⁰ —C	2	0.393 ± 0.017†	0.008 ± 0.179†
Cu ⁺ —C	6	0.427 ± 0.023†	0.949 ± 0.259†
Cu ⁺ —N	54	0.431 (7)	0.997 (98)
Cu ⁺ —O	9	0.432 ± 0.018†	1.092 ± 0.258†
Cu ⁺ —P	5	0.482 ± 0.022†	0.998 ± 0.213†
Cu ⁺ —S	33	0.489 (5)	1.008 (73)
Cu ²⁺ —N	65	0.496 (6)	2.006 (85)
Cu ²⁺ —O	39	0.482 (5)	1.989 (70)
Cu ²⁺ —F	13	0.466 (3)	1.996 (41)
Cu ²⁺ —S	29	0.566 (6)	1.964 (85)
Cu ³⁺ —N	3	0.548 ± 0.007†	2.998 ± 0.093†
Cu ³⁺ —O	3	0.538 ± 0.077†	3.072 ± 0.213†
Cu ³⁺ —S	7	0.651 ± 0.018†	3.040 ± 0.173†
Ni ⁰ —C	9	0.309 ± 0.009†	0.031 ± 0.140 †
Ni ⁰ —N	3	0.339 ± 0.009†	0.066 ± 0.185†
Ni ⁰ —P	4	0.360 ± 0.013†	0.003 ± 0.135†
Ni ⁰ —S	4	0.373 ± 0.020†	0.013 ± 0.077†
Ni ⁺ —C	1	0.381	1.002
Ni ⁺ —N	6	0.414 ± 0.017†	1.001 ± 0.196†
Ni ⁺ —S	1	0.450	1.000
Ni ²⁺ —C	5	0.501 ± 0.006†	1.995 ± 0.035†
Ni ²⁺ —N	38	0.485 (6)	2.030 (105)
Ni ²⁺ —O	37	0.473 (4)	1.979 (74)
Ni ²⁺ —S	32	0.545 (4)	1.965 (97)
Ni ³⁺ —N	4	0.539 ± 0.024†	3.007 ± 0.066†
Ni ³⁺ —S	3	0.625 ± 0.025†	2.998 ± 0.027†
Ni ¹⁻ —C	—	0.206‡	—

† Not standard deviation; the range within which all the values lie. ‡ Extrapolated value (see text and Fig. 1).

have been obtained when $N = 1$ and $K' = 20$. Thus, we propose (8) as a general relation between V_i and r_{ij} , where $R = R_{4,20}$

$$V_i + 4 = (1 + 20/n) \sum_j^n R/r_{ij}. \quad (8)$$

In principle, (8) can be applied to any atom. Here we have estimated the R values for several $M-L$ (M : metal; L : binding atom of a ligand) bonds involving Cu and Ni in oxidation states 0–3 (Table 1) from the reported X-ray structures of appropriate homoleptic complexes (except for Cu³⁺—O, Ni⁰—N and Ni^{0/1+}—S bonds). For Cu³⁺—O, Ni⁰—N and Ni^{0/1+}—S bonds, we have not found any homoleptic compound with known structure. The R value of the Cu³⁺—O bond has been estimated from the few available structures of Cu³⁺N_xO_y chromophores, with separately determined $R(\text{Cu}^{3+}\text{—N})$. From some structurally characterized Ni⁰N₂C₂, Ni⁰NP₃ and Ni⁰S_xP_yC_z moieties the $R(\text{Ni}^0\text{—N})$ and $R(\text{Ni}^0\text{—S})$ have been calculated with prior knowledge of $R(\text{Ni}^0\text{—C})$ and $R(\text{Ni}^0\text{—P})$. At present, to our knowledge, the structure of only one nickel(I) complex with a Ni¹⁺—S bond is known; the ligand is a diphenyldi-*p*-tolyl 21-thiaporphyrin (Latos-Grazynski, Olmstead & Balch, 1989). The r_{ij} values of this complex have been used to evaluate

$R(\text{Ni}^{1+}\text{—S})$ with known $R(\text{Ni}^{1+}\text{—N})$. Most of the crystallographic data pertaining to our present study have been collected at random from the recent literature. Structures having disorder have been carefully avoided. As stated above, we have also avoided extended solids to the extent possible. A total of 415 structures have been analysed to optimize the R values; all the relevant bond distances and references are given in Tables S1 (copper complexes; supplementary material) and S2 (nickel complexes; supplementary material).† With the R values listed in Table 1, the oxidation numbers calculated for all the 415 complexes except one [(NET₄)₂Ni(S—Ph)₄], where Ph—S⁻ is the thiophenolate anion and NET₄⁺ the tetraethylammonium cation] are found to lie strictly within ± 0.25 valence units of the actual ones (see Tables S1 and S2). In metal oxides and halides, which are extended solids, (3) usually gives rise to an error of ± 0.10 valence units; in fact, if the average deviation in such a system exceeds 0.2 valence units, the structure is unstable and transforms to a lower symmetry or the structure is wrong (Brown, 1992). However, such high accuracy is lost in the type of coordination complexes considered here (Tables S1 and S2); in such inorganic complexes, (3) reproduces the actual oxidation numbers within ± 0.40 valence units (Hati & Datta, 1995). In our random sampling we have encountered two examples of Cu⁺N₂ chromophores (Ehlert, Retting, Storr, Thompson & Trotter, 1990; Kitagawa, Munakata & Tanimura, 1992), where the BVS values yielded by (8) are 0.556 and 0.627; we believe the large steric effects operative in these two cases are responsible for the observed deviations from the actual oxidation number (which is +1). That steric effects can considerably affect the BVS value calculated by (3) is known (Whangbo & Torardi, 1990; Hati & Datta, 1995). For [Ni(S—Ph)₄]²⁻, which contains a distorted square planar NiS₄ moiety, (8) gives a BVS of 1.707 for Ni, while the oxidation state of the metal in this ion is reported to be +2 (Yamamura, Miyamae, Kitayama & Susaki, 1985); the reason for this deviation is not clear.

In Tables S1 and S2 we have shown that our BVS method based on (8) gives good agreement with the known oxidation states. We now discuss its ability to discriminate between various oxidation states with some examples taken from Tables S1 and S2. In [Cu(2,4,6-trimethylpyridine)₃]PF₆, where a Cu⁺N₃ chromophore exists with Cu—N distances 3 × 2.01 Å (Habiakare, Lucken & Bernardinelli, 1992), the BVS values for Cu calculated using (8) by assuming +1, +2 and +3 oxidation states are as follows: 0.932, 1.676 and 2.271 valence units; clearly the N₃ coordination sphere is compatible only with the +1 oxidation state for the Cu atom. However, in the course of our studies we have found that

† Lists of full geometry and references, and BVS values calculated by (8) have been deposited with the IUCr (Reference: BR0057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

such clear-cut discrimination is not always possible by (8) alone. For example, in 1,4,8,11-tetrathiacyclotetradecanenickel(II) tetrafluoroborate, where the Ni^{2+}S_4 chromophore has $\text{Ni}^{2+}\text{—S}$ bond lengths as 2×2.177 and 2×2.175 Å (Davis, White & Belford, 1975), the BVS values computed *via* (8), assuming 0, +1, +2 and +3 oxidation states for Ni, are 0.114, 0.963, 2.011 and 2.893 valence units, respectively, indicating that in this case (8) cannot discriminate between 0, +1, +2 or +3 oxidation states for the metal as the BVS values lie within ± 0.25 valence units of the initially assumed oxidation state. In order to discriminate between the oxidation states by (8) alone, we introduce here a second criterion – the correct assignment of the oxidation state is that where the BVS is closest to the assumed atomic valence. By this criterion, we can correctly assign the oxidation state of nickel in 1,4,8,11-tetrathiacyclotetradecanenickel(II) tetrafluoroborate as +2. Working with the second criterion, we have found that the assignments of the oxidation states are correct in 90% of the cases. The main systematic deviants are five of the six Ni^+N_4 chromophores studied here (Table S2). An example of such a deviation is the Ni^+N_4 chromophore in (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) perchlorate with Ni—N bond distances 2×2.063 and 2×1.988 Å (Furenlid, Renner, Szalda & Fujita, 1991). In this case, the BVS values estimated with the help of (8), assuming 0, +1, +2 and +3 oxidation states for the metal, are 0.018, 0.907, 1.749 and 2.389, respectively. Accordingly, one would incorrectly assign an oxidation state of 0 to the Ni atom in (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) perchlorate.

We have also tried to accommodate $V = 0$ to -3 in a function such as (2). It is found that the best results are obtained through (9), where

$$V_i + 4 = (1 + 8/n) \sum_j^n \exp(r_o - r_{ij}) \quad (9)$$

b takes a value of 1 Å. However, the error rendered by (9) in the calculated bond-valence sums for the various complexes analysed in the present study is rather large (± 0.5 valence units). Thus, (9) is not viable.

3. General discussion

It is apparent from (8) that in the BVS method the lengths of the bonds around an atom are governed by the oxidation state of the atom; in the interrelation between the bond length and oxidation state, the angle between the bonds does not appear explicitly.† Thus, the ideal bond lengths for a particular central atom in any

† Very recently, Wang & Liebau (1996) found a correlation between bond valences calculated by (2) with $b = 0.37$ Å and bond angles in a number of Sb^{III} chalcogen compounds.

oxidation state and in a bonding environment of interest can be determined by (8) very easily. For example, the ideal $\text{Cu}^{2+}\text{—O}$ bond lengths in symmetric O_4 , O_5 and O_6 environments are derived as 1.93, 2.01 and 2.09 Å, respectively.‡ These values show that the optimum $M\text{—}L$ bond length increases as the coordination number of M increases. Such a conclusion is also drawn from (3).

It follows from (8) that for a given central atom the sensitivity of V to the type of bonded atom is directly proportional to the respective R value. Consequently, since for a particular oxidation the state of a metal $R(M\text{—}O)$ and $R(M\text{—}N)$ are almost same (see Table 1), it is not possible to distinguish between oxygen and nitrogen binding ligands by (8). To elaborate this point, here we calculate the ideal $\text{Cu}\text{—}N$ bond lengths in symmetric N_4 , N_5 and N_6 environments also *via* (8); 1.98, 2.07 and 2.15 Å, respectively,‡ which are very close to the corresponding $\text{Cu}^{2+}\text{—O}$ distances. In fact, at least for copper and nickel, (8) cannot properly distinguish between coordinating atoms of a particular row of the Periodic table; on the other hand, (8) can easily discriminate between binding atoms of different rows of the Periodic table. The situation is reminiscent of the nature of sensitivity of the EXAFS spectroscopy (Riggs-Gelasco, Stemmler & Penner-Hahn, 1995). Similar problems also occur while working with (3) (Liu & Thorp, 1993; Hati & Datta, 1995).

The R value for a given $M\text{—}L$ bond is found to be linearly related to the oxidation state V of the atom M . See Table 1 for examples. In Fig. 1 we have depicted such variations explicitly for Ni—N and Ni—C bonds only. Such plots can be used to determine the R value of an M,L pair for any desired oxidation state of M which is not obtainable otherwise. For example, from Fig. 1, $R(\text{Ni}^-\text{—C})$ is estimated (by extrapolation) as 0.206 Å.

From the analyses of the bond distances in extended ionic solids, no definite pattern in the variation of the r_o value of an $M\text{—}L$ bond with the oxidation state of M emerges; in some cases r_o increases and in some cases r_o decreases as the oxidation state of M increases, the difference being most marked for Cu. Still, there have been attempts to simplify the situation by assuming the $r_o(M\text{—}L)$ to be independent of the oxidation state of M and to correlate the resulting r_o values to the sizes of the constituent atoms (Brese & O'Keeffe, 1991; O'Keeffe & Brese, 1991). However, when (3) is applied to the coordination complexes, r_o is found to be dependent on the oxidation state of M (Liu & Thorp, 1993; Hati & Datta, 1995). The r_o value of a given M,L pair in a coordination complex generally increases with an increase in the oxidation state of M . An example of such a trend (Hati & Datta, 1995) is provided by the r_o values of the Ni,S pair: $\text{Ni}^0\text{—S}$ 1.098, $\text{Ni}^+\text{—S}$ 1.649, $\text{Ni}^{2+}\text{—S}$ 1.963, $\text{Ni}^{3+}\text{—S}$ 2.040 Å. Similar trends are also

‡ In view of the very recently recognized 'apparent flexibility' of metal complexes in crystals (Martin & Orpen, 1996), we have restricted such calculations to the second place of the decimal point.

observed for our R values (see Fig. 1 and Table 1 for examples). It may be noted that our R values are much smaller than the corresponding r_o values.

We now address the problem of 'which atoms are bonded'. Generally, when r_{ij} is greater than the sum of the van der Waals radii of the two atoms i and j , it can be assumed that i and j are not bonded. However, in cases of non-metals, secondary bonds may become important. For an appraisal of secondary bonds which are much longer than the primary ones, the reader is referred to the works of Alcock (1972) and Troemel and co-workers (Troemel, 1986; Alig & Troemel, 1992). In an earlier section we have stated that the error produced by (8) in estimating V is only ± 0.25 valence units. If for a certain coordination geometry of an atom i in an unambiguously known oxidation state, say V' , the BVS does not lie within $V' \pm 0.25$, then it would mean that there is some error in identifying the actual coordination sphere of the atom i . This 'rule of thumb' can be used to find out which atoms are bonded to a central atom. In terms of (3) there is a bonding interaction between any given pair of atoms at all distances. In Fig. 2 we have described the variation of bond valence for a Cu^{2+} —O bond as per (3), which shows that the valence of a bond approaches 0 as r_{ij} approaches infinity. This cannot be justified by any quantum mechanical calculations. In our model, the valence of a bond is given by

$$v_{ij} = (1 + 20/n)(R/r_{ij}) - 4/n, \quad (10)$$

indicating that bond valence changes sign with the increase in r_{ij} and is dependent on the assumed

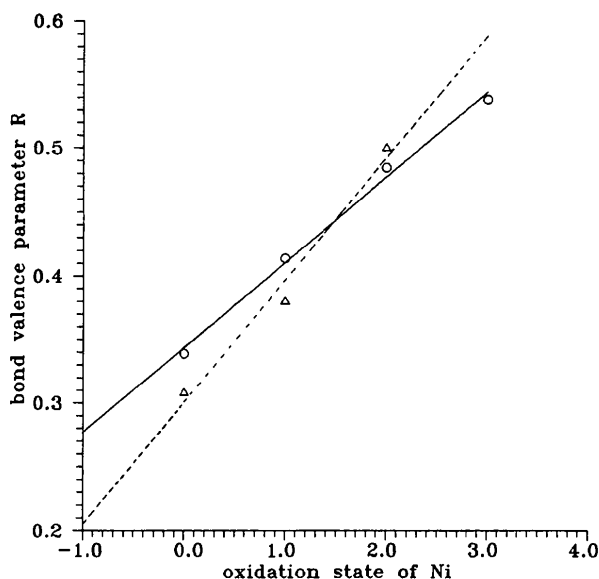


Fig. 1. Variation of the bond-valence parameter R for Ni—N (full line; circles; correlation coefficient = 0.995) and Ni—C (dashed line; triangles; correlation coefficient = 0.990) bonds with the oxidation state of the Ni atom.

coordination number. For a symmetric Cu^{2+}O_6 chromophore, v_{ij} becomes negative when $r_{ij} > 3.131 \text{ \AA}$ (Fig. 2). It is tempting to say that oxygen is not bonded to Cu^{2+} in an O_6 environment when the Cu^{2+} —O distance exceeds 3.131 \AA . Incidentally, the sum of the van der Waals radii for Cu and O is 3.05 \AA (1.70 \AA for copper and 1.35 \AA for oxygen), as found in the Corey–Pauling–Koltun' models. However, the value of r_{ij} beyond which $v_{ij} < 0$ depends on the coordination number n . This is illustrated in Fig. 2 by plotting v_{ij} versus r_{ij} for symmetric Cu^{2+}O_5 and Cu^{2+}O_4 chromophores. From Fig. 2 it follows that for a Cu^{2+}O_5 moiety, $v_{ij} < 0$ when $r_{ij} > 3.012 \text{ \AA}$ and for a Cu^{2+}O_4 moiety, $v_{ij} < 0$ when $r_{ij} > 2.892 \text{ \AA}$. Further, according to (8), the upper limit of the bonding distance between an M, L pair depends on the lengths of the other existing bonds around M . Our calculations using (8) reveal that the maximally elongated Cu^{2+}O_6 chromophore can have the following dimensions: $r_{\text{eq}} = 1.85$ and $r = 3.38 \text{ \AA}$ [the BVS produced by (8) with these distances is 1.751 , which is the lowest value of calculated V that is permitted for an M^{II} centre by our stipulated error limit of ± 0.25 valence units]. Thus, it seems that in our model the bond-valence sum is more meaningful than the valences of the individual bonds. It is also apparent from the behaviour of v_{ij} of an M, L pair when the oxidation state of M is negative. For example, in a symmetric $\text{Ni}^{-1}\text{C}_{10}$ chromophore, the valence of an Ni^{-1} —C bond becomes negative when $r_{ij} > 1.545 \text{ \AA}$, which probably means that in this case the bonds cannot be shorter than 1.545 \AA . In the case of an M^0L_n moiety, the r_{ij} at which $v_{ij} = 0$ can be regarded as the optimum M — L bond distance; in practice the actual bond lengths will be

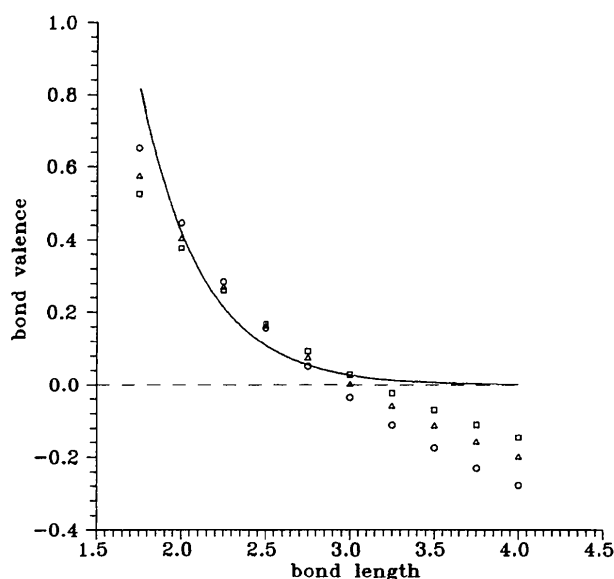


Fig. 2. Dependence of the valence of a Cu^{2+} —O bond on its length: full line, according to (3); circles, in terms of (8) in a symmetric Cu^{2+}O_4 chromophore; triangles, according to (8) in a symmetric Cu^{2+}O_5 moiety; squares, in terms of (8) in a symmetric Cu^{2+}O_6 chromophore.

Table 2. Illustration for the effect of coordination number on the BVS calculated by (3) and (8) by adding additional axial Cu^{2+} —O bond(s) to a hypothetical regular square-planar Cu^{2+}O_4 chromophore

r_{eq} indicates equatorial bond length; r_{ax} indicates axial bond length.

r_{eq} (Å)	r_{ax} (Å)	4 eq bonds		BVS assuming 4 eq + 1 ax bonds		4 eq + 2 ax bonds	
		(3)	(8)	(3)	(8)	(3)	(8)
1.93	—	2.030	1.994	—	—	—	—
—	1.8	—	—	2.751	2.334	3.472	2.649
—	2.0	—	—	2.450	2.200	2.870	2.417
—	2.2	—	—	2.274	2.090	2.519	2.227
—	2.4	—	—	2.172	1.999	2.315	2.069
—	2.6	—	—	2.113	1.922	2.196	1.935
—	2.8	—	—	2.078	1.855	2.126	1.820
—	3.0	—	—	2.058	1.798	2.086	1.721
—	3.2	—	—	2.046	1.748	2.063	1.634
—	3.4	—	—	2.039	1.704	2.049	1.557
—	3.6	—	—	2.035	1.664	2.041	1.489
—	4.0	—	—	2.032	1.597	2.033	1.373
—	5.0	—	—	2.030	1.477	2.030	1.164

around this value of r_{ij} . The loss of the meaning of the valence of a particular bond in our model is actually due to the appearance of a factor of $4/n$ in (10) with a negative sign. However, this factor is very crucial here as it enables us to include 0 and some negative oxidation states (formally up to $V = -3$) in the BVS formalism. Nevertheless, Fig. 2 shows that in the bonding region (2), with $b = 0.37$ Å, and (10) behave in a similar manner.

The BVS calculated by (3) or (8) is dependent on the n assumed. In terms of (3), the addition of an extra bond always means a finite increase (however small) in the BVS. However, according to (8), depending on the length(s) of the bond(s) being added to and on the lengths of the bonds already present around a central metal atom, the BVS for the metal may increase or decrease with the addition of extra bond(s). The situation is explained in Table 2, where one or two axial Cu^{2+} —O bonds of various lengths are added to a hypothetical symmetric square-planar Cu^{2+}O_4 chromophore arbitrarily assigned a value of 1.93 Å as $r(\text{Cu}^{2+}$ —O). Equation (8) shows that in the chosen example, while inclusion of bonds shorter than ~ 2.5 Å in the coordination sphere of Cu^{2+} gives rise to an increase in the BVS, inclusion of bonds longer than ~ 2.5 Å leads to a decrease in the BVS. Further, (8) allows the addition of one axial bond with length in the range 2.0–3.2 Å and two axial bonds of equal length in the range 2.2–2.9 Å. On the other hand, (3) allows the addition of two axial bonds longer than 2.4 Å to the Cu^{2+}O_4 chromophore chosen in Table 2. These observations raise some ambiguity regarding the coordination number n of copper in some of the coordination spheres considered in Table 2. For example, in a Cu^{2+}O_6 moiety with Cu^{2+} —O bond lengths as 4×1.93 and 2×2.80 Å, it is not clear what should be regarded as the value of $n = 4, 5$ or 6.

The bond valences determined by (3) or (7) are unique. However, this is not so in our approach. The R value and consequently v_{ij} determined by (10) depend on which of the two atoms defining a bond is considered. The R for $A^*—B$ (where A^* is the central atom) is not the same as R for $A—B^*$ (where B^* is the central atom) unless the oxidation state of both atoms are the same. This is exemplified by calculating the bond-valence sums of copper and chlorine in $\text{Cs}_2\text{CuCl}_2\text{Cl}'_2$, where Cu^{2+} —Cl = 2.21 and Cu^{2+} —Cl' = 2.24 Å (Helmholtz & Kruh, 1952). Here, R for Cu^{2+} —Cl is 0.555 Å and that for Cl'— Cu^{2+} is 0.318 Å; $\text{BVS}(\text{Cu}) = 2.000$, $\text{BVS}(\text{Cl}) = -0.978$ and $\text{BVS}(\text{Cl}') = -1.019$. Owing to this problem of (10), which again arises due to the presence of a factor of $4/n$, it seems that our approach should be restricted only to the central metal atoms in coordination complexes.

As pointed out in earlier sections, (3) and (7) are basically designed for extended binary solids where bonds are found between cation and anion and the bonds are assumed to be directed from anion to cation. It is true that the RHS of (3) or (7) is a positive quantity. However, the directionality of the bond ensures a negative bond-valence sum around the anion. Consequently, in extended solids, since the bond valences are unique, (3) and (7) imply that

$$\sum V_i = 0. \quad (11)$$

In our approach, since the bond valences are not unique, the bond-valence sums around the cation and the anion are to be calculated separately to show that (11) is satisfied.

4. Implications

Application of (8) to axially distorted octahedral homoleptic complexes of a metal ion leads to

$$1/r_{\text{eq}} = 0.346/R - 0.5/r_{\text{ax}}, \quad (12)$$

where r_{eq} represents the average equatorial bond length and r_{ax} the average axial bond length. Equation (12) predicts a linear variation between $1/r_{\text{eq}}$ and $1/r_{\text{ax}}$ in ML_6 chromophores with a slope of -0.5 and an intercept which can be calculated beforehand with the knowledge of appropriate R . Earlier, from an extensive study, Gazo *et al.* (1976) found that the relative variation in the r_{eq} and r_{ax} in some MO_6^{2+} and MN_6^{2+} chromophores, which they termed the plasticity of a coordination sphere, depends on the metal ion; the degree of distortion in the coordination polyhedra decreases as $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. The examples collected in Table S2 indicate that such distortions in the octahedral nickel(II) homoleptic complexes are not very significant. Hence, we have tested (12) in $\text{Cu}^{2+}X_6$ chromophores for $X = \text{F}, \text{O}, \text{N}$ and S . The results are summarized in Table 3. It is found that in Cu^{2+}F_6 , where the ligand is homogeneous, the fit is excellent (see Fig. 3 also), but in the other three

Table 3. Various data for the linear variation between $1/r_{eq}$ and $1/r_{ax}$ in some octahedral $Cu^{2+}X_6$ chromophores

n is the number of structures used for regression analysis and r the correlation coefficient; for the meanings of the other symbols used, see text.

X	n	Range of bond lengths		r	Intercept		Slope	
		r_{ax}	r_{eq}		Found	Calc.	Found	Calc.
F	13	2.37–1.85	2.08–1.864	0.964	0.735	0.742	–0.485	–0.5
O	18	3.00–1.93	2.145–1.88	0.953	0.651	0.718	–0.352	–0.5
N	18	2.652–2.055	2.229–1.99	0.924	0.655	0.698	–0.405	–0.5
S	5	3.141–2.343	2.495–2.317	0.942	0.516	0.611	–0.258	–0.5

cases where the ligand environments are quasi-homogeneous (we call it so because the binding atom in such cases is only a part of different molecules having various electronic structures, e.g. an O atom can be of the types aquo, hydroxo, phenolato, carboxylato *etc.*), the fits are only satisfactory.

The structural non-rigidity of $Cu^{2+}X_6$ chromophores in the solid state has been recognized long ago. The observed tetragonal distortions originate from the Jahn–Teller effect (Burdett, 1981; Huheey, 1983*b*; Orpen *et al.*, 1989; Burton & Deeth, 1995). Still, in the past, Hathaway (1973) has tried to explain the tetragonality in terms of the ‘asymmetry’ of the effective radius of the Cu^{2+} ion; he has argued that in a regular octahedron, Cu^{2+} is spherically symmetric, but in an elongated octahedron it becomes prolate ellipsoid. Later Gazo *et al.* (1976, 1982, 1983) and Boca & Pelican (1981) have concluded that r_{ax} and r_{eq} are correlated along a smooth curve, which is the projection of the minimum in the $E(r_{ax}, r_{eq})$ curve [$E(r_{ax}, r_{eq})$ is the total energy E as a function of r_{ax} and r_{eq}] on the plane defined by r_{ax} and r_{eq} , such that as r_{ax} increases r_{eq} decreases and *vice versa*. Very recently the relation between r_{ax} and r_{eq} has been recognized as hyperbolic

(Boca, 1995). Here we have demonstrated the existence of a satisfactorily linear variation between $1/r_{ax}$ and $1/r_{eq}$ in octahedral $Cu^{2+}X_6$ chromophores.

Similarly for a square-pyramidal MX_5 moiety a linear variation of the type described by (13) is expected

$$1/r_{eq} = 0.300/R - 0.25/r_{ax}. \quad (13)$$

The examples of $Cu^{2+}X_5$ chromophores given in Table S1 are only of square-pyramidal type; these show that the distortions in the coordination polyhedra are significant only for $X = O$. For some 12 copper(II) complexes containing square-pyramidal O_5 coordination spheres (Table S1), we have found that there does exist a considerable linearity between $1/r_{eq}$ and $1/r_{ax}$ (Fig. 4; correlation coefficient = 0.916). The observed intercept (0.566; from Fig. 4) matches quite well with the theoretical one [0.621; calculated by (13)]. However, the slope (–0.121) in Fig. 4 is somewhat higher than that expected [–0.25; see (13)]; this may be due to the quasi-homogeneous nature of the O_5 sphere.

The results obtained in Table 3 and Fig. 4 in a way support the use of (8) for calculating bond-valence sum.

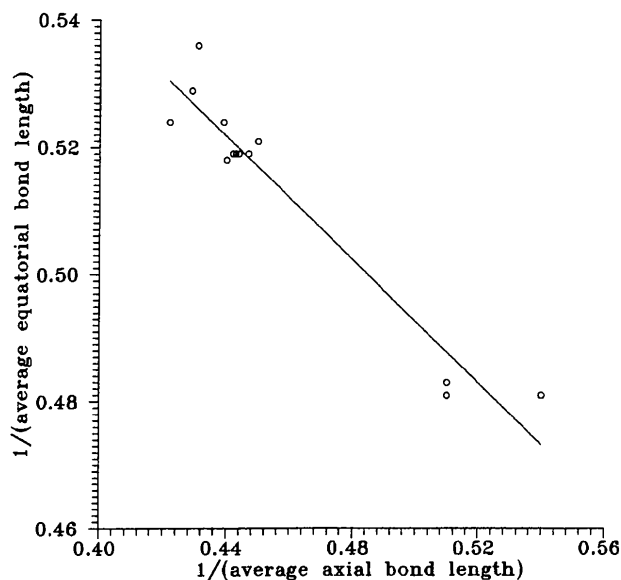


Fig. 3. Variation of $1/r_{eq}$ with $1/r_{ax}$ for the octahedral $Cu^{2+}F_6$ chromophore, where r_{eq} and r_{ax} are, respectively, the average equatorial and axial bond lengths; correlation coefficient = 0.964.

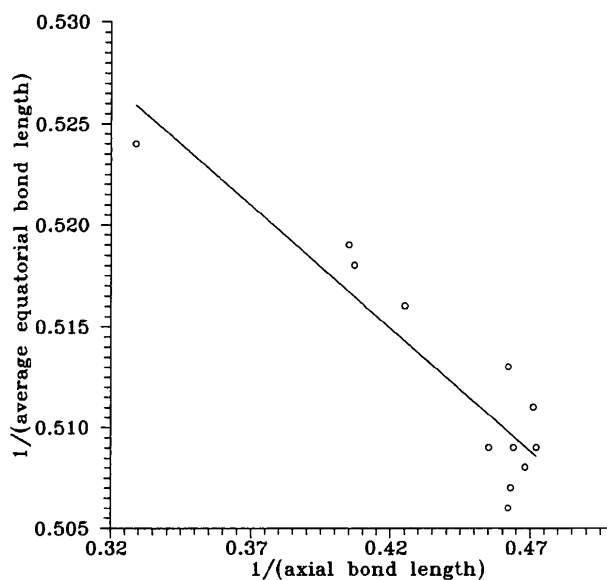


Fig. 4. Variation of $1/r_{eq}$ with $1/r_{ax}$ for the square-pyramidal $Cu^{2+}O_5$ chromophore, where r_{eq} is the average equatorial and r_{ax} the axial bond lengths; correlation coefficient = 0.916.

5. Applications

Equation (8) can be applied to determine the compatibility between a given oxidation state and a particular bonding sphere model for a central atom. In cases of the transition metal ions, although the geometries of the coordination spheres are sometimes known exactly from X-ray crystal structure determinations, it becomes difficult to specify the oxidation states of the metals. In an earlier section we have indicated how (8) can be useful in assigning the oxidation state of the metal ion in a complex. However, conclusions drawn from (8) alone are not always infallible (*vide infra*). Consequently, (8) should be used together with other physico-chemical properties (*e.g.* magnetic susceptibility). To elucidate this point we once again refer to the case of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) perchlorate. In a preceding section we have pointed out that according to (8) the NiN_4 moiety is actually compatible with Ni^0 , Ni^{I} or Ni^{II} . When the knowledge of one unpaired electron in this complex (Furenlid, Renner, Szalda & Fujita, 1991) is coupled with the conclusions drawn *via* (8), the possibility of Ni^0 or Ni^{II} is excluded and we can clearly assign the oxidation state of the metal as +1.

Owing to the crystallization problems it is not always possible to have single crystals suitable for X-ray diffraction. Moreover, for large molecules like most of the proteins and enzymes, even if single crystals are grown, it is very difficult to solve the X-ray diffraction patterns for the actual structure. For metal complexes, in the event of non-availability of single crystals of appropriate quality and for metal-containing proteins and enzymes, EXAFS spectroscopy is often employed to probe the immediate vicinity of the metal centres. However, in EXAFS spectroscopy it is not always possible to determine the exact number of donor atoms around a metal ion, resulting in several alternative models for its coordination sphere. In such situations, if the oxidation state of the metal ion involved is known exactly, (8) can be used to determine the most probable coordination model. This is illustrated below by exemplary applications of (8) to azurin and urease.

5.1. Azurin

This is a blue copper protein (molecular weight: 14–15 kDa) found in certain bacteria. It has only one copper centre of type 1 and acts as an electron-transfer agent by operating through a $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ couple having a redox potential of ~ 0.3 V (Fee, 1975; Solomon, Baldwin & Lowery, 1992; Guckert, Lowery & Solomon, 1995).† The X-ray structures of the oxidized and reduced forms of azurin isolated from *Alcaligenes denitrificans* are now known with a fair amount of accuracy (Shepard,

† 'Type 1' copper is characterized by the following properties: paramagnetism, an intense charge-transfer band at ~ 1600 nm and unusually small hyperfine splitting constant in the EPR spectra.

Anderson, Lewandoski, Norris & Baker, 1990). In both forms the geometry of the coordination sphere around the Cu atom is almost the same, in keeping with the fast electron transfer behaviour of this protein. The basic feature of the coordination sphere is that two histidine N atoms and a cysteine S atom are almost coplanar with the Cu atom forming a trigonal equatorial plane, and there are two long axial bonds (with lengths > 3.0 Å) – one with the thioether S atom of a methionine residue and another with the peptide carbonyl O atom of a glycine moiety; consequently, a $\text{Cu}^{1+/2+}\text{N}_3\text{S}_2$ chromophore is implicated. Our BVS analysis of the structural data for this chromophore in the two forms of azurin (in *A. denitrificans*) by (8) shows (Table 4) that in both forms the axial bonds are too long; neither the carbonyl O nor the thioether S is bonded to the metal. Hence, the chromophore in *A. denitrificans* azurin should be regarded as $\text{Cu}^{1+/2+}\text{N}_2\text{S}$. In cases of simple inorganic complexes, although very recently a copper(I) compound with a copper–carbonyl O bond has been characterized structurally (Munakata *et al.*, 1994), such a copper(II)–carbonyl O bond, to our knowledge, has not yet been identified. Previously, from model molecular orbital calculations, Solomon and co-workers have suggested that there is no net bonding between the copper(II) centre and the axial ligands in oxidized azurin (Solomon, Baldwin & Lowery, 1992; Lowery & Solomon, 1992*a,b*) and at a distance larger than 2.8 Å, it is unlikely that a thioether S is bonded to a reduced type 1 copper (Guckert, Lowery & Solomon, 1995). Thus, it appears that the axial dispositions of the thioether S and the peptide carbonyl O atoms on the metal centre result from the requirements of the tertiary structure of *A. denitrificans* azurin. In contrast, according to (3), contributions from both the axial bonds are to be taken into account to match the BVS of copper with the metal oxidation state in the oxidized form of *A. denitrificans* azurin (see Table 4).

5.2. Urease

This is an enzyme which catalyses the hydrolysis of urea to ammonia and carbon dioxide. It occurs in bacteria and plants. Its active site consists of two high-spin nickel(II) centres separated by a distance of 3–4 Å and the oxidation state of the metal is believed to remain unchanged throughout the catalytic cycle (Andrews, Blakeley & Zerner, 1988; Halcrow & Christou, 1994; Wang *et al.*, 1994). Recently the crystal structure of the active site in *Klebsiella aerogenes* urease has been reported by Karplus and co-workers (Jabri, Carr, Hausinger & Karplus, 1995). Two types of Ni^{II} centres have been found – one (Ni_A) is pentacoordinate and the other (Ni_B) tricoordinate. However, in terms of our equation (8) the reported metal–ligand bond distances for Ni_A and Ni_B are not consistent with an oxidation state of II for nickel (Table 4). It seems that the $M-L$ bond lengths have been somewhat overestimated. For example,

Table 4. Bond-valence sums for copper in azurin and nickel in urease

The bond-valence parameters r_o for $\text{Cu}^+—\text{O}$, $\text{Cu}^+—\text{S}$ and $\text{Cu}^{2+}—\text{S}$ bonds are, respectively, 1.578, 1.856 and 2.015 Å (estimated by us); r_o values for $\text{Cu}^{2+/1+}—\text{N}$ and $\text{Ni}^{2+}—\text{N}$ are taken from Hati & Datta (1995) and $r_o(\text{Ni}^{2+}—\text{O})$ from Liu & Thorp (1993).

Species	Form	Coordination sphere	BVS	
			From (8)	From (3)
Azurin from <i>A. denitrificans</i>	Oxidized†	$\text{N}_2\text{SS}'\text{O}$	1.425	1.611
		$\text{N}_2\text{SS}'$	1.586	1.591
	Reduced‡	N_2S	1.743	1.539
		$\text{N}_2\text{SS}'\text{O}$	0.565	0.888
		$\text{N}_2\text{SS}'$	0.674	0.876
Urease from <i>K. aerogenes</i>	Ni_A §	N_2S	0.815	0.852
		N_2O_3	1.585	1.461
			1.865¶	1.913¶
	Ni_B ††	N_2O	1.267	0.966
			1.835‡‡	1.658‡‡

† $\text{Cu}—\text{N}$ 2.08, 2.00, $\text{Cu}—\text{S}$ 2.15, $\text{Cu}—\text{S}'$ 3.11, $\text{Cu}—\text{O}$ 3.13 Å; from Shepard, Anderson, Lewandowski, Norris & Baker (1990). ‡ $\text{Cu}—\text{N}$ 2.13, 2.05, $\text{Cu}—\text{S}$ 2.26, $\text{Cu}—\text{S}'$ 3.23, $\text{Cu}—\text{O}$ 3.22 Å; from Shepard, Anderson, Lewandowski, Norris & Baker (1990). § $\text{Ni}—\text{N}$ 2.3, 2.2, $\text{Ni}—\text{O}$ 2.1, 2.1, 2.0 Å; from Jabri, Carr, Hausinger & Karplus (1995). ¶ $\text{Ni}—\text{N}$ 2.2, 2.1, $\text{Ni}—\text{O}$ 2.0, 2.0, 1.9 Å; see text. †† $\text{Ni}—\text{N}$ 2.1, 2.2, $\text{Ni}—\text{O}$ 2.0 Å; from Jabri, Carr, Hausinger & Karplus (1995). ‡‡ $\text{Ni}—\text{N}$ 1.9, 2.0, $\text{Ni}—\text{O}$ 1.8 Å; see text.

if all the five bonds for Ni_A are uniformly shortened by 0.1 Å, the resulting coordination sphere becomes quite compatible with a Ni^{II} formulation (see Table 4). Here it is important to mention that in the determined structure, the coordinate accuracy in the active site region is reported to be only 0.2 Å (Jabri, Carr, Hausinger & Karplus, 1995), which means that the error in the derived bond lengths is $\pm 3 \text{ \AA}$. † The situation seems to be similar for the other nickel centre. For Ni_B , after shortening all the three bonds by 0.2 Å, the BVS matches with a Ni^{II} centre (Table 4).

6. Conclusions

Here for the first time we have tried to develop a procedure to accommodate 0 and some negative oxidation states in the BVS formalism. The result is (8), a new expression for the bond-valence sum. However, in the process the meaning of the valence of an individual bond around a central atom appears to be lost. Moreover, the bond-valence parameter involved no longer remains unique – it depends on which of the two atoms defining a bond is considered. Thus, (8) should be used only to specify the coordination sphere of the central metal atom

† However, for Ni_A , if all the bond lengths are uniformly shortened by 0.3 Å, the BVS becomes 2.510, which shows that the resulting bond lengths are too short for a Ni^{II} centre. Anyway, the conclusion is that in the work of Jabri, Carr, Hausinger & Karplus (1995) the bond lengths around Ni_A have been overestimated.

in an inorganic complex. Equation (8) can be applied when the oxidation state of a central metal atom is greater than or equal to -3 . An implication of our equation is the linear variation between $1/r_{\text{eq}}$ and $1/r_{\text{ax}}$ in the octahedral and square-pyramidal homoleptic metal complexes, where r_{eq} and r_{ax} are, respectively, the average equatorial and axial bond lengths. This is verified in the copper(II) complexes where significant variations are observed in the axial and equatorial bond lengths. With the help of several worked-out examples, we have shown the usefulness of (8) in assessing the compatibility of a bonding sphere and an oxidation state for the metal ion in coordination complexes and biological molecules.

The BVS method, as evident from (8) or (3), is essentially based on the concept of ligand additivity. There is evidence for the effects of ligand additivity on several solution properties (especially the redox potential) of a metal ion. However, such observations in solution are limited only to metal ions having closed-shell electronic configurations [mainly octahedral d^6 (Datta, 1986; Fielder, Osborne, Lever & Pietro, 1995)]. However, the BVS approach shows that ligand additivity holds in the solid state, irrespective of the electronic configuration of the central atom.

Financial assistance received from the Department of Science and Technology, Government of India, New Delhi, is gratefully acknowledged. Thanks are due to Dr H. H. Thorp for checking a draft of the manuscript. We wish to thank the reviewers for their valuable comments.

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