The correlation between metal oxidation state and bond valence parameters for M−O bonds (M = V, Fe and Cu). A simple method to search for the metal oxidation-state independent parameter pairs

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Abstract. Based on the latest available crystal data and the reported bond valence parameters, the linear correlation between the bond valence parameter R_0 with $B = 0.37$Å for M−O bonds (M = V, Fe and Cu) and the metal oxidation state n is shown for the first time. For V−O bonds, a linear equation of $R_0 \sim n$ is perfectly established as $R_0 = 0.0250n + 1.674$ ($n = 2$–5). Similarly, a linear equation for Fe−O bonds is fitted as $R_0 = 0.0335n + 1.648$ ($n = 2$–4), as well as $R_0 = 0.0855n + 1.482$ ($n = 1$–3) for Cu−O bonds fitted properly. In addition, the linear correlation between R_0 and n within certain range of B values for V−O and Fe−O bonds is also established. Consequently, the oxidation-state independent parameters (R_0, B) of (1.788, 0.32 Å) for V−O bonds and (1.795, 0.30 Å) for Fe−O bonds can be derived from the zero slope of the $R_0 \sim n$ straight lines. However, a similar parameter pair for Cu−O bonds cannot be found using this unique approach.

1. Introduction

The bond valence sum, henceforth BVS, surrounding the jth atom is equal to the oxidation state, n_j, as shown in equation (1), an idea that can be traced back to Pauling's second rule [1]. The bond valence, s_{ij}, in equation (1) can be easily calculated from the observed bond length, r_{ij}, using the most commonly adopted expression (2) below:

$$n_j = \Sigma s_{ij}, \tag{1}$$

$$s_{ij} = \exp\left[(R_0 - r_{ij})/B\right] \tag{2}$$

where R_0 and B are the bond valence parameters dependent of the nature of the ij pair [2]. A "universal" value for B of 0.37 Å [3] has been accepted for a long period of

time. Using this value along with the published bond lengths, empirical values of R_0, the bond length of unit valence, can be fitted for different pairs of atoms in a variety of crystal structures.

The BVS method was first applied to pure inorganic structures, but in the last decade bond valence parameters have been proposed for use with metal-organic compounds as well as metalloproteins [4]. Recently a comprehensive compilation of about 1500 parameter pairs of R_0 and B has been made available on the internet with B in some cases differing from 0.37 Å. Most of these values are associated with a specific oxidation state, but in some cases no oxidation state is specified [5(a)]. These conventional bond valence data, as well as the bond valence tables based on the flexible B values, are also available on the web pages [5(b)].

Equations 1 and 2 have been shown empirically to work for all kinds of chemical bonding and are soundly based on empirical, semi-empirical and quantum mechanical studies [6]. Though there are vast number of papers where the BVS is used to confirm metal oxidation states in a variety of metal complexes, however, few reports on developing the possible correlation between parameter R_0 or B and metal oxidation state n. It has been assumed that R_0 is not very different for different oxidation states in general, except for few bonds like Cu−O, Cr−O and Mn−O etc. [7]. Nevertheless, whether the bond lengths of unit valence exhibit some dependence on valence is of great interest and worth investigating.

Historically, determinations of R_0 with $B = 0.37$ Å were based on bond lengths for specific oxidation states found in the Inorganic Crystal Structure Database (ICSD), however, the oxidation state was often ignored in the later values proposed for cation-anion and anion-anion pairs [3, 8]. Because the BVS has been proposed as a method of determining the metal oxidation state in transition metal complexes in the last decade, the advantage of using oxidation-state independent bond valence parameters in these studies is obvious. For example, using $B = 0.37$ Å, values of $R_0 = 1.713$ Å have been proposed for Fe(II)−O bonds and 1.751 Å for Fe(III)−O bonds, but if the oxidation

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state is not initially known, it has been suggested to use a value of 1.745 Å [9]. It seems to us that the parameter $B = 0.37$ Å could be partnered with either value of oxidation state dependent and independent R_0 for Fe−O bonds simultaneously.

Recently, it has been developed that R_0 for Mo−O bonds is linearly dependent on the oxidation state for $3 \leq n \leq 6$, and that the slope of this correlation depends on the value of B chosen [10]. By fitting the value of B giving a zero slope of the line, a parameter set (B/R_0) which is really independent of oxidation state is derived consequently. For example, if B is chosen as 0.37 Å, $R_0 = 0.022n + 1.768$ Å with a positive slope, but if it is chosen as 0.27 Å, then $R_0 = -0.0109n + 1.9353$ Å with a negative slope. A zero slope is derived for $B = 0.30$ Å, and the value of R_0 does correspond with the intersection of the lines at 1.880 Å. This parameter set (1.880/0.30) is close to the oxidation-state independent parameters of $B = 0.314$ and $R_0 = 1.890$ Å previously proposed by Zachariasen [11], and actually identical with that of $B = 0.3046$ and $R_0 = 1.8788$ Å for all Mo oxidation states from +3 to +6 recently proposed by Zocchi [12]. Therefore the oxidation-state independent bond valence parameter set for Mo−O bonds is just a special case in the $R_0 \sim n$ linear relations, which has been developed for the first time to the best of our knowledge.

In this paper we extend this study to see if oxidation-state independent bond valence parameters can be defined for certain first-row transition metals such as the M−O bonds where M = V, Fe and Cu. To do this, we found it necessary to determine bond valence parameters first for V(II)−O and Fe(IV)−O bonds for which accurate values have not previously been reported, see below. Using bond valence parameters in literature together with the values

Table 1. Evaluation of the R_0 values with $B = 0.37$ Å for V(II)−O and Fe(IV)−O bonds.

	Compound		V(II)−O Distance (Å)	Temp. (K)	R_0 (Å)	Ref.
1	$[V(H_2O)_6]SO_4 \cdot 7\,H_2O$	mol. 1	$2.115(2) \times 2$, $2.150(2) \times 2$, $2.141(2) \times 2$	11	1.729	[a]
		mol. 2	$2.125(2) \times 2$, $2.139(3) \times 2$, $2.170(3) \times 2$	11	1.738	
2	$[V(H_2O)_6]SO_4$	mol. 1	$2.131(2) \times 2$, $2.123(2) \times 2$, $2.136(2) \times 2$		1.723	[b]
		mol. 2	$2.150(2) \times 2$, $2.120(2) \times 2$, $2.124(2) \times 2$		1.725	
3	$[V(H_2O)_6]SiF_6$		$2.1214(7) \times 6$	213	1.715	[c]
4	$(ND_4)_2[V(H_2O)_6](SO_4)_2 \cdot 6\,D_2O$		$2.130(5) \times 2$, $2.111(7) \times 2$, $2.114(6) \times 2$	5.8	1.712	[d]
5	$(NH_4)_2[V(H_2O)_6](SO_4)_2$		$2.133(1) \times 2$, $2.136(1) \times 2$, $2.116(1) \times 2$		1.722	[c]
6	$[V(H_2O)_6](CF_3SO_6)_2$		$2.118(2) \times 4$, $2.120(3) \times 2$		1.714	[e]
7	$[V(THF)_4][V(CO)_6]_2$		$2.079(8) \times 2$, $2.163(8) \times 2$, $2.18(1) \times 2$		1.730	[f]
8	$[V(pic)_2(H_2O)_2] \cdot 2\,H_2O$		$2.134(1) \times 6$		1.728	[g]
				Average	1.724(8)	

	Compound		Fe(IV)−O Distance (Å)	Temp. (K)	R_0 (Å)	Ref.
1	$SrFeO_3$		$1.9254(1) \times 6$		1.775	[h]
2	$CaFeO_3$ in $P2_1/n$	Fe1	1.923×2, 1.925×2, 1.926×2	130	1.775	[i]
		Fe2	1.910×2, 1.922×2, 1.927×2	130	1.770	
	$CaFeO_3$ in $Pnma$		1.918×2. 1.922×2, 1.925×2		1.772	
3	Sr_2FeO_4		$1.932(1) \times 4$, $1.950(9) \times 2$ $1.931(1) \times 4$, $1.943(3) \times 2$	100	1.788 1.785	[j]
			$1.931(1) \times 4$, $1.948(2) \times 2$	4.2	1.787	
4	Ba_2FeO_4		1.759, 1.778, 1.779, 1.786		1.775	[k]
5	Na_4FeO_4		1.790, 1.805, 1.808, 1.825		1.807	[l]
6	$Sr_3Fe_2O_7$		$1.927(1) \times 4$, 1.936(4), 1.958(2) $1.922(1) \times 4$, 1.940(5), 1.952(2)	4.2	1.783 1.780	[j]
7	$Sr_4Fe_4O_{11}$	Fe1	$1.855(2) \times 4$, 1.900(1)		1.781	[h]
8	$Sr_8Fe_8O_{23}$	Fe1 Fe2	$1.851(2) \times 4$, 1.926(1) $1.912(3) \times 4$, $1.925(1) \times 2$		1.782 1.766	[h]
				Average	1.780(10)	

a: Cotton, F. A.; Falvello, L. R.; Murillo, C. A.; Pascual, I.; Schultz, A. J.; Tomas, M.: Inorg. Chem. **33** (1994) 5391.
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j: Dann, S. E.; Weller, M. T.; Currie, D. B.; Thomas, M. F.; Alrawwas, A. D.: J. Mater. Chem. **3** (1993) 1231.
k: Delattre, J. L.; Stacy, A. M.; Young, V. G.; Long, G. J.; Hermann, R.; Grandjean, F.: Inorg. Chem. **41** (2002) 2834.
l: Weller, M. T.; Hector, A. L.: Angew. Chem. Int. Ed. **39** (2000) 4162.

determined in this work, we do find a positive correlation between R_0 and n for all three bond types using $B = 0.37$ Å, but the correlation decreases smoothly as the value of B decreases. And like the method described for Mo−O bonds above, we have been able to determine oxidation-state independent values of R_0 and B for V−O and Fe−O, but we are unable to find values that work for Cu−O bonds to date.

2. Data retrieval and selection

To determine bond valence parameters for V(II)−O and Fe(IV)−O bonds we selected from the ICSD and the Cambridge Structural Database (CSD) cation environments in which all the ligands were O, and there was no disorder and for which the crystallographic agreement index $R < 0.1$. Despite the limited available data we rejected a few high temperature data which might show thermal expansion of the bonds [13], as well as structures showing strain or an incorrect oxidation state assignment which are detectable from the BVS analyses. For example, ICSD-41123 is described as $H_4V_2O_4$. No hydrogen atom positions were reported, and according to the BVS analysis around both V and O, this compound should be reformulated as V_2O_4. ICSD-28917 is $BaFeO_3$, but the bond valence sum around Fe is only 3.5 rather than 4.0, either an indication of the strain frequently found in perovskite materials, or the Fe(IV) has disproportionated to Fe(III) and Fe(V) as that in $SrFeO_3$ [14]. Data for Ba_2FeO_4 like ICSD-26301, −28918 and −29096 were also rejected for the reasons given. The results obtained from those reliable bond length data are listed in Table 1. All calculations were performed with the program *VALENCE* [15].

The R_0 value of 1.78 Å with $B = 0.37$ Å for Fe(IV)−O was first calculated from the only perovskite $SrFeO_3$ as 1.78 Å in 1991 [3], which is consistent with what we have got here. Besides, we also found that the value of $R_0 = 1.753$ Å with $B = 0.37$ Å for Cu(III)−O in the text should read 1.738 Å [24]. Though it was unable to retrieve any new reliable structures containing Cu(III)−O bonds from the CSD and CCDC, we have found that this value of 1.738 Å is acceptable, see below.

3. Linear correlation between bond valence parameter R_0 and oxidation state n

3.1 V−O bonds

Published values of the bond valence parameters for V−O bonds are given in Table 2, including the value 1.724 Å determined in the present work for the V(II)−O bonds. Values in bold type are either parameters for which the oxidation state is not specified, or intended to apply to all oxidation states. Earlier values tended to be based on a limited number of structures, and more recent values adopt the value of $B = 0.37$ Å without any question. Figure 1 illustrates the values of R_0 determined for $B = 0.37$ Å. The linear correlation can be expressed by equation (3)

$$R_0 = 0.025n + 1.674 . \qquad (3)$$

The value of R_0 for $n = 4$ is the same as the oxidation-state independent value of 1.774 Å ($B = 0.37$ Å) proposed by Palenik [21], but this is merely the average of the values of R_0 with $B = 0.37$ Å for $n = 3$, 4 and 5 according to equation (3), see Fig. 1.

Recently, Zocchi has shown that one can alternatively keep R_0 fixed and vary B, proposing the linear relation as $B = 0.0173n + 0.2646$ ($2 \leq n \leq 5$) with $R_0 = 1.7884(5)$. As this R_0 value is close to those shown in bold type in Table 2, one might propose $R_0 = 1.7884$, $B = 0.325$ Å, an

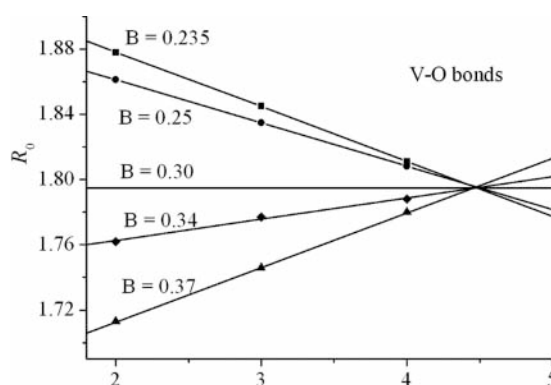**Fig. 1.** Linear relationship between R_0 and n for V−O bonds.

Table 2. Bond valence parameters R_0 (B) in Å for V−O bonds.

Date	Author	V^V−O	V^{IV}−O	V^{III}−O	V^{II}−O	Ref.
1951	Byström *et al.*	**1.77(0.332)**				[16]
1960	Evans	**1.81(0.339)**				[17]
1971	Wilhelmi *et al.*	**1.789(0.339)**				[18]
1976	Waltersson	**1.791(0.313)**				[19]
1978	Zachariasen	**1.790(0.319)**				[11]
1985	Brown *et al.*	1.803(0.37)	1.784(0.37)	1.743(0.37)		[2, 5]
1993	Liu *et al.*		1.780(0.37)	1.749(0.37)		[20]
1997	Palenik	**1.774(0.37)**				[21]
1999	Tytko *et al.*	1.799(0.37)	1.779(0.37)			[22]
2002	Zocchi	1.7882(0.3511)	1.7888(0.3334)	1.7885(0.3167)	1.7879(0.2991)	[23]
	This work	**1.788(0.32)**			1.724 (0.37)	

Table 3. Bond valence parameters R_0 (B) in Å for Fe$-$O and Cu$-$O bonds.

Date	Author	Fe^{II}$-$O	Fe^{III}$-$O	Fe^{IV}$-$O	Cu^{I}$-$O	Cu^{II}$-$O	Cu^{III}$-$O	Ref.
1975	Allmann	**1.74(0.38)**						[25]
1985	Brown *et al.*	1.734(0.37)	1.759(0.37)		1.610(0.37)	1.679(0.37)	1.739(0.37)	[2, 5]
1991	Bress *et al.*			1.78(0.37)	1.593(0.37)			[3]
1993	Thorp *et al.*	1.700(0.37)	1.765(0.37)			1.649(0.37)		[20]
1996	Mahapatra *et al*						1.738(0.37)	[24]
1998	Kanowitz *et al.*	1.713(0.37) **1.745(0.37)**	1.751(0.37)					[9]
2000	Shields *et al.*			1.798(0.37)	1.567(0.37)	1.655(0.37)		[26]
2002	Delattre *et al.*							[27]
	This work	**1.795(0.30)**		1.780(0.37)				

average of the B values, as the reliable oxidation-state independent parameters.

We have chosen to approach this problem in a different way by calculating values of R_0 for a number of different values of B. Like the case of Mo$-$O bond [10, 12], we select one reference structure of each oxidation state of V, namely V^{II}(H$_2$O)$_6$SO$_4 \cdot$ H$_2$O [28], Ba$_3$V$^{III}_2$(HPO$_4$)$_6$, [29] K$_4$[V^{IV}O(cit)]$_2 \cdot$ 6 H$_2$O [30] and K$_2$(NH$_4$)$_4$[V^{V}O$_2$(cit)]$_2 \cdot$ 6 H$_2$O [31] to determine values of R_0 for the V$-$O bond with various choices of B, and the fitting results are also shown in Fig. 1. The line set intersects at $R_0 = 1.788$ Å according to the optimization, and then a zero-slope value of B of 0.32 Å obtained. This parameter set is identical to the values evaluated in the work of last paragraph, $R_0 = 1.7884$ and $B = 0.325$ Å on the one hand, and quite close to the values of $R_0 = 1.790$ and $B = 0.319$ Å proposed by Zachariasen [11] independent on the oxidation state of V in the range from $+3$ to $+5$ on the other hand.

3.2 Fe$-$O and Cu$-$O bonds

Literature values of the bond valence parameters for Fe$-$O and Cu$-$O are given in Table 3, including the values determined in the present work for the Fe(IV)$-$O bonds (Table 1). Unlike the cases for Mo$-$O and V$-$O bonds where four oxidation states were available, bond valence parameters for Fe$-$O and Cu$-$O are only known for three oxidation states. Again, the latest sets of R_0 parameters with $B = 0.37$ Å do fall on straight lines with a maximum error of 0.002 Å, in nearly perfect agreement with equations (4) and (5) below.

$$R_0 = 0.0335n + 1.648, \qquad (4)$$

$$R_0 = 0.0855n + 1.482. \qquad (5)$$

The crystal structures of [Fe^{II}(H$_2$O)$_6$] $\cdot$ [Fe(C$_6$H$_6$N$_3$O$_4$)$_3$]$_2$ $\cdot$ 12 H$_2$O[32], [Fe^{II}Fe$^{III}_2$(CH$_2$BrCO$_2$)$_6$(H$_2$O)$_3$] [33] and Sr$_4$Fe$^{III}_2$Fe$^{IV}_2$O$_{11}$ [34] were selected as reference structures for each Fe oxidation state, and values of R_0 were calculated for different values of B as also shown in Fig. 2. Thus it can be optimized to fit the oxidation-state independent value of $R_0 = 1.795$ Å with $B = 0.30$ Å as before. It may be of interest to note that this parameter set (1.795/0.30) is quite different from that previous proposed by Allmann (1.74/0.38) [25] and Kanowitz (1.745/0.37) [9]. Actually the latter two are close to each other, and the set

(1.745/0.37) corresponds to an average of R_0 in $n = 2$ (1.713 Å) and $n = 4$ (1.780 Å) with $B = 0.37$ Å.

On the other hand, we are unable to determine oxidation-state independent values for Cu$-$O bonds because there is no value of B within a large range that could give a negative slope. This is most likely related to the very steep positive slope 0.0855 for $B = 0.37$ Å, more than 2$-$3 times of that for Fe$-$O and V$-$O, as shown in equations (3)$-$(5) and Figs. 1$-$3. Consequently, it is most unlikely that the average R_0 of 1.653 Å, for $n = 2$ in equation (5), with $B = 0.37$ Å will work well as an tentative oxidation-state independent set of the Cu$-$O bond valence parameters, and the oxidation-state dependent values should be required in such a case.
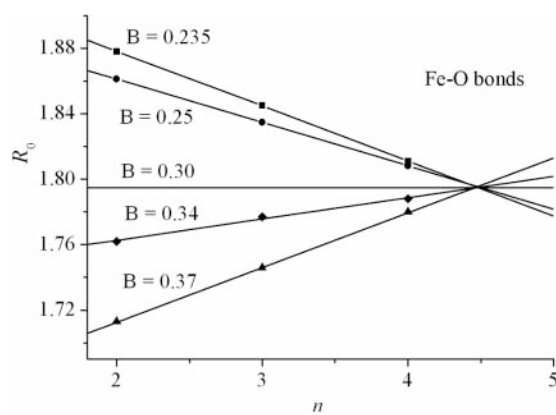

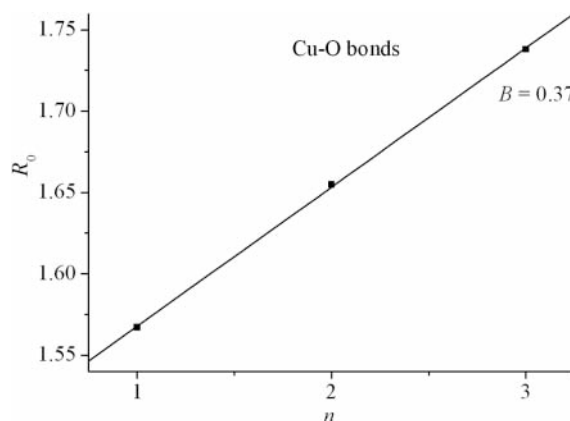**Fig. 2.** Linear relationship between R_0 and n for Fe$-$O bonds.

Fig. 3. Linear relationship between R_0 and n for Cu$-$O bonds.

4. Sample BVS calculations for V−O and Fe−O bonds

In this section we compare the ability of oxidation-state dependent and -independent parameters to give the expected bond valence sums. These are shown for an arbitrary selection of several structures as sample calculations for V−O bonds in Table 4 and Fe−O bonds in Table 5. In each case the root mean square deviation between the BVS and the oxidation state is given. For V−O bonds the best agreement (0.08 Å) is obtained using the oxidation-state dependent parameters given by the $R_0 \sim n$ correlation in equation (3), but our proposed oxidation-state independent bond valence parameters at 0.16 Å can be recommended to calculate the oxidation state of a metal ion in an unknown compound without any assumptions. Less effective are Zocchi's oxidation-state dependent and Palenik's oxidation-state independent parameters.

In respect of Fe−O bonds our oxidation-state independent parameters give better agreement for the selected structures than the values taken from the correlation given by eq (4). The difference is not large and may be the result of using a fairly small sample structures. It is of interest to note that for the only Fe(V) compound K_3FeO_4 available to date [35], the BVS for Fe(V) calculated with our parameter sets (1.795/0.30) and (1.816/0.37) is 5.14 and 5.18, respectively, while the parameters (1.745/0.37) by Kanowitz et al. 4.28 which is too low as might be expected. For the more "exotic" oxidation states like Fe(I) in the only compound K_3FeO_2 [36] and Fe(VI) in the compounds Na_2FeO_4 [37], K_2FeO_4 [38] and Cs_2FeO_4 [39], the BVS calculated with our oxidation-state independent parameters is 2.19, 6.73, 6.45, and 6.54, while the parameters by Kanowitz et al. 1.88, 5.33, 5.15 and 5.21, respectively. Interestingly, if the bond lengths are thermally corrected using the rigid-body model [40], the value of BVS for

Table 4. Comparison of the BVS calculations using different parameters in Å for V−O bonds.

Compound	$n = 2$	This work [eq. (3)] $n = 3$	Zocchi's $n = 4$	$n = 5$	This work 1.788/0.32	Palenik's 1.774/0.37	n	Ref.
1. $V(H_2O)_6]SO_4 \cdot H_2O$								[a]
V1	2.04 *1.95*				2.11	2.33	2	
V2	1.99 *1.90*				2.05	2.28	2	
2. $[V(pic)_2(H_2O)_2] \cdot 2 H_2O$	1.98 *1.88*				2.04	2.27	2	[b]
3. $Ba_3V_2(HPO_4)_6$								[c]
V1		2.81 *2.80*			2.83	3.01	3	
V2		3.05 *3.08*			3.11	3.26	3	
4. $NaV(SO_4)_2$		3.07 *3.11*			3.13	3.28	3	[d]
5. $K_4[VO(cit)]_2 \cdot 6 H_2O$			4.04 *4.12*		4.08	4.04	4	[e]
6. $Ni(VOPO_4)_2 \cdot 4 H_2O$			3.96 *4.09*		4.09	3.96	4	[f]
7. $K_2(NH_4)_4[VO_2(cit)]_2 \cdot 6 H_2O$				5.05 *4.93*	5.00	4.72	5	[g]
8. $Na_2[H_2V_{10}O_{28}][hmtH]_2 \cdot 8 H_2O$								[h]
V_1				4.97 *4.80*	4.78	4.64	5	
V_2				5.00 *4.84*	4.85	4.68	5	
V_3				4.96 *4.80*	4.80	4.64	5	
V_4				4.94 *4.78*	4.77	4.62	5	
V_5				4.97 *4.81*	4.81	4.64	5	
9. BaV_3O_8								[i]
V_1			4.85 *5.18*	5.19 *5.10*	5.27	4.89	5	
V_2			4.12 *4.20*	4.41 *4.24*	4.18	4.14	4	
V_3			4.75 *5.06*	5.08 *4.99*	5.15	4.87	5	
10. $K_6(VO)_4(SO_4)_8$								[j]
V_{1a}			4.05 *4.16*	4.33 *4.18*	4.16	4.10	4	
V_{1b}			4.67 *4.85*	5.00 *4.85*	4.87	4.74	5	
V_{2a}			4.65 *4.82*	4.97 *4.82*	4.83	4.71	5	
V_{2b}			4.11 *4.23*	4.40 *4.24*	4.23	4.17	4	
$[\Sigma \Delta^2/m]^{1/2}$				0.08 *0.15*	0.16	0.26		

a: Cotton, F. A.; Falvello, L. R.; Murillo, C. A.; Pascual, I.; Schultz, A. J.; Tomas, M.: Inorg. Chem. **33** (1994) 5391.
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Table 5. Comparison of the BVS calculations using different parameters in Å for Fe−O bonds.

Compound		This work, eq. (4)			This work 1.795/0.30	Kanowitz's 1.745/0.37	n	Ref.
		$n = 2$	$n = 3$	$n = 4$				
1 $[Fe(H_2O)_6] \cdot [Fe(C_6H_6N_3O_4)_3]_2 \cdot 12\ H_2O$		1.93			1.93	2.09	2	[a]
2 $[Fe^{II}(OCMes^*)_2]_2$	Fe1	1.64			1.88	1.78	2	[b]
	Fe2	1.63			1.87	1.77	2	
3 $[Fe^{II}(THF)_4] \cdot [HFe_3(CO)_{11}]_2$		1.91			1.92	2.07	2	[c]
4 $[Fe^{III}_3(salpn)_2(O_2CCH_3)_2 \cdot (DMF)_2$		1.88			1.88	2.04	2	[d]
5 $[Fe^{II}Fe_2^{III}O(CH_2BrCO_2)_6 \cdot (H_2O)_3]$	Fe1		2.93		2.92	2.90	3	[e]
			3.01		3.03	2.99	3	
		2.11			2.17	2.29	2	
6 $(pyH)[Fe^{III}(hfac)_2(hfptH_2)]$			3.00		3.00	2.97	3	[f]
7 $Sr_4Fe_2^{III}Fe_2^{IV}O_{11}$	Fe1			4.00	3.98	3.63	4	[g]
	Fe2	3.00			2.99	2.97	3	
8 $Sr_8Fe_2^{III}Fe_6^{IV}O_{23}$	Fe1			3.99	3.97	3.62	4	[g]
	Fe2	3.29			3.35	3.26	3	
	Fe3			4.16	4.00	3.78	4	
9 $Na_4Fe^{IV}O_4$				3.73	3.85	3.38	4	[h]
10 $Ba_2Fe^{IV}O_4$				4.06	4.27	3.69	4	[i]
$[\Sigma \Delta^2/m]^{1/2}$		0.18			0.14	0.26		

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Fe(VI) of K_2FeO_4 [38], for example, calculated with our and Kanowitz *et al.*'s parameters is down to 6.14 and 4.95, respectively.

5. Conclusions

We have shown that the proposed "universal" value of $B = 0.37$ Å, which was determined by ensuring that the bond valence sums were correct for different coordination numbers, does not in general work well for different oxidation states. For V−O and Fe−O bonds we propose a set of oxidation-state-independent parameters that work well with all oxidation states but we were unable to find a similar set for Cu−O bonds. It is not clear that a single value of B can be made to fit different coordination numbers and different oxidation states, so the oxidation-state-dependent parameters are expected to give better agreement than oxidation-state-independent parameters. However, our examination of the BVS analyses in a selection of V and Fe compounds shows that both work very well as the case of Mo previously studied, especially that of oxidation-state-independent can safely be used in cases where the oxidation state of metal is not already known. To further exploring and understanding of the BVS parameters and the $R_0 \sim n$ correlation many more elements would be worthy of consideration, as well as the $B \sim n$ correlation emerged studied alternatively.

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