# Notes

## Bond Valence Sums in Coordination Chemistry Using Oxidation State Independent $R_0$ Values.  A Simple Method for Calculating the Oxidation State of Manganese in Complexes Containing Only Mn−O Bonds

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### Introduction

The postulate that the bond valence sum, henceforth BVS, surrounding the *j*th atom or ion is equal to the oxidation state $z_j$, as shown in eq 1, can be traced to Pauling.[1]  The valences

$$z_j = \sum_i s_{ij} \qquad (1)$$

$$s_{ij} = \exp[(R_0 - r_{ij})/b] \qquad (2)$$

$$s_{ij} = (r_{ij}/R_0)^{-N} \qquad (3)$$

of the individual bonds, $s_{ij}$ in eq 1, can be calculated from the observed bond lengths using eq 2 or 3, where $r_{ij}$ is the observed bond length, $R_0$ and $N$ are constants that are dependent upon the nature of the *ij* pair, and *b* is usually taken to be 0.37.  The $R_0$ value can be viewed as a bond length of unit valence.  The usual procedure was to assume an oxidation state and to use a previously determined $R_0$ value appropriate to the bond being considered.  A more extensive discussion of the BVS method can be found elsewhere.[2−4]

Although the concept appears to be extremely useful in coordination chemistry, it has not been applied routinely.  My interest has been in exploring the question of whether the BVS could be used to calculate the oxidation state of a metal ion in a coordination compound without any assumptions.[5]  The present report examines the usefulness of oxidation state independent $R_0$ values as applied to Mn complexes with O donors.  The Mn case was chosen because of the different $R_0$ values, summarized in Table 1, that have been proposed for Mn−O bonds depending on the Mn oxidation state.[6−10]

### Experimental Section

The Mn−O bond length data were from the June 1996 release of the Cambridge Structural Database (henceforth CSD) containing 160 091 entries.[11]  For a given coordination number, those entries containing only O atoms were retrieved, i.e., $MnO_n$ where $n = 3−8$.  A total of 202 entries from the CSD gave a starting set of 250 $MnO_n$ complexes.  An oxidation state for each entry was calculated using eq 2 with $b = 0.37$ and an $R_0$ value of 1.75 Å.[9]  Any obvious erroneous oxidation states were corrected at this point;[12] see the discussion below.  Then, an $R_0$ value which minimized the sum of the squares of the

**Table 1.**  Values of $R_0$ for Mn−O Bonds for Oxidation States 2, 3, 4, and 7[a]

| ref | $R_0$ (Å) | | | |
|-----|-----|-----|-----|-----|
|  | +2 | +3 | +4 | +7 |
| 6 | 1.790 | 1.760 | 1.753 | 1.79 |
| 7 | 1.765 | 1.732 | 1.750 | |
| 8 | 1.790 | 1.760 | 1.753 | |
| 9 | 1.750 | 1.750 | 1.750 | 1.750 |
| 10 | 1.798 | 1.769 | 1.774 | 1.780 |
| *N* | 5.6 | 5.5 | 5.2 | 5.43 |

[a] Equation 2 with $b = 0.37$ was used in refs 6−9, and eq 3 in ref 10 with the corresponding $N$ values.

**Table 2.**  The Experimental values of $R_0$, for Mn−O Bonds as a Function of the Coordination Number of the Mn Atom[a]

| CN | no. | $R_0$ (Å) |
|-----|-----|-----|
| 3 | 3 | 1.837 |
| 5 | 14 | 1.762 |
| 6 | 201 | 1.753 |
| 7 | 8 | 1.766 |
| 8 | 3 | 1.761 |
| all | 229 | 1.759 |
| 5−8 | 226 | 1.754 |

[a] CN is the coordination number, no. is the number of complexes used for that coordination number, and $R_0$ is the value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

**Table 3.**  Summary of Mn−O distances, Used in the Analysis as a Function of Oxidation State, ox., and coordination number, CN[a]

| ox. | CN | no. | Mn−O (Å) | | |
|-----|-----|-----|-----|-----|-----|
|  |  |  | min | max | av |
| 2 | 5 | 45 | 1.993 | 2.240 | 2.121 |
| 2 | 6 | 858 | 1.977 | 2.375 | 2.176 |
| 2 | 7 | 56 | 2.097 | 2.574 | 2.242 |
| 2 | 8 | 24 | 2.168 | 2.396 | 2.286 |
| 3 | 5 | 35 | 1.851 | 2.268 | 1.959 |
| 3 | 6 | 252 | 1.823 | 2.372 | 2.015 |
| 4 | 6 | 90 | 1.835 | 1.988 | 1.899 |

[a] The number of bonds found is no., min is the minimum Mn−O distance found for that oxidation state and coordination number, max is the maximum Mn−O distance found for that oxidation state and coordination number, and av is the average Mn−O distance found for that oxidation state and coordination number.

differences between the reported and calculated oxidation states was determined.  The resulting $R_0$ values for $n = 3−8$ are given in Table 2.  The final $R_0$ value of 1.754 Å was calculated using only the $MnO_n$ data for $n = 5−8$, for reasons given below.  An analysis of the Mn−O bond length data used in our study is given in Table 3.  A complete listing of the compounds is available.  The BVS was calculated using FORTRAN programs written by the author.[13]

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(1) Pauling, L. *J. Am. Chem. Soc.* **1929,** *51,* 1010−1026.

(2) Palenik, G. J. *Inorg. Chem.* **1997,** *36,* 122.

(3) Urusov, V. S. *Acta Crystallogr., Sect. B* **1995,** *B51,* 641−649.

(4) O'Keeffe, M. *Modern Perspectives in Inorganic Crystal Chemistry*; Kluwer Academic Publishers:  Netherlands, 1991; pp 163−175.

(5) We are currently studying the Li, V, Cr, Fe, and Mo systems.

(6) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991,** *B47,* 192−197.

(7) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993,** *32,* 4102−4105.

(8) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985,** *B41,* 244−247.

(9) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991,** *113,* 3226−3229.

(10) Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B* **1976,** *B32,* 1957−1959.

(11) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993,** *8,* 31−37.

(12) These and the other corrections noted below have been sent to the CSD and will be included in a later release of the file.

(13) Copies of the FORTRAN programs can be obtained from the author.

## Results and Discussion

The BVS was calculated for 250 Mn−O complexes using an initial $R_0$ value of 1.75 Å,[9] and only 31 had values that differed by 0.25 or more from an integer value. In 10 of the 31 the complex had been misclassified in the CSD file; see below. One other case had been discussed in an earlier paper.[2] The question was whether there were features of the remaining 20 that caused the BVS to have a noninteger value or whether the BVS was not accurate to more than about 10%. All 20 examples were not examined in detail since in many cases only a minimum of crystallographic data was reported or the original journal article was not readily available. However, as shown below, a noninteger BVS frequently signaled problems either with the CSD entry or with the crystal structure determination.

The five $MnO_3$ complexes recovered from the CSD provide excellent examples of some of the pitfalls in the CSD file, as well as the usefulness of the BVS. Three of the "hits", GIRPOM,[14] VOPLIV,[15a] and VOPLIV01,[15b] gave a BVS that was less than 1. Examination of the original papers showed that these were polymeric structures involving $MnO_6$ fragments and were difficult to encode properly in the CSD file. These data were then included in the $MnO_6$ data set and the BVS was in good agreement with the reported values. While the remaining three $MnO_3$ fragments, JIXKEG[16] and JIXLIL,[17] gave an $R_0$ value of 1.837 Å, see Table 2, the BVS for the "best" $R_0$ value of 1.754 Å was less than the expected value of 2. However, these complexes were prepared to produce low coordination numbers and are sterically hindered. Steric effects will produce longer bonds and a lower BVS.

All 10 of the $MnO_4$ complexes retrieved from the CSD had a noninteger BVS that differed by more than 0.25 from an integer or expected value. Four of the 10 involved the permanganate ion, and three had a BVS that was greater than the expected value of 7. In the series of alkyltriphenylphosphonium permanganate complexes, the authors noted "substantial librational motion", with approximate thermal corrections to the Mn−O bond lengths of 0.13 Å.[18] The fact that large thermal motions can lead to apparently shorter bond lengths is well-known. The corresponding BVS is therefore larger than the expected valence.

In the cases of AMPMNC,[19] COYLEH10,[20] MCOPEC,[21] VUCXUM,[22] and ZUZNOX,[23] the initial BVS values were 1.30,

1.40, 1.30, 1.79, and 1.28, much less than the expected 2. According to the CSD, the Mn ion in each case had a total coordination number of 4. However, in all cases the original reports showed two additional bonds to Cl ions in AMPMNC, O atoms in MCOPEC and VUCXUM, and N atoms in COYLEH10 and ZUZNOX. MCOPEC and VUCXUM were included in the $MnO_6$ case with the two additional Mn−O bonds. The net result was that, of the remaining $MnO_4$ entries, none actually contained a four-coordinate Mn.

Finally, PARSMN[24] and HEHSES[25] were retrieved as $MnO_6$ complexes and had BVS 1.49 and 1.48. PARSMN was really an $MnO_8$, case and the addition of two Mn−O bonds gave a BVS of 1.84. The complex HEHSES was actually a $MnO_6N_2$ case and was labeled as invalid. We see that a low and/or noninteger value of the BVS can indicate possible problems with the reported structure or with the data in the CSD.[12]

A fascinating example was BUPWEO,[26] a $MnO_5$ case where the BVS was 1.00. Although the complex could be considered octahedral with one long Mn−O bond being left out of the CSD file, the BVS did not improve appreciably. The structure had been refined with a 40% occupancy for the Mn atom, which seemed rather unusual. Since the authors also had prepared Mg salts of the same ligand, the identity of the sample may be suspect. The structure is presently being reinvestigated.[27]

The Mn−O system presents an unusual problem in that some polynuclear Mn complexes have been prepared where the Mn ions have different oxidation states. LIHXUV[28] is a linear $Mn_3$ complex formulated as Mn(III)−Mn(II)−Mn(III) with hydroxo and acetato bridges. The BVS for the central Mn(II) ion was 2.48, which is reasonable for a weakly coupled system.

BOZZAR[29] is an example of a Mn(IV) complex where the BVS was 4.26, slightly larger than the 0.25 limit that was considered acceptable. The result is interesting because the complex could be formulated as a Mn(III) and a reduced catechol ligand but the experimental evidence favored the Mn(IV) formulation, which is in agreement with the BVS. Thus, the BVS can be useful in deciding between alternate formulations involving different oxidation states of the ligand and/or the metal ion.

Table 3 contains a summary of the Mn−O distances used in the BVS analysis as a function of oxidation state and coordination number. The average Mn−O distance increases with an increase in coordination number at a constant oxidation state, as expected. Similarly, the Mn−O distance decreases with increasing oxidation state at a constant coordination number, also as expected. However, the important point is the large range of values at any fixed combination of oxidation state and coordination number. The large variation in the Mn−O distance is understandable in terms of the BVS. Ligand constraints can

(14) GIRPOM is *catena*-((μ₂-formamido-*O*)bis(μ₂-methylphenylphosphinato-*O,O'*)manganese formamide solvate. Betz, P.; Bino, A. *Inorg. Chim. Acta* **1988**, *149*, 171−175.

(15) VOPLIV and VOPLIV01 are *catena*-tris(betaine)manganese(II) tetrachloromanganate(III). (a) Chen, X.-M.; Mak, T. C. W. *Inorg. Chim. Acta* **1991**, *189*, 3−5. (b) Schreuer, J.; Haussühl, S. *Z. Kristallogr.* **1993**, *205*, 309−310.

(16) JIXKEG is bis(μ₂-2,4,6-tri-*tert*-butylphenolato-*O*)bis(2,4,6-tri-*tert*-butylphenolato-*O*)dimanganese toluene solvate. Bartlett, R. A.; Ellison, J. J.; Power, P. P.; Schoner, S. C. *Inorg. Chem.* **1991**, *30*, 2888−2895.

(17) JIXLIL is bis(μ₂-bis(2,4,6-triisopropylphenyl)boryl oxide-*O*)bis(2,4,6-triisopropylphenyl)boryl oxide-*O*)manganese hexane solvate. Chen, H.; Power, P. P.; Schoner, S. C. *Inorg. Chem.* **1991**, *30*, 2884−2888.

(18) Karaman, H.; Barton, R. J.; Robertson, B. E.; Lee, D. G. *J. Org. Chem.* **1984**, *49*, 4509−4516.

(19) AMPMNC is bis(α-(aminomethyl)methylphosphinic acid)diaquadichloromanganese(II). Glowiak, T.; Sawka-Dobrowolska, W. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2763−2766.

(20) COYLEH10 is bis[(nitrato-*O*)(pyrrole-2-carboxaldehyde *N*-acetylhydrazone-*O*)]manganese(II). Ianelli, S.; Nardelli, M.; Pelizzi, C. *Gazz. Chim. Ital.* **1985**, *115*, 375−383.

(21) MCOPEC is bis(dichlorophosphato)bis(ethyl acetate)manganese(II). Danielsen, J.; Rasmussen, S. E. *Acta Chem. Scand.* **1963**, *17*, 1971−1979.

(22) VUCXUM is hexakis(μ₂-*tert*-butoxy)di-*tert*-butoxydimanganeseditin. Veith, M.; Kafer, D.; Koch, J.; May, P.; Stahl, L.; Huch, V. *Chem. Ber.* **1992**, *125*, 1033−1042.

(23) ZUZNOX is bis(4-aminobenzenesulfonato)diaquamanganese(II). Gunderman, B. J.; Squattrito, P. J.; Dubey, S. N. *Acta Crystallogr., Sect. C* **1996**, *C52*, 1131−1134.

(24) PARSMN is tetraphenylarsonium tetranitratomanganese(II). Drummond, J.; Wood, J. S. *J. Chem. Soc. A* **1970**, 226−232.

(25) HEHSES is *catena*-[μ₂-pyrazine-2,3,5,6-tetracarboxylato]diaqua manganese(II)] dihydrate. Marioni, P.-A.; Marty, W.; Stoeckli-Evans, H.; Whitaker, C. *Inorg. Chim. Acta* **1994**, *219*, 161−168.

(26) BUPWEO is bis[μ-(2,4,5-trichlorophenoxy)acetato-*O*]bis[*trans*-diaqua-(2,4,5-(trichlorophenoxy)acetato)manganese(II)]. Kennard, C. H.; Smith, G.; O'Reilly, E. J.; Chiagjin, W. *Inorg. Chim. Acta* **1983**, *69*, 53−59.

(27) C. H. Kennard, private communication.

(28) LIHXUV is tetrakis(μ₂-acetato)bis(μ₂-hydroxo)bis(hydrogen tris[3,5-diisopropylborato])trimanganese(III,II,III)−3,5-diisopropylpyrazole−acetonitrile solvate. Kitajima, N.; Osawa, M.; Imai, S.; Fukisawa, K.; Moro-oka, Y.; Heerwegh, K.; Reed, C. A.; Boyd, P. D. W. *Inorg. Chem.* **1994**, *33*, 4613−4614.

(29) BOZZAR is tris(3,5-di-*tert*-butylcatecholato)manganese(IV) acetonitrile solvate. Chin, D.-H.; Sawyer, D. W.; Schaeffer, W. P.; Simmons, C. J. *Inorg. Chem.* **1983**, *22*, 752−758.

limit the range of Mn−O distances that are possible so that the other ligands must assume distances that are compatible with the BVS being equal to the oxidation state. The principle of the BVS being equal to the oxidation state of the metal ion is an important principle that must be satisfied at the expense of a constant bond radius. Under these conditions, the calculation of the BVS is much more meaningful than bond distance comparisons.

## Conclusions and Recommendations

The BVS is a relatively simple calculation if the appropriate $R_0$ values are available. For the Mn case with O donor atoms, an $R_0$ of 1.754 Å can be used to calculate the oxidation state of the Mn atom with no prior assumptions. The results are in good agreement for oxidation states of Mn(II), Mn(III), and Mn(IV).[30] The agreement with Mn(VI) and Mn(VII) is not very good, which may be a reflection of few good examples or problems with high oxidation states and low coordination numbers. We are pursuing the question of BVS for high oxidation states and low coordination numbers in other metal ions.

The deviation of the BVS from an integer value usually indicates either problems with the structure, possible steric constraints, or excessive thermal motion. A number of examples have been provided to illustrate these points.

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(30) One of the referees noted that the "best" $R_0$ values for Mn +2, +3, and +4 were 1.761, 1.739, and 1.747 Å, which are very close to the values given by Liu and Thorp in ref 7.

In cases where the ligand oxidation state is ambiguous, the BVS can be used as a guide for the oxidation state of the metal and therefore, by inference, the ligand. The BVS can be extremely useful to chemists in evaluating the results of a crystal structure analysis or in attempting to resolve conflicts regarding oxidation states. Structural chemists should be able to utilize the BVS to support the crystal structure analysis. The concept can be applied without assumptions regarding the oxidation state and can help avoid serious errors prior to publication.

There are an increasing number of papers published in which the authors neither name their compound nor give the proposed oxidation state for the metal ion. The absence of these data places the onus on the reader to determine the missing information. In studying the various compounds used in preparing this report, there were numerous occasions where the oxidation state was not easily determined from the data given. Certainly, the authors of any publication are in a better position to ascertain the possible oxidation state of a metal ion in a complex that they have prepared. Furthermore, the authors should be more knowledgeable regarding the rules of nomenclature in their area of expertise.