Bond Valence Sums in Coordination Chemistry. A Simple Method for Calculating the Oxidation State of Cobalt in Complexes Containing Only Co−O Bonds

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Introduction

Although the bond valence sum, henceforth BVS, appears to be extremely useful to coordination chemists, it has not been applied routinely. The BVS has been applied to extended X-ray absorption fine structure data for metalloenzymes, but an assumption was required regarding the oxidation state of the metal ion.[1,2] The determination of the oxidation state of the metal ion in biological molecules and other complexes without any assumptions would be a more valuable tool; thus, our interest has been in exploring whether the oxidation state of a metal ion could be calculated from the bond distances with no assumptions.[3] Good agreement between the calculated and postulated oxidation states would provide support for the chemical formula and the accuracy of a crystal structure determination. However, if the oxidation state calculated from the bond distances obtained from a crystal structure differs markedly from the postulated chemical formula, usually problems in the crystal structure determination, possible steric effects, or incorrect formulations are indicated.

The postulate that the BVS surrounding the jth atom or ion is equal to the oxidation state z_j, as shown in eq 1, can be traced

$$z_j = \sum_i s_{ij} \tag{1}$$

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

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

to Pauling.[4] The valences 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. Since $s_{ij} = 1$ if $r_{ij} = R_0$, the R_0 value can be viewed as a unit valence bond length. Consequently, there is a unique R_0 value for each ij pair. 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.[5−8]

Table 1. Values of R_0 for Co−O bonds for Oxidation States +2 and +3[a]

ref	oxidn state of Co +2	oxidn state of Co +3
8	1.680	1.680
9	1.692	1.70
10	1.692	
WP	1.685	1.637

[a] Equation 2 with $b = 0.37$ was used in refs 8, 9, and 10, and WP is the present work.

Our efforts have been directed toward determining new and more accurate R_0 values, as well as exploring the possibility of determining an R_0 value for an element pair that could be used in eq 2 without assuming an oxidation state for the metal ion. One of the problems in developing new R_0 values is the necessity to evaluate the crystallographic data that is being used.

The present report examines the usefulness of oxidation state independent R_0 values as applied to Co complexes with O donors and suggests how a BVS can be used to identify suspect crystal structure determinations. There are also only a few R_0 values that have been determined for the Co−O pair, and these are summarized together with our results in Table 1.[8−10]

Experimental Section

The Co−O bond length data were from the June 1997 release of the Cambridge Structural Database (CSD) containing 167 797 entries.[11] For a given coordination number (CN), those entries containing only O atoms were retrieved i.e., CoO_n where $n = 3-8$. A total of 199 entries from the CSD gave a starting set of 227 CoO_n complexes. An initial R_0 value[8] of 1.680 Å was used to calculate an oxidation state for each entry. Any obvious erroneous oxidation states were corrected at this point,[12] see the discussion below, and duplicate entries were removed. Then, an R_0 value which minimized the sum of the squares of the differences between the reported and calculated oxidation states was determined for each CN and for oxidation states 2 and 3 for all coordination numbers. The R_0 values determined for CN's 3−8 are given in Table 2 and appear to decrease from coordination number 3 to 6 and then increase slightly to CN 8.

A complete listing of the BVS calculated for all of the CoO_n data for $n = 3-8$ using the average R_0 value of 1.661(16) Å is available. An analysis of the Co−O bond length data used in our study is given in Table 3. The BVS was calculated using FORTRAN programs written by G.J.P.[13]

Results and Discussion

The BVS was calculated for 227 CoO_n fragments, $n = 3-8$, using an initial R_0 value of 1.680 Å.[8] Two CoO_3 entries,

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(1) Hati, S.; Datta, D. *J. Chem. Soc., Dalton Trans.* **1995**, 1177−1182.
(2) (a) Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585−1588. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102−4105.
(3) (a) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 122. (b) Palenik, G. J. *Inorg. Chem.* **1998**, *36*, 3394−3397. (c) Palenik, G. J. *Inorg. Chem.* **1998**, *36*, 4888−4890. (d) Browning, K.; Abboud, K. A.; Palenik, G. J. *J. Chem. Crystallogr.* **1995**, *25*, 851−855.
(4) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010−1026.
(5) Urusov, V. S. *Acta Crystallogr., Sect. B* **1995**, *B51*, 641−649.
(6) O'Keeffe, M. *Modern Perspectives in Inorganic Crystal Chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; pp 163−175.
(7) Brown, I. D. In *Structure and Bonding in Crystals*; Academic Press: New York, 1981; Vol. II, pp 1−30.
(8) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226−3229.
(9) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991**, *B47*, 192−197.
(10) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *B41*, 244−247.
(11) Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 31−37.
(12) All of the corrections have been sent to the CSD and will be included in a later release of the database.
(13) Copies of the FORTRAN programs can be obtained from the author.
(14) GIRPUS is *catena*-(μ_2-formamido-*O,O′*)bis(μ_2-methylphenylphosphinato-*O,O′*)cobalt formamide solvate. Betz, P.; Bino, A. *Inorg. Chim. Acta* **1988**, *149*, 171.

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Table 2. Experimental Values of R_0 (in Å) for Co−O Bonds as a Function of the Coordination Number of the Co Atom[a]

CN	no.	R_0
3	4	1.748
4	22	1.704
5	6	1.686
6	190	1.670
7	5	1.684
8	1	1.695
5−8	226	1.754

[a] CN is the coordination number, no. is the number of complexes used for that CN, 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 Co−O Distances Used in the Analysis[a]

ox.	CN	no.	min	max	avg(σ)
2	3	12	1.763	1.981	1.906(82)
2	4	84	1.845	2.073	1.960(41)
2	5	30	1.893	2.453	2.043(116)
2	6	1002	1.874	2.450	2.093(56)
2	7	28	2.018	2.251	2.152(60)
2	8	8	2.033	2.538	2.260(217)
3	6	132	1.866	2.168	1.895(30)

[a] Ox. is the oxidation state, CN is the coordination number, no. is the number of bonds found, min is the minimum Co−O distance, max is the maximum Co−O distance, avg is the average Co−O distance, and σ is the standard deviation of the average value for the given oxidation state and CN.

GIRPUS[14] and JIJPIB,[15] both gave a BVS of 0.98 rather than the expected 2.0. Both GIRPUS[14] and JIJPIB[15] have a polymeric structure in the solid state with a CoO_6 coordination and were not classified correctly in the CSD file.[16] The two entries were removed from the CoO_3 set and included in the CoO_6 set, and the final BVS sums were 1.82 and 1.83, respectively. The complex TBACCO[17] gave a BVS of 2.57 versus the reported 2.0. Since the crystallographic *R* value was given as 0.00 and a detailed report was not readily available, this entry was not included in subsequent calculations.

The BVS values calculated using an R_0 of 1.661 Å for the two complexes FIRSII[18] (BVS = 1.58 and 1.68) and FIRSOO[19] (BVS = 1.54 and 1.52) with CN = 3 illustrate the problems with low CN's. Metal complexes with low CN's are usually synthesized by using very bulky ligands. Under these circumstances, the bonds are unusually long, the BVS is lower than expected, and the complexes also are usually very reactive. Any reactions of these complexes usually increase the CN and would presumably yield a BVS closer to the proposed oxidation state. There is a slight improvement for FISRII[18] (BVS = 1.69 and 1.79) and for FIRSOO[19] (BVS = 1.65 and 1.62) if one uses the Co(II) R_0 value of 1.685 Å.

The anion in the complex BAMNIM[20] is octahedral (BVS = 2.31), but the structure was refined using only isotropic thermal parameters to a relatively high crystallographic *R* value of 0.109, "... ignoring the contribution of seven reflections with large values of $|F_o - F_c|$...". The authors noted that attempts to refine the structure anisotropically gave unreasonable thermal parameters. Therefore, the structure should be viewed as suspect.

In both HAZDOB10[21] (BVS = 2.36) and ZAXHIP[22] (BVS = 1.58), the cation is a radical tetrathiafulvalene derivative and the Co(II) is in a Keggin type polyoxotungstate anion, $CoW_{12}O_{40}{}^{6-}$. The authors note that the anions "... appear as centrosymmetric units as a result of disorder...". Therefore, the Co−O bond lengths are not as accurate as one might hope and the deviation of the BVS from 2.0 is not unreasonable.

COPTOX[23] is a one-dimensional paramagnetic conductor and was formulated as $Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$. The fractional occupancy of the Co(II) could account for the low BVS of 1.38 compared to an ideal value of 2.

The high crystallographic *R* value of 0.12 for GLYCCO10[24] (BVS = 1.75) could have justified not using this entry. However, on inspection of the original report we found that the Co was five and not four coordinate as indicated in the CSD file. Including the fifth Co−O bond increased the BVS to 2.07, in good agreement with the presence of Co(II) in the complex.

The ions in PASFCO[25] and PASCON10[26] are very similar and provide an example of the use of the BVS in examining the bonding in coordination compounds. While the refinements of PASFCO[25] and PASCON10[26] (the crystallographic *R* values are 0.105 and 0.098, respectively) are not up to present day standards, a comparison is still informative since in both cases the question is whether the CN is 4 or 8. The ion $Co(CF_3COO)_4{}^{2-}$ has D_{2d} symmetry, and there are 4 Co−O at 2.00 Å and 4 more at 3.11 Å. The ion was classified as 4 coordinate in the CSD with a BVS = 1.62. Adding the additional 4 long Co−O distances increases the BVS slightly to 1.68. In $Co(NO_3)_4{}^{2-}$ the symmetry is C_2 and the Co−O distances are 2.03, 2.11, 2.36, and 2.54 Å, giving a BVS of 1.82. If the Co(II) R_0 value is used for PASFCO[25] and PASCON10,[26] the BVS is 1.81 and 1.94, respectively. These results suggest that both ions should be considered as 8 coordinate species. The fact that the BVS is slightly lower than the expected 2.0 may involve steric problems with the high CN or reflect the fact that the structure determinations are not particularly accurate.

An intriguing example is VORTOL,[27] where the BVS of 1.51 was one of the lowest for a Co(II) complex. There are a number

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(15) JIJPIB is *catena*(bis(μ_2-aqua)(μ_2-*p*-methylbenzoato-*O,O′*)cobalt(II) bis(*p*-methoxybenzoate) dihydrate. Antsyshkina, A. S.; Chyragov, F. M.; Porai-Koshits, M. A. *Koord. Khim.* **1989**, *15*, 1098−1103.

(16) The CSD is aware of the problem with polymeric coordination compounds and is working on a solution.

(17) TBACCO is tetrabutylammonium tris(acetylacetonato)cobalt(II). Granoff, B. *Diss. Abstr. B.* **1967**, *27*, 4131.

(18) FIRSII is bis(μ_2-tricyclohexylmethoxo-*O,O*)bis(tricyclohexylmethoxy)dicobalt(II) methanol cyclohexane tetrahydrofuran solvate. Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773−1780.

(19) FIRSOO is bis(μ_2-triphenylmethoxo-*O,O*)bis(triphenylmethoxy-*O*)dicobalt(II) *n*-hexane solvate in ref 18.

(20) BAMNIM is pentakis(4-methylpyridinylisocyanide)cobalt(I) tris(nitromalonaldehydo)cobalt(II). Albertin, G.; Bordignon, E.; Orio, A.; Pellizzi, G., Tarasconi, P. *Inorg. Chem.* **1981**, *20*, 2862−2868.

(21) HAZDOB10 is octakis(bis(ethylenedithio)tetrathiafulvalene) tetracontaoxocobalt(II) dodecatungsten−5.5-water. Gomez-arcia, C. J.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; Le Magueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaes, P. *Inorg. Chem.* **1995**, *34*, 4139−4151.

(22) ZAXHIP is octakis(bis(ethylenedithio)tetrathiafulvalene) tetracontaoxocobalt(II)dodecatungsten acetonitrile solvate trihydrate in ref 21.

(23) COPTOX is hexaaquacobalt(II) bis(oxalato)platinate(II) monohydrate. Schultz, A. J.; Underhill, A. E.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 1313−1315.

(24) GLYCCO10 is cobalt(II) monoglycerolate. Slade, P. G.; Radoslovich, E. W.; Raupach, M. *Acta Crystallogr., Sect. B* **1971**, *B27*, 2432−2436.

(25) PASFCO is tetraphenylarsonium tetrakis(trifluoroacetato-*O*)cobalt(II). Bergman, J. G., Jr.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1420−1424.

(26) PASCON10 is tetraphenylarsonium tetrakis(nitrato-*O,O′*)cobalt(II). Bergman, J. G., Jr.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1208−1213.

(27) VORTOL is sodium tris(1-ethyl-4(1*H*)-oxo-[1,3]dioxolo[4,5-*g*]cinnoline-3-carboxylato-*O,O′*)cobalt(II) hexahydrate or sodium tris(cinoxacinato-*O,O′*)cobalt(II) hexahydrate. Chulvi, C.; Munoz, M. C.; Perello, L.; Ortiz, R.; Arriortua, M. I.; Via, J.; Urtiaga, K.; Amigo, L. M.; Ochando, L. E. J. *Inorg. Biochem.* **1991**, *42*, 133−138.

of points in the report that raise suspicion about the structure determination. Although the crystal size appeared adequate (0.18 × 0.18 × 0.31 mm), only $^1/_3$ of the unique reflections were observed. The heavy atoms were refined anisotropically and the hydrogen atoms isotropically so that the ratio of observed reflections to variables is about 5 or 6. Figure 2[27] used only small spheres for the anisotropically refined atoms, and the thermal parameters are not available. However, the isotropic B_{eq} values which were reported are rather strange in two respects. The accuracy of the B_{eq} varied by a factor of about 2, with the Co and Na ions having larger esd's than some of the lighter atoms. The Na^+ B_{eq} (9.34(2) Å^2) seemed rather large compared to those of the Co^{2+} (4.18(3) Å^2) and the lighter atoms (3.0−6.0 Å^2). Furthermore, neither the Na−O distances nor a description of the Na^+ coordination was given. The parameters were retrieved from the CSD file and used to calculate all the intra- and interatomic distances involving the Co and Na ions. While the Na^+ appears to be 9 coordinate, the distances of 3 at 2.999 Å, 3 at 3.073 Å, and 3 at 3.290 Å are all too long.[28] The BVS around the Na^+ ion is only 0.23, which is much smaller than the expected 1.0. In essence the Na^+ ion does not appear to be in contact with any other atom. The final conclusion is that the crystal structure determination has serious flaws.

Table 3 contains a summary of the Co−O distances used in our BVS analysis as a function of oxidation state and CN. The majority of the data refers to Co(II), and we see that the average Co−O distance increases with an increase in CN at a constant oxidation state, as expected. For Co(III), the only data involved 6-coordinate complexes, and the average value is smaller than that for Co(II), as expected. An important point is the large range of values at any fixed combination of oxidation state and CN. The large variation in the Co−O distance is understandable in terms of the BVS. Ligand constraints can limit the range of Co−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 for that CN. 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 may be more meaningful than bond distance comparisons or the usual crystallographic R value in assessing the accuracy of a crystal structure determination.

Conclusions and Recommendations

We have shown that an R_0 of 1.661 Å can be used to calculate the oxidation state of the Co atom in coordination complexes containing only Co−O bonds with no prior assumptions. The BVS is a relatively simple calculation, and the results are in good agreement for oxidation states of Co(II) and Co(III). The deviation of the BVS from an integer value usually indicates either possible steric constraints, excessive thermal motion, problems with the crystal structure report, or some combination of all of these effects. We have provided a number of examples to illustrate these points.

In cases where the ligand coordination is ambiguous, the BVS can be used as a guide for assigning the total CN. The ability to calculate the oxidation state of the metal and therefore, by inference, the ligand should be an important tool for both coordination chemists and biochemists. The BVS can be extremely useful to noncrystallographers 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 in the literature.

Supporting Information Available: Listings of the BVS calculations for the 227 Co complexes used in the analysis (13 pages). Ordering information is given on any current masthead page.

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(28) Preliminary results for alkali metal oxygen complexes found Na−O distances that averaged 2.56 Å, close to the sum of the ionic radii for Na^+ and O^{2-}. Therefore, to have all the Na−O distances greater than 3.0 Å is unreasonable.