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# Bond Valence Sums in Coordination Chemistry Using Oxidation State Independent $R_0$ Values

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## Introduction

Bond valence sums have not been used routinely in coordination chemistry even though they are potentially very useful; nevertheless, there are a small number of recent papers that have utilized bond valence sum calculations.[1−3] The basic concept (eq 1) that the valence of the *j*th atom or ion, $z_j$, can be defined

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

in terms of the sum of the individual bond valences, $s_{ij}$, can be traced to Pauling.[4] The valences of the individual bonds are not known but can be calculated from the observed bond lengths using eq 2, where $R_{ij}$ is the observed bond length, $R_0$ is a

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

constant dependent upon the nature of the *ij* pair, and $b = 0.37$. A more extensive discussion can be found in a recent review.[5] The question is whether $R_0$ is dependent upon the oxidation state or only upon the nature of the two atoms. Our interest has been in exploring the latter idea as applied to coordination compounds since the oxidation state could then be calculated without any assumptions. Several examples of how these calculations can be used in coordination chemistry are presented in this note.

## Experimental Section

The bond valence sums were all calculated using Fortran programs written by the author. The various $R_0$ values (Å) were calculated using reported parameters[6] and are as follows: V−O, 1.774; Mn−O, 1.750; Co−O, 1.680; Co−N, 1.790. The bond length data were from the literature[7] or from the Cambridge Structural Database (henceforth CSD).[8]

## Results and Discussion

We were very interested in the reported structure[7] of "$Co^{III}$-Hedta" since there are very few, if any, seven-coordinate cobalt(III) complexes. Therefore, using the published parameters[6] for Co−O and Co−N bonds, the bond valence sum was calculated to be 1.90, suggesting that the complex contained Co(II). A survey of the Cambridge Structural Database[8] revealed that the complex was indeed identical to the previously reported $Co^{II}(H_2edta)\cdot 2H_2O$.[9] A correction will appear shortly.[10]

That the bond valence sum offers a relatively simple method for determining the oxidation state and assessing the correctness of reported structures can be further illustrated by the case of "manganese(III) acetylacetonate".[11] The BVS was calculated to be 4.32, but if we used the values for Co−O, the BVS became 3.46 which is closer to the expected value of 3.0. Two redeterminations of the $Mn(acac)_3$ structure[12] gave BVS values of 3.22 and 3.18. As noted in ref 12, there is little doubt that the earlier determination was actually carried out on $Co(acac)_3$.

The Cambridge Structural Database contains over 150 000 entries which are very carefully checked for accuracy and consistency. Nevertheless errors, while rare, can occur. The anion in POCANC,[13] acetonitrile[trinitratocobalt], was reported to contain Co(III) but the BVS was 1.99. In the published article the anion included Co(II) but was incorrectly entered into the database.[14] Similarly, in the vanadium complex AOXOVA,[15] triammonium bis(oxalato)dioxovanadium(III), the CSD entry gave a calculated value of 3.78 vs an expected value of 5.0. Once again inspection of the original article revealed that one of the V−O bond lengths in the CSD differed from that in the original because of an error in one of the published coordinates.[14]

In summary the use of oxidation state independent $R_0$ values for BVS calculations provides important and useful information regarding the oxidation state of the metal ion. The results are surprisingly good in view of the empirical nature of the calculation of the $R_0$ value. Although other $R_0$ values[16,17] may be more accurate, we have found that the values used are applicable to any element pair and have provided good agreement between the postulated and calculated oxidation states in most cases. We are in the process of examining data in the CSD for several $MO_6$ systems to establish better $R_0$ values and the limits under which the BVS is applicable.

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