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Bond Valence Sums in Coordination Chemistry. The Calculation of the Oxidation State of Samarium in Complexes Containing Samarium Bonded Only to Oxygen

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A simple method is presented for calculating the oxidation state of Sm in complexes where Sm is bonded only to O ligands. A total of 88 SmO_n fragments with $n = 4–12$ were retrieved from the Cambridge Structural Database and were analyzed using the bond valence sum (BVS) method. New R_0 values for Sm(II)–O of 2.116(21) Å and for Sm(III)–O of 2.055(13) Å were derived. The average R_0 value of 2.086 Å gives a good approximation of the oxidation state of the Sm ion, either +2 or +3, from the observed distances without any assumptions. The Sm–O distances for +2 and +3 complexes with coordination numbers of 4–11 are tabulated and reflect the requirement that the BVS must equal the oxidation state. The distances for CN = 12 were not included because of problems with the reported crystal structures. Several X-ray structure determinations where the BVS and the oxidation state did not agree are discussed.

Introduction

We have been exploring whether the oxidation state of a metal ion in a coordination compound could be calculated from the bond distances determined from a crystal structure without any assumptions and trying to learn what information could be derived from the calculation.[1] Agreement between the calculated and postulated oxidation states would provide additional support for the accuracy of the structure determination. However, when the calculated and postulated values differ markedly, possible steric effects or problems in the crystal structure determination are indicated. The bond valence sum, henceforth BVS, can also be used to determine the oxidation state of the metal ion in metalloenzymes using EXAFS data, extended X-ray absorption fine structure, without any assumptions. Although the concept appears to be extremely useful in coordination chemistry, it has not been applied routinely.

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 to Pauling.[2] 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 and R_0 and N are constants that are dependent upon the nature of the ij pair.

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

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

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

The constant b was determined to be 0.37 Å,[3] and the value has been generally accepted.[4−8] 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.[6−14]

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The present report examines the problems in establishing an R_0 value for Sm complexes with O donors. The Sm−O case was chosen because of the existence of +2 and +3 oxidation states, the fact that coordination numbers greater than 6 should be relatively common, and the paucity of the different R_0 values for the lanthanides. There was one value for Sm(III)−O using eq 2 with $b = 0.337$ Å and one using eq 3 in a compilation of R_0 values.[10] An extrapolated value of 2.088 Å was found in a more recent listing.[15] However, no R_0 value for Sm(II)−O has been reported. One of the difficulties in determining an R_0 is the requirement for accurate bond length data which can be obtained from crystal structure data provided the determination has been carried out properly. Conversely, we have found that one of the best guides for assessing the accuracy of a structure determination has been the BVS. Therefore, the procedure we have been using is to use structural data only from those compounds where the BVS agrees with the expected value. Thus, determination of the "best" R_0 value requires a careful assessment of the crystallographic data and of experimental details in those cases where there is a discrepancy between the calculated BVS and the postulated oxidation state.

Experimental Section

The Sm−O bond length data were from the October 2001 release of the Cambridge Structural Database (CSD).[16] Those 88 entries containing only O atoms bonded to Sm, i.e., SmO_n, where n (4−12) is the number of O's and also the coordination number (CN), were retrieved. Duplicate entries were removed to give a starting set of 80 SmO_n complexes. An oxidation state was assigned to each entry on the basis of a BVS calculated using an R_0 value of 2.10 Å[10] and by comparison with the CSD entry. In those cases where there was a question about the oxidation state, the original reference was consulted. An R_0 value was determined for each entry so that the BVS was equal to the postulated oxidation state. Then an average value was calculated together with an estimated standard deviation, σ. Those R_0 values that differed by more than 2.0σ from the mean value were deleted and flagged for further examination: a new R_0 value and σ were calculated. The resulting R_0 values are given in Table 1 and show no trends with CN. The R_0 determined in this way did not differ significantly from the R_0 value that minimized the sum of the squares of the differences between the reported and calculated oxidation states. An analysis of the Sm−O bond length data used in our study is given in Table 2. The BVS was calculated using FORTRAN programs written by GJP.[17]

Results and Discussion

Table 1. Summary of the R_0 Values for Sm−O Bonds as a Function of Coordination Number and Oxidation State[a]

CN	3+	2+	CN	3+	2+
4	2.072(6)	2.138	9	2.054(15)	2.111
n/*t*	2/2	1/1	*n*/*t*	18/18	1/1
5	2.056(16)	2.122(18)	10	2.057(10)	
n/*t*	10/10	2/2	*n*/*t*	7/7	
6	2.054(16)		11	2.080	
n/*t*	9/9		*n*/*t*	1/1	
7	2.061(15)	2.087	12	2.174(10)	
n/*t*	5/5	1/1	*n*/*t*	6/6	
8	2.048(14)		all	2.055(13)	2.116(21)
n/*t*	13/17		*n*/*t*	62/75	5/5

[a] The average R_0 value given is that which makes the observed and calculated oxidation states equal, with the estimated standard deviation in parentheses. CN is the coordination number, n is the number of complexes used, and t is the total number of complexes for that coordination number and oxidation state.

Table 2. Summary of Sm−O Distances Used in the Analysis[a]

ox	CN	no.	min	max	av(σ)	val	CN•val
2	4	4	2.320	2.635	2.414(149)	0.448	1.79
2	5	10	2.290	2.640	2.487(144)	0.361	1.80
2	7	7	2.506	2.580	2.551(22)	0.304	2.12
2	9	9	2.653	2.675	2.667(11)	0.222	2.00
3	4	8	2.099	2.434	2.195(117)	0.684	2.74
3	5	45	2.087	2.495	2.262(111)	0.570	2.85
3	6	54	2.033	2.699	2.340(150)	0.462	2.77
3	7	28	2.222	2.494	2.378(86)	0.416	2.91
3	8	104	2.155	2.597	2.419(75)	0.373	2.98
3	9	153	2.277	2.756	2.470(79)	0.325	2.92
3	10	70	2.194	3.074	2.527(142)	0.279	2.79
3	11	11	2.493	2.686	2.565(66)	0.251	2.76

[a] Ox is the oxidation state, CN is the coordination number, no. is the number of bonds found, min is the minimum Sm−O distance found for that oxidation state and coordination number, max is the maximum Sm−O distance found for that oxidation state and coordination number, av(σ) is the average Sm−O distance found for that oxidation state and coordination number, with the estimated standard deviation in parentheses, val is the valence of the average distance using eq 2 with $b = 0.37$ and $R_0 = 2.116$ Å for Sm(II) and $R_0 = 2.055$ Å for Sm(III).

The first R_0 value for Sm(II)−O bonds of 2.116(21) Å was determined using the data from 5 Sm(II)−O complexes, while the corresponding value for Sm(III)−O was determined to be 2.055(13) Å from 75 Sm(III)−O complexes. The larger value for Sm(II)−O is reasonable since the radius of Sm(II) is larger than that of Sm(III), and R_0 can be viewed as a length of unit valence. An analysis of a recent compilation of M−O R_0 values[15] indicated that the higher oxidation state usually had the smaller R_0 value. There are a very few exceptions in the case of some high oxidation state transition metal−oxygen bonds which may be related to different spin states and/or π-bonding. Our value R_0 for Sm(III)−O can be compared to the extrapolated value of 2.088 Å[15] determined from ionic salts. One conclusion is that the BVS method originally formulated for ionic species can be applied to coordination compounds.

The BVS calculated for 5 Sm(II) and 75 Sm(III) complexes with coordination numbers 4−12 using eq 2 has only 11 examples, all Sm(III), where the value differs by 0.25 vu, vu = valence units, or more from the expected integer oxidation state. Of the 11, 6 were for CN = 12, vide infra. The value of 0.25 vu is arbitrary since the difference expected will depend on the value of σ for R_0 and the number of bonds. However, past studies[1] have suggested that 0.25−0.30 vu is a reasonable guide to those structural studies that should be examined in more detail. We have examined a large number

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of structures with differences less than 0.25−0.30 vu and have found them to be free of obvious errors. We feel that this approach is reasonable since one goal of our studies has been to determine whether the BVS is a guide to the correctness of a crystal structure determination. Thus, we have focused our efforts on those structures where the BVS and oxidation state do not agree.

The BVS calculated using the average R_0 value of 2.086 Å, presented in the Supporting Information, gives a reasonably good approximation of the oxidation state of the Sm ion without any assumptions if there are no problems with the structure determination. Consequently, one can obtain the oxidation state of the Sm ion in Sm−O complexes using only the observed bond distance data.

The BVS results for SmO_{12} complexes were disturbing since none of the 6 entries were in very good agreement. The question was whether the BVS model fails for high coordination numbers or whether there was a problem with the data. Most of our studies have involved coordination numbers of 10 or less, and in these cases, the model works very well. Some preliminary calculations were carried out involving Ce and CN = 12, and they suggest that the model is also valid for high coordination numbers.[18] Therefore, we decided to examine the SmO_{12} case in more detail.

The SmO_{12} complexes are from two publications of one group,[19,20] and all have surprisingly high symmetry. The space group *F*23 has been reported only 25 times in the 257162 entries in the April 2002 CSD file, and 7 of the 25 are the SmO_{12} complexes in refs 19 and 20. The data presented in ref 19 are somewhat misleading. The authors give only one figure which is presumably for the ClO_4^- salt, and they state "... showing 50% thermal ellipsoids..."; however, only an outline is found. A careful inspection of the CIF files in the available supporting data for ref 19 finds that some of the carbon atoms in the pyrrolidine ring have B_{eq} values of 10.0−20.0, and the distances in the pyrrolidine ring range from 1.18 to 1.87 Å. Both the large B_{eq} values and the distances are indicative of either disordered or incorrectly placed atoms, suggesting that the reported crystal structures have serious problems. A simple explanation is that a lower symmetry space group should have been used and/or that the crystals are of lower symmetry, but twinned. In either case, the gross features of the structures are probably correct, but the geometrical data should be used only with caution. In support of this conclusion are reports of somewhat similar metal complex−lanthanide adducts which were all of lower symmetry.[21,22] In one case with Pr,[22] the calculated BVS was 2.85.[18]

In QIVBOM,[23] BVS = 2.73, the Sm(III) ion is bonded to four oxygens from two Si_7 clusters with the fifth ligand being the bulky 2,6-di(*tert*-butyl)phenol. The slightly lower BVS value may reflect the crowded nature of this cluster complex. However, the esd of our value of R_0 was 0.013 Å, corresponding to 0.034 valence units; for 5 bonds this would be 0.17 vu. Therefore, the value of 2.73 is probably within the error limits of our calculation, as is CIDJUU,[24] BVS = 3.25, which contains a SmO_9 fragment.

Three compounds with CN = 8, GEMHIP,[25] BVS = 3.45, YOVDES,[26] BVS = 3.23 and 3.53, and ZUVMUY,[27] BVS=3.41, are the only others that have a relatively large difference between the observed and expected values. In the case of GEMHIP, the *R* value of 0.130 is high by present day standards, but only an isotropic thermal parameter refinement was carried out, not the currently accepted standard.

The situation with YOVDES is difficult to assess because of the paucity of data in the publication and the absence of thermal ellipsoids in the two figures.[26] In Figure 1 of ref 26, the atoms are spheres, and in Figure 2, only the outlines of the ellipsoids are shown. For the two independent Sm ions, the BVS is larger than the expected value, suggesting that the bonds are too short. The thermal ellipsoid outlines indicate large thermal motion for several of the atoms which will lead to apparently short bonds and a larger BVS. Although the authors stated that the positional and thermal parameters had been filed with the CSD, apparently only a hard copy of the positional parameters was submitted. Consequently, an assessment of the magnitude of the thermal parameters is not possible.

ZUVMUY presents an interesting problem in data collection.[27] The fairly large crystals were sealed in capillaries together with the appropriate solvent; however, no absorption corrections were applied. The U_{eq} for the Sm ion was similar to, and in some cases smaller than, those of some of the carbon and oxygen atoms in the ligands which is not physically reasonable. Consequently, the structure should be viewed with caution, as implied by the BVS value.

Distances in Sm Complexes. The bond distance data for those complexes used in our analysis are summarized in Table 2. We see that for a given oxidation state and coordination number there is a wide range of Sm−O distances, but the average bond distance corresponds to a valence per bond equal to the oxidation number divided by the CN. One of the implications of this observation is that a comparison of bond distances in a structure per se may be

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either not relevant nor indicative of the accuracy and correctness of the structure. However, the BVS seems to be a relatively sensitive measure of the accuracy of a structure determination. The main drawback is that suitable R_0 values may not be available.

Conclusions and Recommendations

The BVS is a relatively simple calculation if the appropriate R_0 values are available. For the Sm case with O donor atoms, an R_0 of 2.086 Å can be used to calculate the oxidation state of the Sm atom with no prior assumptions. A further refinement would be to use the value of 2.116 Å for Sm(II) or 2.055 Å for Sm(III). The results are in good agreement for coordination numbers from 4 to 11. When the BVS for a CSD entry deviates from the expected value, a problem is usually indicated. The problem could be additional interactions that were not reported by the authors and/or were not included in the CSD file. In addition, possible steric constraints, disorder, or excessive thermal motion can contribute to a BVS that does not agree with the postulated value. In all cases, the BVS provides a good indication of the reliability of the structure report.

Supporting Information Available: Listings of the BVS calculations for the SmO_n ($n = 4-12$) used in the analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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