Inorg. Chem. **2003**, *42*, 118–121

Inorganic Chemistry
Article

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

Petra L. Roulhac and Gus J. Palenik*

Chemistry Department, The University of Florida, P.O. Box 117200,
Gainesville, Florida 32611-7200

Received August 27, 2002

A total of 119 CeO_n fragments with $n = 3–12$ were analyzed by using the bond valence sum, or BVS, method to yield new R_0 values for Ce(III)–O of 2.121(13) Å and for Ce(IV)–O of 2.068(12) Å. These R_0 values can be used to calculate the oxidation state of Ce in complexes where Ce is bonded only to O ligands. Furthermore, the average R_0 value of 2.094 Å gives a good indication of whether the oxidation state of the Ce ion is +3 or +4 from the observed distances without any assumptions. The fact that complexes with coordination numbers of 10–12 are in agreement is significant since this study is the first example which indicates that high coordination numbers also follow BVS rules. The Ce–O distances used in deriving the R_0 values for the +3 and +4 complexes are tabulated as a function of coordination number and have a wide range of values, but the average Ce–O distance reflects the requirement that the BVS must equal the oxidation state. Several examples are given where the oxidation state of the Ce ion is apparently incorrectly assigned, as well as cases where problems with the X-ray structure determinations are indicated by a disagreement between the postulated and calculated oxidation state.

Introduction

We have been exploring the concept of whether the oxidation state of a metal ion in a coordination compound can be calculated from the bond distances determined in a crystal structure without any assumptions. We have also been trying to learn what information could be derived from the calculation.[1] If there is agreement between the calculated and postulated oxidation states, the accuracy of the structure determination is supported. However, when the calculated and postulated values differ markedly, problems in the crystal structure determination are frequently indicated. Although the concept appears to be extremely useful in coordination chemistry, the bond valence sum, henceforth BVS, has not been applied routinely, in part because of the lack of accurate constants for a variety of bond types.

The empirical postulate that the 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.[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

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

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

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

R_{ij} is the observed bond length and R_0 and N are constants that are dependent upon the nature of the *ij* pair. The R_0 value can be viewed as a bond length of unit valence. The constant b was determined to be 0.37[3] and the value has been generally accepted.[4−8] The usual procedure is to assume an oxidation state and to use a previously determined R_0

---

* To whom correspondence should be addressed. E-mail: palenik@chem.ufl.edu.

[1] (a) Wood, R. M.; Abboud, K. H.; Palenik, R. C.; Palenik, G. J. *Inorg. Chem.* **2000**, *39*, 2065−2068. (b) Jensen, W. P.; Palenik, G. J.; Tiekink, E. R. T. *Polyhedron* **2001**, *20*, 2137−2143 and references therein.

[2] Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010−1026.

[3] Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244−247.

[4] Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B* **1976**, *32*, 1957−1959.

[5] Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991**, *47*, 192−197.

[6] Jansen. L.; Chandran, L.; Block, R. *J. Mol. Struct.* **1992**, *260*, 81−98.

[7] Naskar, J. P.; Hati, S.; Datta, D. *Acta Crystallogr., Sect. B* **1997**, *53*, 885−894.

[8] (a) Urusov, V. S. *Acta Crystallogr., Sect. B* **1995**, *51*, 641−649. (b) Burdett, J. K.; Hawthorne, F. C. *Am. Miner.* **1993**, *78*, 884−892.

10.1021/ic025980y CCC: $25.00
© 2003 American Chemical Society
Published on Web 11/28/2002

value appropriate to the bond being considered. An example of the calculation can be found in the supporting data. A more extensive discussion of the BVS method can be found elsewhere.[8−13] The usefulness of the BVS method has prompted attempts to provide a theoretical basis for eqs 1−3.[8]

The present report examines the problems in establishing R_0 values for Ce complexes with O donors. The Ce−O case was chosen because of the existence of +3 and +4 oxidation states, the fact that for the relatively large Ce ion, coordination numbers greater than 6 should be common, and finally, the paucity of the R_0 values for the lanthanides in various oxidation states. In one compilation of R_0 values,[10] there was a value for Ce(III)−O using eq 2 with $R_0 = 2.180$ Å and $b = 0.338$ and one for Ce(IV)−O of $R_0 = 2.117$ Å and $b = 0.326$. There was also a value for Ce(III)−O using eq 3 with $R_0 = 2.160$ Å and $N = 6.5$. However, there are no values for either Ce(III)−O or Ce(IV)−O using eq 2 with $b = 0.37$.

We have operated under the assumption that the BVS should always be "correct" and have used the crystallographic data only when the observed and calculated oxidation states are in agreement. We have found that any discrepancies can usually be explained by a careful examination of the crystallographic and/or the experimental data, vide infra.

Experimental Section

The Ce−O bond length data for each coordination number (CN) from 3 to10 were retrieved from the April 2001 release of the Cambridge Structural Database (CSD), and the data for CN = 11 and 12 were obtained from the April 2002 release.[14] Those entries containing only O atoms bonded to Ce, i.e., CeO_n, where n (3−12) is the number of O's and also the CN, were retrieved to give a starting set of 117 CeO_n complexes. No restrictions were placed on the crystallographic R value for inclusion in our data set. We have found that if the errors are random in a crystal structure determination with a large R value, the BVS is still consistent with the oxidation state. However, systematic errors such as absorption, disorder, or the neglect of anomalous scattering are usually indicated by a BVS that deviates significantly from the expected value, and a closer look at the published report is initiated. These data were augmented by the data for $Ce_2Mg_3(NO_3)_{12}{\cdot}24H_2O$[15]and $(NH_4)_2Ce(NO_3)_6$[16] which are not in the CSD file. Duplicate entries were flagged, and an initial R_0 value of 2.10 Å[10] was used to calculate an oxidation state for each entry. An R_0 value was determined for each entry so that the BVS was equal to the postulated oxidation state. Those R_0 values that differed by more than 2.0σ from the mean value were deleted, and a new R_0 value and σ were calculated.

Table 1. Summary of the *R₀* Value for Ce−O Bonds as a Function of Coordination Number and Oxidation State[a]

CN	3+	4+	CN	3+	4+
3	2.150		9	2.123(12)	
n/t	1/1		n/t	30/37	
4	2.117(90)		10	2.129(9)	2.081(26)
n/t	1/4		n/t	6/6	4/4
6	2.110(8)	2.065(14)	11	2.125(28)	
n/t	3/3	13/13	n/t	3/3	
7	2.055	2.075(7)	12	2.133(16)	2.096
n/t	1/1	4/4	n/t	7/7	1/1
8	2.112(11)	2.065(7)	All	2.121(13)	2.068(12)
n/t	11/13	11/14	n/t	60/75	32/36

[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 Ce−O Distances Used in the Analysis[a]

Ox	CN	no	min	max	av (esd)	val	CN x val
3	4	4	2.142	2.422	2.270(144)	0.669	2.68
3	6	18	2.208	2.606	2.383(115)	0.493	2.96
3	8	88	2.317	2.662	2.479(61)	0.380	3.04
3	9	279	2.323	2.992	2.538(84)	0.324	2.92
3	10	60	2.451	2.963	2.587(103)	0.284	2.84
3	11	22	2.494	2.860	2.595(71)	0.278	3.06
3	12	72	2.393	2.777	2.645(51)	0.243	2.92
4	4	4	2.083	2.102	2.091(8)	0.940	3.76
4	6	78	2.026	2.588	2.242(149)	0.624	3.74
4	7	28	2.027	2.571	2.329(186)	0.494	3.46
4	8	96	2.272	2.389	2.324(25)	0.500	4.00
4	10	20	2.328	2.494	2.400(49)	0.407	4.07

[a] Ox is the oxidation state, CN is the coordination number is the number of bonds found, min is the minimum Ce−O distance found for that oxidation state and coordination number, max is the maximum Ce−O distance found for that oxidation state and coordination number, Av (σ) is the average Ce−O distance found for that oxidation state and coordination number, with the estimated standard deviation in parentheses, and val is the valence of the average distance using eq 2 with $b = 0.37$ and $R_0 = 2.121$ Å for Ce(III) and $R_0 = 2.068$ Å for Ce(IV).

The resulting R_0 values summarized in Table 1 as a function of CN and oxidation state do not appear to show a dependence on the 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 Ce−O bond length data used in our study is given in Table 2. The BVS was calculated by using FORTRAN programs written by G.J.P.[17]

Results and Discussion

Excluding eight entries with CN = 3, vide infra, the BVS calculated by using eq 2 with $b = 0.37$ and an R_0 value of 2.121 Å for Ce(III) and 2.068 Å for Ce(IV) has only 13 examples where the value differs by more than 0.30 from the expected integer oxidation state. In fact, the average R_0 value of 2.094 Å gives a reasonably good approximation of the oxidation state of the Ce ion without any assumptions, using only the observed bond distance data.

The case of CN = 3 reflects the problems with polymeric-type structures in the CSD, since in eight of the nine entries, Ce actually had a CN greater than three. Only GEGZAT, tris[2,6-di(*tert*-butyl)phenoxy-*O*]cerium(III)[18] (BVS = 2.78),

---

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

(10) Brown, I. D. In *Structure and Bonding in Crystals*; Academic Press: New York, 1981; Vol. II, pp 1−30.

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

(12) (a) Brown, I. D. *J. Chem. Educ.* **2000,** *77*, 1070−1075. (b) Brown, I. D. *The Chemical Bond in Inorganic Chemistry The Bond Valence Model*; Oxford University Press: Oxford, UK, 2002.

(13) Zachariasen, W. H. *J. Less Common Metals* **1978**, *62*, 1−7.

(14) Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 31−37.

(15) Zalkin, A.; Forrester, J. D.; Templeton, D. H. *J. Chem. Phys.* **1963**, *39*, 2881−2891.

(16) Beineke, T. A.; Delgaudio, J. *Inorg. Chem.* **1968**, *7*, 715−721.

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

was a 3-coordinate Ce(III). The BVS is slightly smaller than the expected value because of steric constraints in the molecule.

Steric problems may account for the smaller BVS for the CN = 4 compounds SOZKUN, bis(μ_2-triphenylsiloxo)bis[di{triphenylsiloxy}cerium(III)][19] (BVS = 2.57), and SOZLUO, bis(μ_2-*tert*-butoxo)bis[di{tri(*tert*-butyl)methoxy}cerium(III)][20] (BVS = 2.69), compared to the similar but less bulky KIPLEA, bis(μ_2-[{di-*tert*-butyl}methoxo)])bis[(di{*tert*-butylmethoxy})cerium(III)][21] (BVS = 2.84). In essence, bulky ligands produce longer bonds and hence a smaller BVS. The case of SOZMAV, (μ_2-1,4-hihydroquinonediolato-*O*,*O*′) bis[(tri{*tert*-butylmethoxy}cerium(III)][20] (BVS = 3.76), was interesting since the question of whether the Ce was +3 or +4 was discussed. The final decision was Ce(IV); the BVS supports that conclusion.

The cluster VIXMEU, bis(μ_3-isopropoxo)tetrakis(μ_2-isopropoxo)heptakis(isopropoxy)-2-propanol-(μ_4-oxo)-dicerium(III,IV)-dicerium(IV),[22] has 15+ charges to be distributed among the four Ce ions, two with CN = 6 and two with CN = 7, and was postulated to contain either totally delocalized Ce_4^{15+} or Ce_2^{8+} and Ce_2^{7+}. The BVS of 3.88 for the Ce ions with CN = 6 and the BVS of 3.60 for the pair with CN = 7 suggest that the Ce_2^{8+} and Ce_2^{7+} model is more appropriate and is also reasonable on the basis of the smaller Ce(IV) ion having the smaller CN.

In the report on JAXDUH, tris(tetra-*n*-butylammonium)bis(5-oxo)tetrakis(2-methoxo)octakis(2-oxo)nitrosy l-tetraoxomolybdenum(II) tetramolybdenum(IV)cerium(III)[23] (BVS = 2.51), the authors described problems with the data collection which resulted in a "poor quality" data set. The *R* values (0.0980 and 0.1163) are high, reflecting the poor quality of the intensity data. Consequently, we did not include these data in our determination of the R_0 value.

The situation with KPACCE10, potassium penta(acetato)cerium(III) monohydrate[24](BVS = 3.78), was somewhat peculiar since the calculated BVS was close to Ce(IV), but the formulation was that of Ce(III). However, if the oxidation state were changed to Ce(IV), then the BVS was 3.28, also in poor agreement. We suggest that the very large *R* value of 0.19 coupled with the poor BVS agreement indicates serious problems with the structure determination. A similar situation exists with ACACCE, tetrakis(acetylacetonato)cerium(IV)[25] (BVS = 3.33), where the early determination with a large *R* value was in poor agreement. However, a subsequent redetermination of the α-phase ACACCE02[26] (BVS = 3.97) and determination of the *β*-phase ACACCE01[27](BVS = 4.07) are in good agreement. The initial determination of the structure of GUPCCE, guanidinium pentacarbonatocerium(IV) tetrahydrate[28] (BVS = 3.59), was in poor agreement, although a subsequent refinement of the original data[29] in a centrosymmetric space group resulted in a slight improvement, BVS = 3.67. However, the *R* value of 0.067 is relatively large by today's standards. The above observations point out that earlier structure determinations of lanthanide complexes should be viewed skeptically.

The use of the BVS in assigning and/or supporting oxidation state assignments is illustrated with CECATI, tetrakis(catecholato)cerate(IV)[30] (BVS = 3.64), where the "noninnocent ligand" can exist in a semiquinone form which could give rise to a Ce(III) formulation. The authors concluded from various physical measurements that the complex was Ce(IV), in agreement with the BVS.

Incorrect Oxidation State Assignments. One interesting aspect of the chemistry of Ce(IV) is the strong oxidizing power of Ce(IV) and the instability of acidic solutions.[31] Acidic solutions of Ce(IV) can oxidize water to O_2(g), with the corresponding reduction of Ce(IV) to Ce(III). Therefore, using Ce(IV) as a starting material will not always yield Ce(IV) complexes. Since the difference in charges can frequently be adjusted by the presence or absence of protons, one should take care in assigning the Ce oxidation state. The problem is nicely illustrated with two examples: TINVUH, bis[(2,4,6-tris{4-*tert*-butyl}pyridinium)-1,3,5-trazine] aquapenta(nitrato-*O*,*O*′)cerate(IV) ethoxy penta(nitrato-*O*,*O*′)cerate(IV) hydroxide nitrate,[32] and CILKOX, bisoxonium hexa(nitrato-*O*,*O*′)cerate(IV) trihydrate.[33]

TINVUH was prepared with 2 M HNO_3 and was formulated as containing the anions $[Ce(NO_3)_5H_2O]^-$, $[Ce(NO_3)_5EtO]^{2-}$, $2NO_3^-$, and OH^- to balance the +6 charge of the cations. The formulation of basic species from an acid solution was necessary if the Ce were +4. However, if the Ce were +3 we would have as anions $[Ce(NO_3)_5H_2O]^{2-}$, $[Ce(NO_3)_5EtOH]^{2-}$, and $2NO_3^-$, with a water molecule. Not only is the latter formula more reasonable chemically, but the BVSs of 2.69 and 2.69 for Ce in the two anions are in agreement with this formulation.

The experimental details for the preparation of CILKOX[31] are somewhat less detailed but 2.5 M HNO_3 solution of

---

(18) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 1130−1132.

(19) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963−4968.

(20) Sen, A.; Stecher, H. A.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 473−479.

(21) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1989**, *28*, 3280−3282.

(22) Yunlu, K.; Gradeff, P. S.; Edelstein, N.; Kot, W.; Shalimoff, G.; Streib, W. E.; Vaartstra, B. A.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 2317−2321.

(23) Villanneau, A.; Proust, F.; Robert, F.; Gouzerh, P. *J. Chem. Soc., Dalton Trans.* **1999**, 421−426.

(24) Sadikov, G. G.; Kukina, G. A.; Porai-Koshits, M. A.; Pospelova, L. A. *Zh. Strukt. Khim.* **9**, 145−146.

(25) Matkovic, B.; Grdenic, D. *Acta Crystallogr.* **1963**, *16*, 456−461.

(26) Titze, H. *Acta Chem. Scand. Sect. A* **1974**, *28*, 1079−1088.

(27) Titze, H. *Acta Chem. Scand.* **1969**, *23*, 399−408.

(28) Voliotis, S.; Rimsky, A.; Faucherre, J. *Acta Crystallogr., Sect. B* **1975**, *31*, 2607−2609.

(29) Marsh, R. R.; Herbstein, F. H. *Acta Crystallogr., Sect. B* **1988**, *44*, 77−88.

(30) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611−1616.

(31) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley: New York, 1988; p 976 and ref 22.

(32) Chan, G. Y. S.; Drew, M. G. B.; Hudson, M. J.; Isaacs, N. S.; Byers, P.; Madic, C. *Polyhedron* **1996**, *15*, 3385−3398.

(33) Dvorkin, A. A.; Krasnova, N. F.; Simonov, Yu., A.; Abashkin, V. M.; Yakshin, V. V.; Malinovskii, T. I. *Soviet Phys. Crystallogr.* **1984**, *29*, 282−285 is the English translation of the article in *Kristallogr.* **1984**, *29*, 471−475.

Ce(IV) was used in the synthesis. The BVS of 2.88 agrees with the formulation of the anion as containing Ce(III), and a water becomes another oxonium ion. The Ce(IV) starting material decomposed in the acidic solution to give the Ce(III) species $[Ce(NO_3)_6]^{3-}$, with H_3O^+ as the cations.

Distances in Ce complexes. The bond distance data for those complexes used in our analysis are summarized in Table 2. For a given CN, as expected, the average value for Ce(III) is larger than that of Ce(IV). We also see that for a given oxidation state and coordination number there is a wide range of Ce−O distances, which makes comparisons of bond distances difficult. For example, in CN = 6, the shortest Ce(III)−O distance lies within the range for Ce(IV)−O. A similar situation exists in CN = 8 and 10. One consequence is that assigning the oxidation state of cerium by a comparison of Ce−O distances can be misleading. However, the average Ce−O distance corresponds to a valence per bond equal to the oxidation number divided by the CN. Consequently, a comparison of bond distances in a structure per se may neither relevant nor indicative of the accuracy and correctness of the structure. However, the BVS seems to be a relatively sensitive measure of the oxidation state of the Ce ion, as well as the accuracy of a structure determination. Now that suitable R_0 values for Ce(III)−O and Ce(IV)−O are available, the assignment of the oxidation state should be less susceptible to error.

Conclusions and Recommendations

The BVS is a relatively simple calculation that can be carried out by using eq 2 for any cerium complex containing only Ce−O bonds. We are currently working on extending this to complexes with Ce−N bonds. The R_0 value of 2.094 Å can be used to give an approximate value of the oxidation state without any assumptions from the observed bond distances. A refinement of the calculation can be carried out using the R_0 value for either Ce(III)−O or Ce(IV)−O. The calculation is particularly useful when there is a question of the oxidation state because of the nature of the ligands or when there is the possibility of either an oxidation or reduction of the Ce ion. In the event that the calculated value does not agree reasonably well with the expected value, the crystal structure determination and bond distance data should be scrutinized very carefully.

Supporting Information Available: Listings of the BVS calculations for the CeO_n ($n = 3-12$) used in the analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025980Y