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Notes

Bond Valence Sums in Coordination Chemistry. Sodium−Oxygen Complexes

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Introduction

It is difficult to judge the accuracy of a crystal structure determination when anisotropic thermal parameters and disorder both in the molecule and in solvent molecules can all be used to reduce the crystallographic *R* value[1] to an acceptably low value. One aid in evaluating the report is the bond valence sum or BVS, a relatively simple calculation provided appropriate R_0 values are available (vide infra), since the BVS must be consistent with the reported bond distances. Two pertinent questions then arise: how to determine accurate R_0 values and how to interpret the resulting BVS. There is an interesting relationship between these two problems since the determination of R_0 values requires good bond distance data from crystal structure determinations, but then we find that the calculated BVS appears to be a better indicator of the correctness of a structure than the usual crystallographic *R* value.

Our previous studies have shown that the BVS is a surprisingly good indicator of the correctness of a crystal structure determination in mononuclear complexes.[2−7] When the BVS did not agree with the proposed oxidation state, the oxidation state may have been incorrectly assigned,[2] the metal ion may have been misidentified,[3] there may be unnoticed or unreported interactions,[2−7] or the crystal structure determination may be of poor quality.[2−7] Consequently, in those cases where there is poor agreement between the postulated and calculated BVS, these data should probably not be used in the determination of the corresponding R_0 value. In essence, the determination of useful R_0 values requires not only a compilation of crystallographic data but also a careful assessment of both these data and the experimental sections to explain any discrepancies. This report on the Na−O system illustrates the usefulness of the BVS in explaining chemical features observed in a crystal structure determination, as well as in assessing the correctness of the determination.

The present study of the Na−O complexes was undertaken for several reasons. The reported values of R_0,[8−11] with one exception,[8] were all derived from ionic-type solids, and the question was whether values derived from coordination type complexes would be identical. There are no complications from multiple oxidation and/or spin states; therefore, the Na−O complexes should provide a clear picture of the consequences of a noninteger BVS together with the effect, if any, of the coordination number on the BVS calculation. Finally, discussions of the Na−O distances and the coordination around a Na^+ ion are frequently not given although these data can not only provide chemical information but can be an indicator of the accuracy of the determination. The absence of a discussion of distances in Na−O complexes may be due to the misconception that the bonding is strictly ionic and perhaps uninteresting, as well as the lack of a current compilation of Na−O distances to which reported structures can be compared. This report demonstrates that the bonding in Na−O complexes has a covalent component and also provides a tabulation of the various Na−O distances as a function of coordination number which can be used in a discussion of Na−O bond lengths. Hopefully, our new R_0 values used in a BVS will become a routine calculation for Na compounds in all future crystal structure reports.

The oxidation state, z_j, can be calculated from the sum of the individual bond valences, s_{ij}, as shown in eq 1. The calculation of s_{ij} from the observed bond lengths, R_{ij}, can be carried out using eq 2, provided the constants *b* and R_0 are known. The

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

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

constant *b* is 0.37. This value was determined by Brown and Altermatt[9] and is generally accepted.[10] Since $s_{ij} = 1$ when $R_0 = R_{ij}$, the value of R_0 can be viewed as a bond length of unit valence and is dependent upon the nature of the *ij* pair. Since the R_0 value depends on the two atoms involved in the bond and there is a unique R_0 value for each pair of elements, the problem has been how to determine this value. The question of the dependence of R_0 upon the oxidation states of the *ij* pair and/or the coordination number has been the focus of our endeavors.

Experimental Section

The Na−O bond length data were from the April 1998 release of the Cambridge Structural Database (CSD) containing 181 309 entries.[12] Those entries containing only O atoms bonded to Na were retrieved, i.e., NaO_n, where *n* (from 3 to 8) is the number of O's and also the total coordination number (CN). A total of 327 entries in the CSD gave a starting set of 389 NaO_n complexes after 13 duplicate entries were removed. A BVS for each entry was calculated using an R_0 value[8] of 1.743 Å. The majority of the NaO_3 entries gave a BVS much less than 1 and were obviously erroneous. Inspection of both drawings of the various entries and the original reports revealed that some of these were

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(1) R_0 is a constant used in the calculation of the BVS with eq 1 and is not to be confused with the crystallographic *R* value that is quoted in crystal structure determinations.

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

(3) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 3394−3397.

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(8) Browning, K.; Abboud, K. A.; Palenik, G. J. *J. Chem. Crystallogr.* **1995**, *25*, 851−855.

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

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

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

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

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Table 1. Experimental Values of R_0 (Å) for Na−O bonds as a Function of the Coordination Number of the Na Atom[a]

CN	no.	R_0	CN	no.	R_0
4	44	1.786(20)	7	39	1.754(39)
5	82	1.794(57)	8	51	1.756(56)
6	83	1.726(22)	4−8	301	1.756(42)

[a] CN is the coordination number, no. is the number of complexes used for that CN, and R_0 is the average R_0 value that gives a BVS equal to the oxidation state for each entry, with the estimated standard deviation in parentheses.

Table 2. Summary of Na−O Distances (Å) Used in the Analysis[a]

CN	no.	min	max	avg(sig)	val
4	180	1.914	2.558	2.299(74)	0.230
5	310	2.129	2.679	2.368(75)	0.191
6	648	2.130	2.978	2.415(94)	0.168
7	266	2.250	2.915	2.485(111)	0.139
8	384	2.240	2.991	2.540(137)	0.120

[a] CN is the coordination number, no. is the number of bonds found, min is the minimum Na−O distance, max is the maximum Na−O distance, avg is the average Na−O distance, sig is the standard deviation of the average value for the given CN, and val is the valence calculated for the average distance using eq 2 with $R_0 = 1.756$ Å.

polymeric in nature and had been classified incorrectly in the CSD.[13] In addition, some of the NaO_3 fragments appeared to form additional bonds to other groups (vide infra) and therefore were not included in subsequent calculations. For each coordination number, except $n = 3$, an R_0 value was determined for each entry so that the BVS was equal to the oxidation state, 1. Those individual R_0 values that differed by more than 2σ from the mean R_0 value were deleted, and a new mean and σ were calculated. These results are summarized in Table 1. The final R_0 value of 1.756(42) Å was obtained by considering all coordination numbers from 4 to 8. The resulting set of 301 entries had no R_0 value differing by more than 2σ from the mean value, and the σ for the calculated oxidation state was 0.11 valence unit.

A complete listing of the BVS calculated for 389 NaO_n complexes (n=3−8) using the R_0 value of 1.756(42) Å is available as Supporting Information. A tabulation of the Na−O bond length data as a function of coordination number is given in Table 2. The BVS was calculated using FORTRAN programs written by G.J.P.[14]

Results and Discussion

The R_0 value of 1.756(42) Å for Na−O bonds was derived from 301 NaO complexes with a CN from 4 to 8 by assuming that the oxidation state of Na was +1 and that eqs 1 and 2 were valid with $b = 0.37$. Our value is not significantly larger than an earlier value of 1.743 Å,[8] derived in a slightly different way, and is slightly but not significantly smaller than the values from ionic compounds (1.803 Å[9] and 1.80 Å[10]) and the empirical value of 1.80 Å.[11] The agreement between these values is important in establishing the validity of extending BVS from ionic solids to coordination complexes.

Since for 301 complexes the BVS equaled the oxidation state, the question arose as to the significance of the 88 cases where the BVS differed by more than 0.3 valence unit or 2.7σ from 1. We found that a BVS differing from the oxidation state invariably indicated problems with the crystal structure report, such as an incorrect cation, additional interactions that were overlooked by the original authors or not included in the CSD file, or simply questions about the validity of the structure determination. A discussion of some of the 88 entries that were not used in the determination of R_0 and, in particular, those complexes where the BVS differed by more than 0.3 of a valence unit from 1 can be conveniently divided into two categories: those complexes where the BVS was much larger than 1 and those where the value was much smaller than 1.

The two crystallographically different Na ions in VAXMUC[15] had large BVS values of 2.26 and 2.32. An examination of the experimental section suggested that lithium could have been introduced when $LiPPh_2$ was used in the synthesis. Using R_0 for Li−O bonds as 1.466 Å and the computer program VALENCE,[16] we found the BVS to be 1.02, suggesting that the reported sodium ion is actually lithium. The presence of Li rather than Na could explain the author’s statement that “a rational synthesis” did not yield the title compound. We did not use VAXMUC in our analysis.

In SULZEE10[17] there was a large BVS of 1.49 and a large number of questions about the structure determination. There are presumably three sodium ions in the compound, but only Na1 was retrieved from the CSD file. The Na2 was disordered about the mirror plane and Na3 was presumably not retrieved from the file since the Na−O distances are all very long. The BVS for Na3 was only 0.253, obviously too small. Since the mole ratio of Na:K used in the synthesis was 12:10, partial substitution of Na by potassium is a distinct possibility. If K were assumed, our calculated BVS is 0.67, closer to 1. The report also mentioned that some water molecules in the crystals “were smeared out” due to large thermal parameters. High thermal parameters can lead to bond lengths which appear shorter than they actually are, increasing the BVS. Another possible problem with this complex is that only about half the measured reflections (2162 out of 4215) were used, leading to a limited data set and possibly a poor refinement. Hence, for those reasons we did not use SULZEE10 in our analysis.

YOVCOB[18] had a BVS of 1.49, but there is some question about the existence of the Na^+ ion in the structure. No chemical analysis was given to support the formulation, and a full report has, to our knowledge, not appeared. The authors note “Because of disorder it has not been possible to locate the anion and solvent units precisely and the R factor cannot be reduced below 0.0830.” The existence of the anion is critical to the formulation as a Na salt and the authors cite “...a very similar copper(II) analogue...$[Na\{Cu(mhp)_2\}_6]$...”[19] in support of their structure. However, they noted that the source of the Na^+ in $[Na\{Cu(mhp)_2\}_6]$ was unexplained. The compound $[Na\{Cu(mhp)_2\}_6]$ was found in the CSD file as JODGAK[19] although the entry had not been retrieved in our search for Na−O complexes. In JODGAK the BVS of 1.54, calculated using the reported Na−O distance of 2.26 Å, is also too large. In JODGAK the authors stated “The presence of the central sodium ion is serendipitous.”. This is certainly a true statement since the starting material was the potassium salt of 6-methyl-2-hydroxypyridine. In summary, we feel that both YOVCOB and

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

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

(15) VAXMUC is hexakis(tetrahydrofuran)sodium (η^5-pentamethylcyclopentadienyl)tris(tetrahydroborato)uranium: Ryan, R. R.; Salazar, K. V.; Sauer, N. N.; Ritchey, J. M. *Inorg. Chim. Acta* **1989**, *162*, 221−225.

(16) Brown, I. D. *J. Appl. Crystallogr.* **1996**, *29*, 479−480.

(17) SULZEE10 is pentakis(ammonium)pentasodium bis((μ_6-phenylphosphonato)tris(μ_2-hydroxo)tris(μ_2-phenylphosphonato)hexakis(μ_2-oxo)-hexaoxohexamolybdenum(V)) hexahydrate: Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1995**, *235*, 135−145.

(18) YOVCOB is hexakis[bis(6-methyloxopyridine)cobalt(II)] sodium(I) acetate dichloromethane solvate: McConnell, S.; Motevalli, M.; Thornton, P. *Polyhedron* **1995**, *14*, 459−462.

(19) JODGAK is sodium dodecakis(μ_2-6-methyl-2-hydroxypyridine-*N*,*O*)-hexacopper nitrate hemihydrate: Blake, A. J.; Gould, R. O.; Milne, P. E. Y.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1991**, *14*, 1453−1455.

JODGAK are structure reports that should be regarded with skepticism pending further data to support their formulations as sodium salts.

PEANNA[20] provides an interesting example of how the BVS is a good indicator of the correctness of a crystal structure determination. The Na−O distances in the original report were unusually long, resulting in an extremely low BVS of 0.38. A subsequent redetermination of the structure in PEANNA11[21] was classified with a CN = 5 in the CSD file (BVS = 0.72) but is really an eight-coordinate Na$^+$ with a BVS of 0.90. In PEANNA the authors were studying both the Na$^+$ and Ag$^+$ complexes, and one can speculate that the data were interchanged in some way. Therefore, we did not use PEANNA in our analysis.

In many cases, a BVS much less than 1 indicates that one or more interactions may have been missed in the original report and/or may not have been included in the CSD file. PEZTET,[22] which has CN = 4 and a BVS of 0.60, is a good example of this type of problem. Examination of the original report showed a C_6H_6 ring close to the Na ion. With the Na−C distance estimated to be about 3.00 Å and using 2.079 Å for R_0 for Na−C bonds,[16] we obtained a BVS of 0.21 for three Na−C bonds, which added to the original BVS gives a new value of 0.81. The authors stated that there is a "significant interaction" between the sodium cations and the carbon rings but did not go into detail about the nature of the interaction. The BVS indicates that the aromatic ring is donating some electron density to the sodium ion in a novel covalent interaction. Therefore, the entry PEZTET did not meet our criterion of having only Na−O bonds.

A search of the CSD for other sodium compounds with Na−aromatic ring interactions yielded the complexes LEPHAP,[23] ROQFEI,[24] and YICTAF,[25] all of which feature sodium ions with oxygen atom donors that appeared to be interacting with $C_8H_8^{2-}$ rings. In these cases, the BVS for Na is very low without the contribution of the carbon atoms, and adding the additional valences for an Na−C interaction increased the BVS closer to 1. These results suggest that the carbon atoms of the ring do show a significant contribution to the overall BVS, thus indicating at least a partial covalent Na−C bond. Table 3 gives the BVS values for those complexes with Na−C interactions included. The complex HAHNUZ[26] appeared to have Na−C interactions as well, but a lack of information prevented us from calculating a new BVS, and we did not use this entry in analysis.

Unfortunately, in the case of the Na$^+$, secondary interactions with other electron donors are usually either not noted or not emphasized and frequently not included in the CSD file. For example, the complex FACGIZ,[27] CN = 3 and BVS = 0.64, had two Na−N bonds of 2.766 and 2.757 Å listed in the publication that were not included in the CSD. When R_0 of 1.891 Å is used,[16] the BVS contributions of the Na−N bonds are 0.09 and 0.10 respectively, giving a BVS of 0.93, clearly closer to the expected 1.0. Table 4 provides some additional examples[28−37] showing how other Na$^+\cdots$X (X = electron-donor atom) interactions increase the BVS to the expected value. The interaction of the Na$^+$ with anions has been postulated on the basis of infrared data,[38] and our BVS calculations provide new evidence for this type of interaction.

Table 3. Summary of Structural Data for NaO$_n$ Complexes with Organic Anions[a]

REFCODE	n	Na−O val	Na−C$_{avg}$	Na−C val	BVS-6	BVS-7
PEZTET[22]	4	0.60	3.06	0.07	0.74	0.81
LEPHAP[23]	3	0.49	3.00	0.08	0.73	0.81
ROQFEI[24]	3	0.68	3.07	0.07	0.88	0.95
YICTAF[25]	3	0.71	2.94	0.09	0.98	1.07

[a] REFCODE is the code used in the CSD file, n is the number of O atoms bonded to Na, Na−O val is the valence sum for the O donors, Na−C$_{avg}$ is the average Na−C distance (Å), Na−C val is the valence of the Na−C$_{avg}$ distances using R_0 = 2.419 Å for the Na−C bond, BVS-6 is the BVS assuming a coordination number of 6 for Na achieved by forming 6 − n Na−C bonds, and BVS-7 is the BVS assuming a coordination number of 7 for Na achieved by forming 7 − n Na−C bonds.

The Na(15-crown-5)$^+$ cations[39−51] provide another interesting and chemically informative example of the fact that a BVS of less than 1 usually indicates missing interactions. We see in Table 5 that the BVS is less than 1 if we consider only the five oxygen atoms from the 15-crown-5; however, Na(15-crown-

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(20) PEANNA is antibiotic A204A-sodium acetone solvate: Jones, N. D.; Chaney, M. O.; Chamberlin, J. W.; Hamill, R. L.; Chen, C. *J. Am. Chem. Soc.* **1973**, *95*, 3399−3340.

(21) PEANNA11 was named as the sodium ionophore A204A acetone solvate but is identical to PEANNA: Pangborn, W.; Duax, W.; Langs, D. *Acta Crystallogr., Sect. C* **1987**, *43*, 890−892.

(22) PEZTET is μ_4-bis(*N*,*N*′-*o*-phenylene)bis(salicylideneiminato))hexakis-(dimethoxyethane-*O*,*O*′)dimanganesetetrasodium: Gallo, E.; Solari, E.; De Angelis, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 9850, 9851.

(23) LEPHAP is (μ_2-η^8,η^8-cyclooctatetraenyl)(η^8-cyclooctatetraenyl)tris-(tetrahydrofuran)cerium(III)sodium: Kilimann, U.; Schafer, M.; Herbst-Irmer, R.; Edelmann, F. T. *J. Organomet. Chem.* **1994**, *469*, C15−C18.

(24) ROQFEI is *catena*-((μ_4-η^2-phenoxide)sodium): Kunert, M.; Dinjus, E.; Nauck, M.; Sieler, J. *Chem. Ber.* **1997**, *130*, 1461−1465.

(25) YICTAF is (μ_2-η^8,η^8-cyclooctatetraenyl)(η^8-cyclooctatetraenyl)tris-(tetrahydrofuran-*O*)samariumsodium: Jizhu, J.; Zhongsheng, J.; Gecheng, W.; Wenqi, C.; Zhang, Y. *J. Inorg. Chem. (Wuji Huaxue Xuebao)* **1993**, *9*, 326−333.

(26) HAHNUZ is *catena*-((μ_3-4-methylphenoxo)sodium): Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1993**, *32*, 3041−3051.

(27) FACGIZ is (*meso*-tetraphenylporphinato-*N*,*N*′,*N*′′,*N*′′′)cobalt(0) bis-[tris(tetrahydrofuran)sodium]: Ciurli, S.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 553−554.

(28) FEXBAL10 is (2.2.2)-cryptandsodium (*meso*-tetrakis(*o*-pivalamidophenyl)porphyrinato)acetoxyiron(II) chlorobenzene solvate: Bominaar, E. L.; Ding, X.-Q.; Gismelseed, A.; Bill, E.; Winkler, H.; Trautwein, A. X.; Nasri, H.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1992**, *31*, 1845−1854.

(29) FTPNTF10 is bis[tris(tetrahydrofuran)sodium] (*meso*-tetraphenylporphinato)iron: Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 3192−3196.

(30) GABYAJ is tris(tetrahydrofuran-*O*)sodium tris(μ_2-chloro)bis(dichloro-(tetrahydrofuran-*O*)tungsten): Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182−3186.

(31) HAGYAP is tetrakis((μ_3-hexafluoroisopropoxo)sodium): Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093−5104.

(32) HIDLAH is tris(tetrahydrofuran)sodium (1,2-bis(diphenylphosphino)-ethane)tetraiodomolybdenum tetrahydrofuran solvate: Mattamana, S. P.; Poli, R. *Inorg. Chim. Acta* **1995**, *229*, 55−60.

(33) KIGGAI is hexakis(*p*-tolylthiolato-*S*)niobium tris(tetrahydrofuran-*O*)-sodium. Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844−4846.

(34) KIDSAR is tetrakis(tetrahydrofuran-*O*)sodium (*tert*-butyl)((2,4,6-tri-*tert*-butylphenyl)amino)fluoromethylsilane: Stalke, D.; Pieper, U.; Vollbrecht, S.; Klingebiel, U. *Z. Naturforsch., B* **1990**, *45*, 1513−1516.

(35) YOXTUA01 is hexakis(μ_2-hexafluoroisopropoxo-*O*,*O*)tris(tetrahydrofuran)trisodiumyttrium: Laurent, F.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 3980−3985.

(36) ZAQZII is tetrakis(μ_3-2-perfluoro-*tert*-butoxo)sodium: Samuels, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Chem. Mater.* **1995**, *7*, 929−935.

(37) ZAWMEP is tetrakis(μ_2-hexafluoro-*tert*-butoxo-*O*,*O*)(hexafluoro-*tert*-butoxy)tris(tetrahydrofuran)disodiumyttrium: Laurent, F.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 3980−3985.

(38) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871−876.

Table 4. Summary of Structural Data and BVS for Na^+ Complexes with Various Anions[a]

REFCODE	*n*	BVS Na−O	X, Na-X	X, Na-X	val	BVS
FACGIZ[27]	3	0.64	N, 2.766	N, 2.757	0.19	0.83
FEXBAL10[28]	6	0.41	N, 3.115	N, 3.010	0.09	0.50
FTPNTF10[29]	3	0.64	N, 2.784	N, 2.825	0.17	0.81
GABYAJ[30]	3	0.64	Cl, 2.982	Cl, 2.913	0.27	0.91
HAGYAP[31]	3	0.69	F, 2.641	F, 2.831	0.12	
			F, 2.922	F, 3.009	0.06	
			F, 3.447	F, 2.365	0.16	1.03
		0.76	F, 2.652	F, 2.993	0.10	
			F, 3.379	F, 3.750	0.01	
			F, 2.480	F, 2.993	0.14	1.01
		0.70	F, 2.636	F, 2.635	0.15	
			F, 3.471	F, 2.411	0.15	
			F, 2.745	F, 3.640	0.06	1.06
		0.64	F, 2.698	F, 2.736	0.12	
			F, 2.857	F, 3.337	0.05	
			F, 3.506	F, 2.805	0.05	
			F, 3.375		0.01	0.87
HILDAH[32]	3	0.68	I, 3.301	I, 3.540	0.21	
HILDAH			I, 3.209		0.18	1.07
KIGGAI[33]	3	0.68	S, 3.00	S, 3.00	0.45	
			S, 3.00			1.13
KIDSAR[34]	4	0.57	N, 2.438		0.23	0.80
YOXTUA01[35]	3	0.72	F, 2.621	F, 2.566	0.17	
			F, 2.503		0.11	0.97
	3	0.74	F, 2.751	F, 2.486	0.16	
			F, 2.514	F, 3.095	0.12	1.02
	3	0.69	F, 2.883	F, 2.805	0.09	
			F, 3.178	F, 2.736	0.07	
			F, 3.153	F, 3.323	0.03	0.88
ZAQZII[36]	3	0.65	F, 2.899	F, 2.774	0.09	
			F, 2.960	F, 3.637	0.04	
			F, 2.332	F, 3.746	0.17	0.97
	3	0.68	F, 2.635	F, 2.774	0.08	0.76
ZAWMEP[37]	3	0.54	F, 2.408	F, 2.621	0.22	
			F, 2.658	F, 2.521	0.17	
			F, 2.633		0.08	1.01
	3	0.51	F, 2.520	F, 2.598	0.18	
			F, 2.489	F, 2.589	0.20	
			F, 2.857		0.04	0.93

[a] REFCODE is the code used in the CSD file, *n* is the coordination of the sodium with oxygen atoms, BVS Na−O is the valence sum for the O donors, X, Na−X is the Na−X distance (Å) to the atom X, val is the sum of the valence contribution of the Na−X bonds, and BVS is the sum of BVS Na−O and val, and it is the final valence taking into account all the Na^+ interactions.

5)$^+$ interacts with other negative centers to increase the CN and BVS of the Na^+ ion. Again, in the case of Na^+, these interactions are usually either not noted or not emphasized and usually not included in the CSD file. Our results can be used to explain the gas-phase versus solution stabilities of the Na(15-crown-5) complexes.[51] In the gas phase, Na^+ can coordinate only to 15-crown-5, while in solution other interactions can occur. The overall result is that Na^+ can achieve a BVS of 1 in a solution or solid without undue distortions of the 15-crown-5 molecule. We conclude that while the size of the 15-crown-5 cavity appears to be ideal for Na^+, the electronic distribution in the crown appears to be less than ideal.

Table 5. Summary of Structural Data and BVS for Na(15-crown-5)$^+$ Complexes with Various Anions[a]

REFCODE	*n*	BVS Na−O	X, Na−X	X, Na−X	val	BVS
JAVKAS[39]	5	0.70	F, 2.402	Cl, 2.871	0.31	1.01
	5	0.78	F, 2.265	Cl, 3.189	0.27	1.05
JAZGEW[40]	5	0.68	Cl, 2.86	Cl, 2.85	0.35	1.01
KIYKUY[41]	5	0.75	F, 2.306	F, 2.332	0.35	1.10
KIYLAF[42]	5	0.73	F, 2.333	F, 2.293	0.36	1.09
LEZDAV[43]	5	0.79	I, 3.330		0.18	0.97
POTCOA10[44]	5	0.63	N, 2.396	S, 2.287	0.34	0.97
SAMZUB[45]	5	0.54	Se, 2.981		0.22	0.76
SANBAK[46]	5	0.67	Se, 2.978		0.22	0.89
SANBEO[47]	5	0.75	Se, 3.00		0.21	0.96
TADFUZ[48]	5	0.68	Cl, 2.768		0.22	0.90
	5	0.76	Cl, 2.651		0.30	1.06
VOTCAI[49]	5	0.50	S, 3.084	S, 3.082	0.23	
	5		S, 3.334		0.06	0.79
WAHFAM[50]	5	0.65	F, 2.418	F, 2.301	0.32	0.97

[a] REFCODE is the code used in the CSD file, *n* is the coordination of the sodium with oxygen atoms, BVS Na−O is the valence sum for the O donors, X, Na−X is the Na−X distance (Å) to the atom X, val is the sum of the valence contribution of the Na−X bonds, and BVS is the sum of BVS Na−O and val, and it is the final valence taking into account all the Na^+ interactions.

Distances in Na−O Complexes. The distances used in the analysis are summarized in Table 2 as a function of coordination number. The average Na−O distance increases with coordination number as expected and as we have observed in other systems.[3−7] The reason for the increase in the average distance is understandable in terms of the BVS model. The valence calculated for each average distance is given in Table 2 and is in good agreement with a valence of 1/*n* predicted if all the Na−O bonds were of equal length. The conclusion is that, for any given coordination number, the Na ion will utilize any combination of bond lengths as long as the BVS equals 1, the oxidation state. Since the BVS must be satisfied for all coordination numbers, the sum becomes a better indicator of the correctness of a structure report than the usual *R* value. The large variation in the Na−O distances for a given coordination number indicates the danger in merely comparing bond distances when a Na−O complex is discussed.

Conclusions and Recommendations

We have shown that, for 389 NaO_n complexes, the BVS calculated using eq 2 with an R_0 value of 1.756(42) Å gives a

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(39) JAVKAS is bis((15-crown-5)sodium) difluorotetrachlorozirconium(IV): Hartmann, E.; Dehnicke, K.; Fenske, D.; Goesmann, H.; Baum, G. *Z. Naturforsch., B* **1989**, *44*, 1155−1160.

(40) JAZGEW is tetrakis((μ_2-nitrilo)trichloro(tetrahydrofuran)molybdenum) (bis(15-crown-5)sodium) bis((tetrahydrofuran)sodium) tetrahydrofuran solvate: Figge, R.; Friebel, C.; Patt-Siebel, U.; Muller, U.; Dehnicke, K. *Z. Naturforsch., B* **1989**, *44*, 1377−1384.

(41) KIYKUY is (bis(15-crown-5)sodium) (bis(μ_2-fluoro) bis(difluorodioxotungsten)) acetonitrile solvate: Mollert, R.; Rentschler, E.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *596*, 121−132.

(42) KIYLAF is (bis(15-crown-5)sodium) (bis(μ_2-fluoro)bis(di fluorooxothiotungsten)) acetonitrile solvate: Mollert, R.; Rentschler, E.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *596*, 121−132.

(43) LEZDAV is *catena*-(bis(aqua(15-crown-5)sodium) bis((15-crown-5)-sodium) tetrakis(μ_3-iodo)(bis(μ_2-iodo)tetracopper(I) bis(μ_2-iodo)di-iododicopper(I)): Hu, G.; Holt, E. M. *Acta Crystallogr., Sect. C* **1994**, *50*, 1578−1580.

(44) POTCOA10 is (1,4,7,10,13-pentaoxa-16-thiacyclooctadecane)sodium thiocyanate: Campbell, M. L.; Larson, S. B.; Dalley, N. K. *Acta Crystallogr., Sect. B* **1981**, *37*, 1741−1744.

(45) SAMZUB is bis((15-crown-5)sodium) bis(tetraselenido-*Se*(*1*),*Se*(*4*))-zinc: Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B* **1988**, *43*, 1094−1100.

(46) SANBAK is bis((15-crown-5)sodium) bis(tetraselenido-*Se*(*1*),*Se*(*4*))-mercury: Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B* **1988**, *43*, 1094−1100.

(47) SANBEO is bis((15-crown-5)sodium) bis(tetraselenido-*Se*(*1*), *Se*(*4*)-cadmium: Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B* **1988**, *43*, 1094−1100.

(48) TADFUZ is (15-crown-5)sodium tetrachloronickel: Ruhlandt-Senge, K.; Muller, U. *Z. Naturforsch., B* **1990**, *45*, 995−999.

(49) VOTCAI is *fac*(15-crown-5)sodium tricarbonyltris(phenylthiolato-*S*)-iron: Nagy-Magos, Z.; Marko, L.; Szakacs-Schmidt, A.; Gervasio, G.; Belluso, E.; Kettle, S. F. *Bull. Soc. Chim. Belg.* **1991**, *100*, 445−458.

(50) WAHFAM is (15-crown-5)sodium pentafluoro(triphenylphosphoraniminato)niobium: Nuszhar, D.; Weller, F.; Dehnicke, K.; Hiller, W. *J. Alloys Compd.* **1992**, *183*, 30−44.

(51) Maleknia, S.; Brodbelt, J. *J. Am. Chem. Soc.* **1992**, *114*, 4295−4298.

value of 1 in most cases. When the BVS differs markedly from 1, there are usually problems with the crystal structure, misidentified cations, unnoticed, and/or unreported interactions. Therefore, one use of the BVS is confirmation of the crystal structure determination. However, equally or even more important is the insight into chemical bonding provided by this simple calculation. We have shown that a π-type interaction between Na^+ and delocalized organic π-clouds is supported by the BVS calculations. In addition, the BVS calculations can be used to explain the perplexing problem of the differences in gas-phase and solution stabilities of the alkali metal ions with various crown ethers. In summary, the BVS is a simple calculation that can be used to understand the bonding in these complexes as well as to avoid introducing errors into the literature.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org. Listings of the BVS calculations for the 389 Na−O complexes used in the analysis.

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