Bond Valence Sums in Coordination Chemistry Using New R_0 Values. Potassium−Oxygen Complexes

Richard M. Wood and Gus J. Palenik*

The Center for Molecular Structure, The University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

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Introduction

The bond valence sum or BVS is a relatively simple calculation provided appropriate R_0 values[1] are available, vide infra. Two pertinent questions 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 accuracy of the structure determination than the usual crystallographic *R* value. Although the use of anisotropic thermal parameters, disorder, and the introduction of solvent molecules can be used to reduce the crystallographic *R* value, the bond distances and the corresponding BVS must be consistent with the proposed model.

Our previous studies have shown that in mononuclear complexes the BVS is a surprisingly good indicator of the correctness of a crystal structure determination. When the BVS does not agree with the proposed oxidation state, either the oxidation state is incorrect,[2] the metal ion has been misidentified,[3] or the crystal structure determination is of very poor quality.[2−6] Consequently, in those cases where there is poor agreement between the postulated and calculated BVS, then these data should 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 a careful assessment both of these data and the Experimental Section to explain any discrepancies. Many of these points are nicely illustrated in this report on the K−O system, which also demonstrates how the BVS can be used to explain chemical features observed in the crystal structure determinations.

The present study of the K−O complexes was undertaken for several reasons. There is only one oxidation state and no complications occur from high and low spin configurations. Therefore, the K−O complexes should provide a good example of the effect, if any, of the coordination number on the BVS calculation, together with a clearer picture of the consequences of a non integer BVS.

Discussions of the K−O distances and the coordination around the K^+ ion are usually not given although these data can provide information regarding the correctness of the structure determination. One reason for the absence of a discussion of distances in K−O complexes may be the lack of a recent compilation of K−O distances to which reported structures can be compared. As part of our analysis of K−O complexes, we have tabulated the various K−O distances as a function of coordination number which can be used in a discussion of K−O bond lengths. Hopefully, our new R_0 values used in a BVS will become a routine calculation for K compounds.

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 the s_{ij} from the observed bond lengths, R_{ij}, can be carried out using eq 2,

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

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

provided the constants *b* and R_0 are known. The value of the constant *b* has been assumed to be 0.37. 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 is dependent 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 K−O bond length data were from the April 1998 release of the Cambridge Structural Database (CSD) containing 181 309 entries.[7] Those entries containing only O atoms were retrieved i.e., KO_n, where $n = 3-9$ and is the number of O atoms and also the total coordination number (CN). A total of 196 entries in the CSD gave a starting set of 221 KO_n complexes. An initial R_0 value[8] of 2.154 Å was used to calculate a BVS for each entry. Any obviously erroneous or duplicate entries were removed or corrected at this point,[9] see the discussion below. 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. The R_0 values determined for CN of 3−9 are given in Table 1, but there does not appear to be any trend in the values as a function of coordination number. The R_0 value that gave a BVS equal to 1 (the oxidation state for K) also was determined for each entry and these results are summarized in Table 1. For a given coordination number, there is no significant difference in the R_0 values determined in these two ways.

A complete listing of the BVS calculated for all of the KO_n data for $n = 3-9$ using the R_0 value of 2.113(57) Å is available as Supporting Information. A tabulation of the K−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.[10]

Results and Discussion

A new R_0 value of 2.113(57) Å for K−O bonds was determined from 176 KO complexes with a CN of 3−9. Our value is slightly but probably not significantly different from

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(1) The 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.

(4) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 4888−4890.

(5) Kanowitz, S. M.; Palenik, G. J. *Inorg. Chem.* **1998**, *37*, 2086.

(6) Wood, R. M.; Palenik, G. J. *Inorg. Chem.* **1998**, *37*, 4149.

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

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

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

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

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

CN	no.	R_0[b]	R_0[c]
3	2	2.242	2.243 (11)
4	5	2.134	2.136 (29)
5	9	2.160	2.167 (43)
6	89	2.127	2.135 (45)
7	33	2.082	2.090 (48)
8	35	2.051	2.058 (44)
9	3	2.068	2.069 (16)
3−9	176	2.100	2.113 (57)

[a] CN is the coordination number, and no. is the number of complexes used for that CN. [b] The R_0 value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states. [c] The average R_0 value that makes the observed and calculated oxidation states equal, with the estimated standard deviation in parentheses.

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

CN	no.	min	max	av (σ)
3	6	2.591	2.742	2.654 (68)
4	20	2.568	2.824	2.653 (59)
5	45	2.636	2.958	2.769 (82)
6	534	2.536	3.137	2.801 (69)
7	231	2.461	3.089	2.819 (90)
8	280	2.604	3.168	2.835 (86)
9	27	2.675	3.098	2.892 (93)

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

the reported values of 2.132(4) Å[11a] and 2.13 Å[11b] determined from only ionic solids or from the calculated value of 2.154 Å.[8] The agreement between these values is important since the data used to calculate the R_0 values are different and the important question that we are attempting to answer is the validity of the BVS in coordination complexes. The lower esd's on the previously reported values are probably due to the more uniform sample used to calculate these values. The small variation of R_0 with coordination number and possible interactions that have been missed will contribute to the larger esd of our value. We have retained an extra significant figure for comparison purposes and in keeping with common crystallographic practices. Since the use of the BVS with coordination complexes is relatively new, the question as to the tolerated percent error is still under investigation so that we have chosen 30% as an upper limit. Some of the 10 entries that were not used in the determination of R_0 and the 16 complexes where the BVS differed by more than 0.3 of a valence unit from 1 are discussed below. The discussion can be conveniently divided into two categories, those complexes where the BVS was much larger than 1 and those where the value was 0.7 or lower.

A BVS much greater than one for a KO complex can indicate an incorrect cation, large thermal motions, and/or problems with the crystal structure determination, as we shall illustrate. TOSPUM[12] had a BVS of 2.71 and the synthesis involved both K^+ and Na^+ salts. There was no analysis or supporting evidence for the formulation of the product as the K^+ salt, the U(eq) of 77 for K was larger than that of the coordinated O atoms (U(eq) of 57 to 73), and the average K−O distance of 2.40 Å seemed very short. The authors noted that the $K(THF)_6^+$ species had been observed only once before in WADGOX.[13] In WADGOX the K−O distances averaged 2.741 Å and the BVS was 1.07. In TOPDIL,[14] a slightly later report, the $K(THF)_6^+$ was also reported with K−O distances averaging 2.698(30) Å and the BVS was 1.20, in reasonable agreement with the expected value. Assuming that the cation was $Na(THF)_6^+$ and using the R_0 value for Na^+ of 1.743 Å,[15] a BVS of 1.06 was calculated for TOSPUM. Therefore, we felt that there was strong evidence that in TOSPUM the cation was really $Na(THF)_6^+$ and that the entry should not be used in the K−O analysis.

Another structure that gave a large BVS of 2.93 was SEGSOM10.[16] While the R value of 0.066 appeared reasonable because of the 3 Re and 7 Br atoms in the cell, the errors for the light atoms were very large. The K−O distances were not well determined, with errors of ±0.03 Å. Although it is not clear whether the large BVS is a result of poorly defined K−O distances, or of the large thermal motion in the K−O bonds (B_{iso}^{eq} for O was 8(2)), or of a Na^+ introduced into the product (the BVS was 1.10 assuming Na^+), we decided to exclude these data.

A similar but somewhat more complicated case is that of TACGEJ,[17] where the BVS was 1.74. Once again the synthesis was carried out using both Na^+ and K^+ salts, and the main evidence for the formulation was the 5.2/1 excess of K^+/Na^+ and a Au, Br, C, H, and N analysis. However, substituting Na for K produced only a 1% change in the FW and only small changes in the calculated analysis. The space group was not determined uniquely from the systematic absences(there are three possible space groups), and the reported structure solution seemed unduly complicated for a compound in which the Au and K positions were fixed by symmetry considerations. In the final structure there was a 3-fold disorder in the $AuBr_4^-$ anions, and the authors noted that the K−O distance of 2.56 Å appeared to be short versus other KO complexes. A simple substitution of Na^+ for K^+ is probably not the answer, but there are so many questions regarding the structure determination that we felt the complex should not be included in our analysis.

The BVS of 2.83 for KUHYOB[18] was one of the largest calculated for K−O complexes. KUHYOB was the unexpected product from the reaction of 18-crown-6 in CH_2Cl_2 with K_2 tartrate$\cdot 0.5H_2O$ in $CHCl_3$. The chlorine found in the chemical analysis presumably arose from the hydrolysis of the $CHCl_3$. However, there is an unusual asymmetric conformation of the 18-crown-6 around the K^+, and the K−O distances are shorter than in any other 18-crown-6 complex.

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(11) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B.* **1985**, *B41*, 244−247. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B.* **1991**, *B47*, 192−197.

(12) TOSPUM is hexakis(tetrahydrofuran)potassium tetrakis(pyridine-2-thiolato)tantalate(V). Cotton, A.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Bull. Soc. Chim. Fr.* **1996**, *133*, 711.

(13) WADGOX is *trans*-bis(μ_2-η^5,η^5-2,2′-bis(3,4-dimethyl-5-phenyl phospholyl))bis(tetrahydrofuranpotassium) bis((18-crown-6)-bis(tetrahydrofuran)potassium) tetrahydrofuran solvate. Eichofer, A.; Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 242−245.

(14) TOPDIL is bis[hexakis(tetrahydrofuran)potassium] bis[(μ_2-2,6-dimethylphenylamido)tris(2,6-dimethylphenylamido]samarium) tetrahydrofuran solvate. Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1996**, *35*, 5435−5444.

(15) Browning, K.; Abboud, K. A.; Palenik, G. J. *J. Chem. Crystallogr.* **1995**, *25*, 847−851.

(16) SEGSOM10 is hexakis(dimethylacetamido-O)potassium bis(μ_3-bromo)hexakis(μ_2-bromo)hexabromohexarhenium. (a) Koz'min, P. A.; Kotelnikova, A. S.; Surazhskaya, M. D.; Osmanov, N. S.; Larina, T. B.; Abbasova, T. A.; Mekhtiev, M. M. *Koord. Khim.* **1989**, *15*, 1216; (b) *Chem. Abstr.* **1990**, *112*, 47568n; (c) *Coord. Chem.* **1989**, *15*, 1216−1222.

(17) TACGEJ is hexakis(3,5-dicarboxypyridine-O)potassium tetrabromoaurate(III). Goher, M. A. S.; Wang, Ru-ji; Mak, T. C. W. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 245.

(18) KUHYOB is (18-crown-6)triaquapotassium hydronium dichloride dihydrate. Doxsee, K. M.; Wierman, H. R.; Weakley, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 5165−5171.

In PIHXUZ[19] the BVS was 1.73, but the crystallographic *R* value of 0.106 was relatively high by current standards. The corresponding Na^+ and Rb^+ also were prepared, and we inquired as to whether the Na^+ salt could have been used in the determination. An author stated[20] that a refinement replacing K^+ with Na^+ gave unrealistically small thermal parameters. Whether the large BVS reflects large thermal motion is unclear since no thermal ellipsoids were shown in the paper. However, we felt that the large BVS and high *R* value precluded using these data in our R_0 determination.

In many cases a BVS much less than 1 usually indicates a missing interaction in the CSD file which may have been missed in the original report or may not have been included in the CSD entry. Several K-diglyme structures illustrate this point very nicely and also suggest an unusual interaction between the K^+ ion and the pi-molecular orbitals of various organic anions. In KIXXIY[21] and KIXXUK[22] the K(diglyme)$^+$ group is oriented toward a $C_8H_8^{2-}$ ring, and the BVS is 0.51 and 0.49, respectively. Using the Valence program,[23] we calculated that 3 C atoms would contribute 0.36 or 0.30 to the BVS, giving values of 0.87 and 0.79 for KIXXIY and KIXXUK, respectively, much closer to the expected 1.0 and a CN of 6 around the K^+ ion. Assuming 4 bonds from K to the ring would give a BVS even closer to 1. These results suggest an interaction between the K^+ ion and π orbitals of the $C_8H_8^{2-}$ ring. A comparison with a more traditional K(diglyme) complex ZUHZOR,[24] a KO_7 type complex with a BVS of 1.11, supports the argument of a covalent type bond in KIXXIY and KIXXUK. A survey of other K(O donor)$^+$ complexes attached to a $C_8H_8^{2-}$ ring not included in our study supports this view and is summarized in Table 3. For example, in CUBHIQ[25] the BVS was 0.44 using only the three O's bonded to the K ion; however, adding the contribution of three C's from the $C_8H_8^{2-}$ ring increased the values to 1.04. In TIMQOV[30] there is only one O attached to the K^+ ion which is bonded to three different organic groups. If we assume two carbon bonds to the C_8 group, three to the C_5, and two to the allyl group, we calculate that the BVS would be 1.03. The question of whether the final CN for the complex should be 6 or 7 is unclear, but we can see from the data in Table 3 that in either case the BVS value is closer to the expected value. In summary the BVS calculation provides clear evidence for a covalent type bond between the K^+ ion and the pi orbitals of organic ions, an interaction which to our knowledge has not been proposed previously.[33,34]

Table 3. Summary of Structural Data for KO_n Complexes with Some Organic Anions[a]

REFCODE	*n*	K−O val	K−C$_{av}$	K−C val	BVS-6	BVS-7
CUBHIQ[25]	3	0.46	3.017	0.20	1.06	1.24
DULBER[26]	4	0.49	3.14	0.14	0.77	0.91
GILMET[27]	2	0.28	2.957	0.23	1.20	1.43
	3	0.65	2.986	0.22	1.21	1.43
JITSOU[28]	4	0.82	3.20	0.12	1.06	1.04
KECOCE[29]	3	0.53	3.16	0.14	0.95	1.09
KIXXIY[21]	3	0.52	3.191	0.12	0.88	1.00
KIXXUK[22]	3	0.50	3.263	0.10	0.80	0.90
TIMQOV[30]	1	0.21	3.145	0.14		
			3.174	0.13		
			3.342	0.08		0.96[b]
TMOCKE[31]	3	0.46	3.003	0.21	1.09	1.30
ZESREU[32]	3	0.61	3.006	0.20	1.21	1.41

[a] REFCODE is the code used in the CSD file, *n* is the number of O atoms bonded to K, K−O val is the valence sum for the O donors, K−C$_{av}$ is the average K−C distance (in Å), K−C val is the valence of the K−C$_{av}$ distances using $R_0 = 2.419$ for the K−C bond, BVS-6 is the BVS assuming a coordination number of 6 for K achieved by forming $6 - n$ K−C bonds, and BVS-7 is the BVS assuming a coordination number of 7 for K achieved by forming $7 - n$ K−C bonds. [b] Calculated by assuming 2 bonds to the C_8, 3 bonds to the C_5, and 1 bond to the benzyl group.

The fact that a BVS less than 1 usually indicates missing interactions is also illustrated by various K(18-crown-6)$^+$ cations. In Table 4 we have collected some of the structural data for complexes involving the K(18-crown-6)$^+$ cation and various anions. We see that the BVS is less than 1 if we consider only the 6 oxygen atoms from the 18-crown-6; however, the K(18-crown-6)$^+$ interacts with other negative centers to increase the CN and BVS. Unfortunately, in the case of K^+, these interactions are usually either not noted or not emphasized and may not be included in the CSD file. As seen in Table 4, adding other $K^+\cdots$anion interactions increases the BVS to the expected value. The empirical R_0 values[8] were used in the calculations so that the agreement is not as good as we would expect for carefully determined R_0 values. However, these results can be used to explain the gas-phase versus solution stabilities of the K(18-crown-6) complexes.[45] In the gas phase the K^+ can

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(19) PIHXUZ is 2,26,31,41-tetrakis(1,1-dimethylethyl)-35,38-diethoxy-44,45,46-trimethoxy-9,14,19-trimethylcalixspherand-potassium picrate dichloromethane solvate. Bakker, W. I. I.; Haas, M.; Khoo-Beattie, C.; Ostaszewski, R.; Franken, S. M.; den Hertog Junior, H. J.; Verboom, W.; de Zeeuw, D.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 123.

(20) S. Harkema, personal communication.

(21) KIXXIY is (diethylene glycol dimethyl ether)potassium (bis(8)-annulene)ytterbium(III). Boussie, T. R.; Eisenberg, D. C.; Rigsbe, J.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.

(22) KIXXUK is (diethylene glycol dimethyl ether)potassium bis(methyl-(8)annulene)ytterbium(III). Boussie, T. R.; Eisenberg, D. C.; Rigsbe, J.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.

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

(24) ZUHZOR is diglymepotassium (2,4-dimethylpentadienyl)(tricarbonyl)-molybdate(0). Kralik, M. S.; Rheingold, A. L.; Hutchinson, J. P.; Freeman, J. W.; Ernst, R. D. *Organometallics* **1996**, *15*, 551−561.

(25) CUBHIQ is bis(1,2-dimethoxypotassium) bis(η_8-cyclooctatetraenide)-ytterbate(II). Kinsley, S. A.; Streitwieser, A., Jr.; Zalkin, A. *Organometallics* **1985**, *4*, 52−57.

(26) DULBER is *catena*-bis(bis(2-methoxyethyl)ether-*O*,*O*′,*O*″-potassium) *bis*(η_8-*tert*-butylcyclooctatetraenide)ytterbate(II). Kinsley, S. A.; Streitwieser, A., Jr.; Zalkin, A. *Acta Crystallogr., Sect. C.* **1986**, *C42*, 1092−1094.

(27) GILMET is *catena*-bis(μ_2-η_{16}-cyclooctatetraenyl)bis(μ_2-tetrahydrofuran)tetrahydrofuran)dipotassium). Hu, N.; Gong, L.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1988**, *352*, 61−66.

(28) JITSOU is tris(μ_2-η_8-η_8-cyclooctatetraenyl)(η_8-cyclooctatetraenyl)-tetrakis(tetrahydrofuran)dierbiumdipotassium. Xia, J.; Jin, Z.; Chen, W. *J. Chem. Soc., Chem. Commun.* **1991**, 1214−1215.

(29) KECOCE10 is potassium 2,2′-di(methoxy)diethyl ether bis(cyclooctatetraenyl)cerium(III). Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 3030−3035.

(30) TIMQOV is (μ_2-η_5-η_3-benzylcyclopentadienyl) (μ_2-η_8-η_8-cyclooctatetraenyl)bis(η_8-cyclooctatetraenyl)tris(tetrahydrofuran)dineodymiumpotassium. Xia, J.; Zhuang, X.; Jin, Z.; Chen, W. *Polyhedron* **1996**, *15*, 3399−3403

(31) TMOCKE is bis(potassium-2,2′-dimethoxydiethyl ether)-1,3,5,7-tetramethylcyclooctatetraene. Goldberg, S. Z.; Raymond, K. N.; Harmon, C. A.; Templeton, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 1348−1351.

(32) ZESREU is bis (((μ_2-η_8-η_8-cyclooctatetraenyl)tris(tetrahydrofuran)-potassium)europium(II). Evans, W. J.; Shreeve, J. L.; Ziller, J. W. *Polyhedron* **1995**, *14*, 2945−2951.

(33) A review of the structural data on the organic compounds of alkali metals can be found in ref 34.

(34) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, 169−278.

(35) JOMDUK is (18-crown-6)potassium (4-trifluoromethylphenyl)phenyltrifluorosilicate. Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 182−191.

(36) JOMFAS is (18-crown-6)potassium (*p*-tolyl)phenyltrifluorosilicate. *Organometallics* **1992**, *11*, 182−191.

(37) JOMFEW is (18-crown-6)potassium (4-methoxyphenyl)phenyltrifluorosilicate. *Organometallics* **1992**, *11*, 182−191.

(38) JOMFIA is (18-crown-6)potassium (4-dimethylaminophenyl)phenyltrifluorosilicate. *Organometallics* **1992**, *11*, 182−191.

Table 4. Summary of Structural Data and BVS for K(18-crown-6)$^+$ Complexes with Various Anions[a]

REFCODE	BVS K−O	X, K−X	X, K−X	val	BVS
JOMDUK[35]	0.83	F, 2.882	F, 2.661	0.25	1.08
JOMFAS[36]	0.81	F, 2.846	F, 2.653	0.27	1.08
JOMFEW[37]	0.82	F, 2.902	F, 2.622	0.26	1.08
JOMFIA[38]	0.81	F, 2.984	F, 2.596	0.26	1.07
JOMFOG[39]	0.76	F, 2.760	F, 2.731	0.26	1.02
JOMFUM[40]	0.77	F, 2.512		0.24	1.01
SEYBUT10[41]	0.70	F, 2.780	F, 3.042	0.18	
		F, 3.073		0.05	0.93
KEGXID[42]	0.92	Cl, 3.225		0.15	1.07
FEHGEE[43]	0.72	I, 3.856	I, 3.904	0.14	
FEHGEE[43]		I, 4.105		0.04	0.90
ZILXUN10[44]	0.92	Se, 3.59	Se, 3.54	0.21	
ZILXUN10[44]		Se, 3.65		0.08	1.21

[a] REFCODE is the code used in the CSD file, BVS K−O is the valence sum for the O donors, X, K−X is the K−X distance (in Å) to the atom X, val is the sum of the valence contribution of the K−X bonds, BVS is the sum of both BVS K−O and val, and it is the final valence taking into account all the K$^+$ interactions.

coordinate only to the 18-crown-6, while in solution other interactions can occur. The overall result is that the K$^+$ can achieve a BVS of 1 without undue distortions of the 18-crown-6 molecule. These results suggest that while the size of the 18-crown-6 cavity based only on hard sphere radii appears to be ideal for K$^+$, the electron distribution appears to be less than ideal for bonding to the K$^+$ ion. To our knowledge the suggestion that the electron distribution is important in the stability of crown ether complexes has not been suggested previously. We might note that in the case of ZILXUN,[44] the compound was retrieved as a KO_3 and the initial BVS was only 0.45. In the original report the K was coordinated to the 18-crown-6 with only three of the six K−O bonds included in the CSD entry, but the addition of three interactions increased the BVS to 0.89.

A summary of the K−O distances used in our analysis is given in Table 2. We see that the average K−O distance increases from CN = 3 to CN = 9 as expected. The average distance is such that the valence contribution calculated using eq 2 times the CN is approximately 1.0, as required. Although the large difference between the minimum and maximum values is somewhat surprising, the result is not unexpected in view of our earlier results[3−6] and the requirement that the BVS = 1 for K−O complexes. The differing steric requirements of the ligands dictates some of the K−O distances, and then the BVS can be satisfied by adjusting those bond distances that can be varied easily. The requirement that the BVS equal 1 is a more important condition than equality of the K−O distances. The large variation in the K−O distances also indicates the dangers in merely comparing K−O distances when discussing a K−O complex.

Conclusions and Recommendations

We have shown that for 195 KO_n complexes the BVS calculated using eq 2 with an R_0 value of 2.113(57) Å gives a 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 K$^+$ 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 versus 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.

Supporting Information Available: Listings of the BVS calculations for the 209 K−O complexes used in the analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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