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Bond Valence Sums in Coordination Chemistry. Calculation of the Oxidation State of Chromium in Complexes Containing Only Cr−O Bonds and a Redetermination of the Crystal Structure of Potassium Tetra(peroxo)chromate(V)

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A simple method for calculating the oxidation state of Cr in complexes containing only Cr−O bonds is presented. A total of 242 CrO_n fragments with $n = 3-6$ were retrieved from the Cambridge Structural Database (CSD) and, together with the data for K_3CrO_8, were analyzed using the bond valence sum method. New R_0 values for Cr(II) of 1.739(21) Å, Cr(III) of 1.708(7) Å, Cr(V) of 1.762(14) Å, and Cr(VI) of 1.793(7) Å were derived. An average R_0 value of 1.724 Å for Cr−O reproduces the oxidation state of 96 of the 110 Cr(II), Cr(III), and Cr(IV) CrO_n complexes ($n = 3-6$) and that of K_3CrO_8 within 0.30 valence units. The crystal structure of K_3CrO_8 was redetermined at 173 K to provide accurate data for a Cr complex with both high oxidation state and coordination number. Potassium tetraperoxochromate(V), K_3CrO_8, is tetragonal, Space group $\bar{I}42m$, $a = b = 6.6940(3)$ Å, $c = 7.7536(5)$ Å, $Z = 2$. The difficulties with fitting the observed valence for Cr(V) and Cr(VI) complexes with coordination numbers 4 and 5 are discussed. The use of bond valence sums in gaining chemical insight into Cr complexes with noninnocent ligands and in establishing oxidation states in Cr clusters is presented. An analysis of the Cr−O bond distances used in the calculations shows a large range of values that can be understood in terms of the bond valence sum calculation.

Introduction

Our interest has been in exploring whether the oxidation state of a metal ion in a coordination compound could be calculated from the bond distances determined in a crystal structure without any assumptions and in determining 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, problems in the crystal structure determination or possible steric effects are usually indicated. In addition, the bond valence sum (BVS) can be used to determine the oxidation state of the metal ion in metalloenzymes using extended X-ray absorption fine structure (EXAFS) data 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

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

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

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

or

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

where r_{ij} is the observed bond length, and R_0 and N are constants that are dependent on the nature of ij pair. The constant b was determined to be 0.37 [3] which has been generally accepted.[4−7] 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.[5−11]

The present report examines the problems in establishing an oxidation state independent of the R_0 value for Cr complexes with O donors. The Cr case was chosen because of the range

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Table 1. Values of R_0 for Cr−O Bonds for Oxidation States[a]

ref	oxidation state of Cr +2	+3	+5	+6
3	1.724			1.794
4	1.730	1.724		1.794
11	1.750	1.750	1.750	1.750
WP	1.739	1.708	1.762	1.793

[a] Equation 2 with $b = 0.37$ was used in refs 3, 4, 11, and WP. WP is the present work.

of oxidation states and the different R_0 values, summarized in Table 1, that have been reported for Cr−O bonds in ionic solids.[3,4,11] 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. 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 Cr−O bond length data were from the May 1999 release of the Cambridge Structural Database (CSD) containing 197 481 entries.[12] Those entries containing only O atoms bonded to Cr were retrieved, i.e., CrO_n, where n (3−6) is the number of O's and also the coordination number (CN). A total of 172 entries from the CSD gave a starting set of 242 CrO_n complexes. In addition, the data for K_3CrO_8 [13−15] were added, and finally our data for that complex, vide infra, were included. An initial R_0 value of 1.737 Å [11] was used to calculate an oxidation state for each entry. Any obvious erroneous oxidation states were corrected at this point,[16] and any duplicate entries were removed. 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 2.5σ from the mean value were deleted, and a new R_0 value and σ were calculated. The resulting R_0 values are given in Table 2. 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 Cr−O bond length data used in our study is given in Table 3. The BVS was calculated using FORTRAN programs written by G.J.P.[17]

Synthesis and X-ray structure determination of $K_3Cr(O_2)_4$. The synthesis of $K_3Cr(O_2)_4$ was carried out using a slight modification of a published procedure.[18] Crystals suitable for an X-ray diffraction study were obtained after cooling the filtrate overnight. Intensity data were collected using a Siemens Smart Platform equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation. (λ = 0.710 73 Å). All calculations were carried out using SHELXTLS,[19] and the details are given in Table 4 and in Supporting Information.

Results and Discussion

Table 2. Experimental Values of R_0 for Cr−O Bonds as a Function of Oxidation State and Coordination Number[a]

CN	oxidation state of Cr +2	+3	+4	+5	+6
3	1.769(10)				
no.	2				
4	1.735(23)		1.773		1.793(7)
no.	15		1		53
5	1.741(4)			1.770(8)	
no.	4			6	
6	1.735	1.708(7)			
no.	1	115			
8				1.738(14)	
no.				4	
best	1.739(21)	1.708(7)		1.762(14)	1.793(7)
	22	115		9	53

[a] Equation 2 with $b = 0.37$ was used. CN is the coordination number and no. is the number of entries used to determine the R_0 value. The estimated standard deviation where appropriate is given in parentheses after the value.

Table 3. Summary of Cr−O Distances Used in the Analysis[a]

ox	CN	no.	min	max	av(σ)	val
2	3	6	1.825	1.986	1.925(73)	0.58
2	4	60	1.943	2.097	1.992(31)	0.48
2	5	20	1.973	2.392	2.099(132)	0.36
2	6	6	2.022	2.499	2.195(236)	0.28
3	4	4	1.824	1.973	1.882(71)	0.65
3	6	810	1.811	2.096	1.967(32)	0.52
4	4	4	1.771	1.775	1.773(2)	0.86
5	5	30	1.533	1.921	1.795(131)	0.83
5	8	24	1.881	1.958	1.920(29)	0.59
6	4	212	1.554	1.881	1.647(72)	1.23

[a] Ox is the oxidation state, CN is the coordination number, no. is the number of bonds found, min is the minimum Cr−O distance found for that oxidation state and coordination number, max is the maximum Cr−O distance found for that oxidation state and coordination number, av(σ) is the average Cr−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 $R_0 = 1.726$ Å.

Table 4. Crystallographic Data for CrK_3O_8

chemical formula = CrK_3O_8	fw 297.30
$a = 6.6940(3)$ Å	space group = $I\bar{4}2m$ (No. 121)
$b = 6.6940(3)$ Å	temp = 173(2) K
$c = 7.5736(5)$ Å	$\lambda = 0.710\ 73$ Å
$V = 339.37(3)$ Å^3	ρ(calc) = 2.909 g/cm^3
$Z = 2$	$\mu = 3.530$ mm^{-1}
$R(F_o)$ with $I > 2\sigma(I) = 0.0149$	$wR2(w(F_o^2)^2) = 0.0408$

The BVS calculated for 163 Cr(II), Cr(III), and Cr(IV) complexes with coordination numbers 3−6 using an average R_0 value of 1.724 Å and eq 2 had only seven examples where the value differed by 0.30 or more from the expected integer oxidation state. In addition, the one example for coordination number 8, $K_3Cr(O_2)_4$, gave the value of 4.74, very close to the expected value. Therefore, the average value can be used to determine the oxidation state of the Cr ion without any assumptions. The oxidation state specific values could be used to check this assignment. However, for Cr(V) and Cr(VI) with CN = 4 or 5, the agreement is much poorer and a discussion is given below.

The BVS may differ from an integer value in the case of low coordination numbers where steric constraints are important. For example, in CUSXET[20] (BVS = 1.82 and 1.86 for the two crystallographically independent Cr(II) atoms), LIBCRA[21] (BVS

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(13) Stomberg, R.; Brosset, C. *Acta Chem. Scand.* **1960,** *14,* 441−452.

(14) Stomberg, R. *Acta Chem. Scand.* **1963,** *17,* 1563−1566.

(15) Swalen, J. D.; Ibers, J. A. *J. Chem. Phys.* **1962,** *37,* 17−20.

(16) All of the corrections have been sent to the CSD and will be included in a later release of the database.

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

(18) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Presss: New York, 1965; Vol. 2, p 1381.

(19) Sheldrick, G. *SHELXTL5*; Siemens Analytical Instrumentation: Madison, WI, 1995.

(20) CUSXET is di-μ-{di(*tert*-butyl)methoxo}-bis{tri(*tert*-butyl)methoxo}-chromium(II). Murray, B. D.; Hope, H.,; Power, P. P. *J. Am. Chem. Soc.* **1985,** *107,* 169−173.

= 2.53), and LIBCRB[22] (BVS = 3.50) the values are all lower than expected. These low values are explicable because of steric constraints involving the bulky *tert*-butoxide and *tert*-butyl ligands that were needed to achieve a low coordination number. Furthermore, in the case of LIBCRA the authors noted "... the specimen finally chosen for the study was still of lower quality than would have been preferred." Thus, the quality of the data in this case may be less than optimum. LIBCRB[22] is of particular interest because it is the only Cr(IV) complex that we retrieved from the CSD file.

The use of BVS in understanding the bonding in coordination compounds can be illustrated with two complexes, CBZQCR[23] and TBZQCR,[24] involving the noninnocent benzoquinone ligand. In both cases, the ligand was assumed to be neutral and Cr was assigned a 0 oxidation state. However, the BVS, by use of our average R_0 value, was 3.27 for CBZQCR and 3.42 for TBZQCR, suggesting that the Cr appears to be +3 in both cases and that each ligand is −1. If the R_0 value for Cr(III) of 1.708 Å was used, the BVS was 3.13 for CBZQCR and 3.28 for TBZQCR, in good agreement with the formulation as Cr(III) and a −1 ligand. The BVS is larger than expected in both cases, perhaps reflecting high thermal motion, which tends to make the observed bond lengths shorter and the BVS larger.

The BVS is also useful in confirming assumptions regarding the oxidation state or identity of metal ions in cluster complexes. There are a number of μ_3-oxo-Cr_3 clusters where the BVS around the Cr ions is very close to 3; for example, KOPNIM[25] (3.01, 2.98, 3.02), WABJUE[26] (2.97, 2.99, 2.91), and COVPOS,[27] although here the BVS at 2.67 was a bit low. COVPOS was formed from a 1:2:6 mixture of Cr(III) and Fe(III) perchlorates and glycine. The thermal parameters from the structural analysis were used to suggest that the Fe_2Cr core was ordered. The BVS around the two Fe atoms of 3.02 and 3.00 (as given in our earlier study of FeO clusters)[1d] supported the postulation of an ordered structure. However, one difficulty with COVPOS was an ambiguity in the space group between *Cc* and *C*2/*c*. The authors used *Cc* without giving any justification for the choice, which may account for the deviation of the BVS from the expected value of 3.

Another cluster complex was PINFOH,[28] but in this case the BVS of 2.60 and 2.53 were in poor agreement with the expected values. In this complex we have a Mn(II) that is coordinated to three $Cr(ox)_3$ ions in a polymeric structure. In addition to a space group ambiguity, the authors did not discuss the assignment of the metal atom types and, in fact, the thermal ellipsoids looked very strange. The U_{eq} for one of the Cr ions was twice that of the other two metal ions and larger than that of virtually all the light atoms, surely unreasonable. Finally, we note that in RUPBEJ[29] there is an identical $MnCr(Ox)_3$ with a different cation and BVS = 2.80 in this case. Consequently, one should view the PINFOH[28] report with some skepticism, and deviant bond valent sums once again are a good indicator of a poor structure determination.

Cr(V) and Cr(VI) Complexes. The situation with Cr(V) and Cr(VI) complexes is much more complicated. In the case of Cr(V) complexes retrieved from the CSD, they all appear to have CN = 5, while the Cr(VI) case has CN = 4. Therefore, in the case of Cr(V) and Cr(VI), we have examples of complexes with high oxidation states but low coordination numbers. This class of compounds does not appear to be amenable to an oxidation state independent value because the O···O contacts are much shorter than van der Waals contacts, and any shortening of the bonds to increase the BVS would be impossible. A somewhat similar conclusion had been reached using a different approach.[5] These conclusions are supported by the Cr−O bond length analysis carried out in conjunction with the structure determination of FURNIP.[30] In going from chromates to dichromates, the increase in the Cr−O bridge bond is accompanied by a decrease in the Cr−O terminal bonds. A similar change occurs from dichromates to trichromates. These changes are understandable in terms of maintaining the BVS around the various Cr atoms. Consequently, the BVS for these complexes are smaller than expected if an average R_0 value is used. A further complication arises in the case of Cr(VI) complexes because a number of the chromates and dichromates are disordered. For example, the complexes ZAWWID,[31] ZAWWOJ,[32] and ZOKYUT[33] were retrieved as having CN = 5 but in reality are disordered CrO_4^{2-} ions. For this reason, we looked for an example of a Cr complex with a high oxidation state and a high coordination number, which led us to $K_3Cr(O_2)_4$.

The structure of the $K_3Cr(O_2)_4$ complex was originally determined using film data and was not well refined.[13] Two subsequent papers refined the same data so that there were three different parameter sets and distances for this complex from only one data set. To resolve the differences and to provide a more accurate determination, we synthesized this interesting complex and redetermined the structure. A view of the complex is given in Figure 1. The O−O distance of 1.452(2) Å is almost the average of the three previous determinations, two of which are longer[13,14] and the other[15] shorter. The O−O distance is very close to the O−O distance in various peroxides,[34] which is in agreement with the formulation as a Cr(V) species. Our results are also in agreement with the proposed bonding in this

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(22) LIBCRB is tetrakis{bis(*tert*-butyl)methoxo}chromium(IV). See ref 20.

(23) CBZQCR is tris(tetrachloro-1,2-benzoquinone)chromium(0). Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1976,** *98*, 4834−4838.

(24) TBZQCR is tris(3,5-di-*tert*-butyl-o-benzoquinone)chromium(0). Sofen, S. R.; Ware, D C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979,** *18*, 234−239.

(25) KOPNIM is μ_3-oxo(hexakis(μ_2-l-valinato-O,O′)triaquachromium(III) heptanitrate pentahydrate. Kato, H.; Nakata, K.; Nagasawa, A.; Yamaguchi, T.; Sasaki, Y.; Ito, T. *Bull. Chem. Soc. Jpn.* **1991,** *64*, 3463−3465.

(26) WABJUE is μ_3-oxo(hexakis(μ_2-chloroacetato-*O*,*O*′) triaquachromium(III) chloroacetate dihydrate. Lim, M.-C.; Chen, W.; An, S.-N.; Jelan, A. M.; Butcher, M. J. *J. Crystallogr. Spectrosc. Res.* **1993,** *23*, 13.

(27) COVPOS is μ_3-oxo(hexakis(μ_2-glycinato-*O*,*O*′)triaquadiiron(III)chromium(III) heptaperchlorate hexahydrate. Clegg, W.; Lam, O. M.; Straughnan, B. P. *Angew. Chem., Int. Ed. Engl.* **1984,** *23*, 434−435.

(28) PINFOH is catena((triphenylphosphonium) tris(μ_3-oxalato)chromium(III)-manganese(II). Decurtins, S.; Schmalle, H. W.; Oswald, H. R.; Linden, A.; Ensling, J.; Gutlich, P.; Hauser, A. *Inorg. Chim. Acta* **1994**, *216*, 65−73.

(29) RUPBEJ is catena((tetra(*n*-propyl)ammonium)tris(μ_3-oxalato)chromium(III)manganese(II). Decurtins, S.; Schmalle, H. W.; Oswald, H. R.; Linden, A.; Ensling, J.; Gutlich, P.; Hauser, A. *Inorg. Chem.* **1997**, *36*, 2301−2308.

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(31) ZAWWID is bis(aquachromato-*O*,*O*′)(bis(pyridine-2,6-bis(ethylimino))bis(*N*,*N*′-ethane-1,2-diamine))europium(III)) dichromate dihydrate. Benetollo, F.; Bombieri, G.; Gilli, P.; Harlow, P. M.; Polo, A.; Vallarino, L. M. *Polyhedron* **1995**, *14*, 2255−2265.

(32) ZAWWOJ is bis(aqua(chromato-*O*,*O*′)(bis(pyridine-2,6-bis(ethylimino))bis(*N*,*N*′-ethane-1,2-diamine))samarium(III)) dichromate dihydrate. See ref 31.

(33) ZOKYUT is bis(aqua-bis(*N*,*N*′-bis(pyridine-2,6-bis(1-ethylimino))-ethylenediamine)(tetraoxochromium(VI)-*O*,*O*′)terbium(III)) dichromate dihydrate clathrate. Ayala, J. D.; Bombieri, G.; Benetollo, F.; Gilli, P.; Vallarino, L. M. *J. Chem. Crystallogr.* **1995**, *25*, 355−360.

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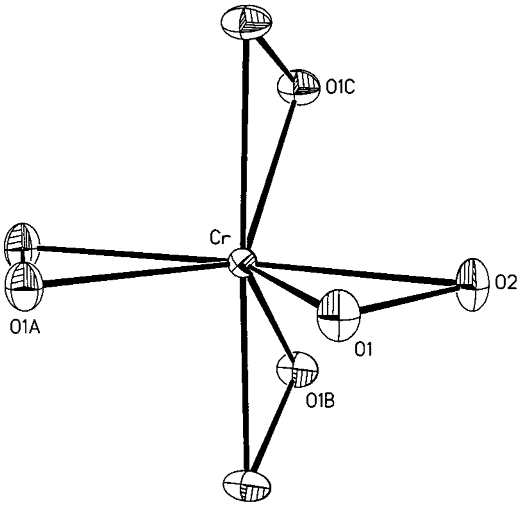

Figure 1. View of the $Cr(O_2)_4^{2-}$ ion showing the atom labeling and 50% thermal ellipsoids. Pertinent distances and angles are the following: Cr−O1, 1.881(1) Å; Cr−O2, 1.958(1) Å; O1−O2, 1.452(2) Å; O1−O2−Cr, 64.99(7)°.

complex.[15] The BVS using our average R_0 is 4.74, in good agreement with the expected value. This result suggests that our average value will provide a good estimate of the oxidation state except for those cases where a combination of high oxidation state and low coordination number exists in the complex. In these cases, the BVS will tend to be low.

Distances in Cr Complexes. The bond distance data for those complexes used in our analysis are summarized in Table 3. We see that for a given oxidation state and coordination number there is a wide range of Cr−O distances, but the average corresponds, in most cases, to a valence per bond equal to the oxidation number divided by the CN. We see that in the case of Cr(VI) with CN = 4, the average valence, calculated using eq 2, is only 1.23, not the 1.5 that might be expected. This observation is in agreement with the fact that the nonbonded O···O distance is very short and that repulsions between the O atoms prevent a shortening of the bond. The fact that these complexes are good oxidizing agents is explicable in terms of the small BVS.

Conclusions and Recommendations

The BVS is a relatively simple calculation if the appropriate R_0 values are available. For the Cr case with O donor atoms, we have shown that an R_0 of 1.724 Å can be used to calculate the oxidation state of the Cr atom with no prior assumptions. The results are in good agreement for oxidation states of Cr(II), Cr(III), and Cr(V). The agreement with Cr(VI) was not very good, which may be a reflection of steric constraints with high oxidation states and low coordination numbers.

The deviation of the BVS from an integer value usually indicates problems with the structure, possible steric constraints, or excessive thermal motion. We have provided a number of examples to illustrate these points.

In cases where the ligand oxidation state is ambiguous, the BVS can be used as a guide for the oxidation state of the metal and therefore, by inference, the ligand. The BVS can be extremely useful to chemists in evaluating the results of a crystal structure analysis or in resolving conflicts regarding oxidation states. Structural chemists should be able to utilize the BVS to support the crystal structure analysis. The concept can be applied without assumptions regarding the oxidation state and can help prevent serious errors prior to publication.

Supporting Information Available: Listings of the BVS calculations for the CrO_n ($n = 3-8$) used in the analysis and the X-ray crystallographic data (in CIF format) for the structure determination of potassium tetraperoxochromate(V), K_3CrO_8. This material is available free of charge via the Internet at http://pubs.acs.org.

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