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Bond Valence Sums in Coordination Chemistry Using Oxidation-State-Independent R_0 Values. A Simple Method for Calculating the Oxidation State of Iron in Fe−O Complexes

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Introduction

We have been exploring the use of the bond valence sum in coordination chemistry, particularly from the viewpoint of using oxidation-state-independent R_0 values.[1] The postulate that the bond valence sum (BVS) surrounding the jth atom or ion is equal to the oxidation state z_j, as shown in eq 1, can be traced to Pauling.[2] The valences of the individual bonds, s_{ij} in eq 1, can be calculated from the observed bond lengths using eq 2 or 3, where r_{ij} is the observed bond length, R_0 and N are constants

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

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

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

that are dependent upon the nature of the ij pair, and b is usually taken to be 0.37. 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.[3−5]

Although the concept appears to be extremely useful in coordination chemistry, it has not been applied routinely. The question is whether the BVS can be used to calculate the oxidation state of a metal ion in a coordination compound or metalloenzyme without any assumptions about the oxidation state. The present report examines the usefulness of oxidation-state-independent R_0 values as applied to Fe complexes with O donors. The Fe case was chosen because of the different R_0 values, summarized in Table 1, that have been proposed for Fe−O bonds depending on the Fe oxidation state.[6−10]

Table 1. Values of R_0 (Å) for Fe−O Bonds for Oxidation States 2 and 3[a]

	oxidation state of Fe			oxidation state of Fe	
ref	2+	3+	ref	2+	3+
6	1.734	1.759	8	1.734	1.759
7a	1.734	1.759	KP	1.713	1.751
7b	1.700	1.765	10	1.764 (5.5)	1.780 (5.7)

[a] Equation 2 with $b = 0.37$ was used in refs 6−8 and the present study, KP. Equation 3 was used in ref 10, with the corresponding N values in parentheses.

Table 2. Experimental Values of R_0 (Å) for Fe−O Bonds as a Function of the Coordination Number of the Fe Atom[a]

CN	no.	R_0	CN	no.	R_0
3	2	1.788	6	229	1.745
4	6	1.740	8	2	1.813
5	10	1.739	all	249	1.745

[a] CN is the coordination number, no. is the number of complexes used for that coordination number, and R_0 is the value that minimizes the sum of the squares of the deviations between the observed and calculated oxidation states.

Table 3. Summary of Fe−O Distances (Å) as a Function of Oxidation State (ox) and Coordination Number (CN)[a]

ox	CN	no.	min	max	av
2	3	6	1.822	2.023	1.950
2	4	4	1.883	2.134	2.009
2	5	25	1.956	2.207	2.065
2	6	396	1.994	2.377	2.120
2	8	16	2.131	2.480	2.356
3	4	20	1.793	1.934	1.855
3	5	25	1.780	2.117	1.957
3	6	1272	1.790	2.376	2.011

[a] The number of bonds found is no., min is the minimum Fe−O distance found for that oxidation state and coordination number, max is the maximum Fe−O distance found for that oxidation state and coordination number and av is the average Fe−O distance found for that oxidation state and coordination number.

Experimental Section

The Fe−O bond length data were from the 1997 release of the Cambridge Structural Database (henceforth CSD) containing 167 797 entries.[11] For a given coordination number, those entries containing only O atoms were retrieved, i.e. FeO_n, where $n = 3$, 4, 5, 6, and 8. A total of 202 entries from the CSD gave a set of 299 FeO_n complexes. Two duplicate entries were removed to give a starting set of 297 FeO_n complexes. An oxidation state for each entry was calculated using eq 2 with $b = 0.37$ and an R_0 value of 1.744 Å.[9] Obvious erroneous oxidation states were corrected at this point. Next, an R_0 value which minimized the sum of the squares of the differences between the reported and calculated oxidation states was determined. The resulting R_0 values for the various n values are given in Table 2. The final R_0 value of 1.745 Å was calculated using all the FeO_n data. Finally, an R_0 value for Fe(II) was determined using 74 complexes and for the Fe(III) using 223 complexes from our CSD data set. An analysis of the Fe−O bond length data used in our study is given in Table 3. A complete listing of the compounds is available. The BVS was calculated using FORTRAN programs written by the one of the authors.[12]

Results and Discussion

The iron complexes examined can be conveniently divided into two groups, mononuclear and polynuclear complexes, since

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(1) (a) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 122. (b) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 3397. (c) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 4888.
(2) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.
(3) Urusov, V. S. *Acta Crystallogr., Sect. B* **1995**, *B51*, 641.
(4) O'Keeffe, M. *Modern Perspectives in Inorganic Crystal Chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; p 163.
(5) Brown, I. D. *Structure and Bonding in Crystals;* Academic Press: New York 1981; Vol. II, p 1.
(6) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr., Sect. B* **1991**, *B47*, 192.
(7) (a) Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.
(8) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *B41*, 244.
(9) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226.
(10) Brown, I. D.; Wu, K. K. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1957.
(11) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
(12) Copies of the FORTRAN programs can be obtained from G.J.P.

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the problems are somewhat different in each case. A BVS that differs by 0.25 or more valence units from the postulated oxidation usually indicates a problem with the crystal structure determination or, in the case of multinuclear complexes, an interaction between the metal atoms. All entries that differed by 0.25 or more valence units were not examined in detail since in many cases the reported X-ray data were extremely abbreviated or the journal was not available.

The mononuclear complex DUDCIO[13] had a large *R* value of 0.112 and the BVS was 1.39, much lower than the expected 2.0. In this case, there is disorder in the $-CH_2CH_2-$ units in the ligand together with the common ambiguity between a centric and acentric space group, in other words, a relatively poor structure determination.

A rather intriguing case was KENZAE[14] where the BVS of 3.51 was much higher than the postulated Fe(III) value. The *R* value of 0.081 is a bit high, but more interesting is the fact that the authors stated that they could not locate the Na^+ ion in the crystal. Considering the fact that Na^+ has 10 electrons, the *R* value is surprisingly low. The high BVS may be understandable in view of the problems with this structure; unfortunately, there are very little data in the report that can be used to evaluate the structure determination.

An example of the usefulness of the oxidation-state-independent BVS is provided by the $Fe^{II}Fe^{III}{}_2(SO_4)_4{\cdot}2H_2O$, which contained separated FeO_6 octahedra.[15] Using the R_0 value of 1.745 Å, the BVS is 2.175 for one octahedron and 3.14 for the other, supporting the presence of both oxidation states in the same crystal.

In multinuclear iron complexes with extensive electron delocalization, the concept of a fixed oxidation state is less meaningful and the BVS may differ from an integer value. For example, in EL[16] which contains the $[FeW_{12}O_{40}]^{5-}$ ion together with organic donor molecules, the BVS for the Fe(III) was 2.63, lower than the expected 3.0.

SEVWOF[17] was a trinulear oxo complex consisting of two Fe(III) atoms and one Mn(II) at the vertexes of a triangle with a central oxo group and bridging carboxyl groups. Complexes of this type usually have a stoichiometry $M_3OA_6L_3$, where A is a carboxylic acid, L is a Lewis base, and the coordination around M is octahedral. However, the authors reported that one Fe(III) was five-coordinated and the other Fe(III) and Mn(II) were octahedral. The BVS for the five-coordinate Fe(III) was 2.52, suggesting a missing coordination site. The *R* value of 0.098 is high and no indication of how the authors distinguished between the Fe and Mn ions is given in the abstract. In essence, one should probably view this report with some skepticism.

Complexes of the type $Fe_3OA_6L_3$ or (μ_3-oxo)hexakis(μ_2-bidentate ligand)tris(monodentate ligand)triiron, similar to SEVWOF[17] (vide supra), can have a BVS that differs significantly from an integer value but is still consistent with the postulated bonding. In the case of a simple Fe(III) core such as that found in HEDROX[18](BVS = 3.02, 3.02, 3.05) or OXFGLY[19](BVS = 2.98, 2.99, 2.88, 2.87, 2.99, 2.98), the BVS reflects the oxidation state of the Fe atoms. If there are two Fe(III) atoms and one Fe(II) in the triiron core and there is complete delocalization, the BVS is close to the expected value of 2.67; for example, the BVS for FUFRON01[20] was 2.75 and that for WEGGUK[21] was 2.71. In WEGGUK[21], the bidentate ligand was cyanoacetate, and in another study of the complex reported recently,[22] the BVS at 296 K was 2.72 and that at 135 K was 2.71. These values indicate delocalization of the valence electron over the three Fe atoms at these two temperatures. However, at 100 K there is valence electron trapping, and the BVS values are 2.47, 2.85, and 2.91 for the three independent Fe atoms. Similarly, in ZUSHUR[23] the BVS values of 2.99, 2.89, and 2.28 reflect the fact that the electron is not delocalized over the three Fe atoms but is valence trapped. In ZUSJOM01,[24] the BVS values are 2.73, 2.25, and 2.88, indicating electron trapping. However, in this determination, which was carried out at 298 K, the electron was to have been delocalized while the reported determination at 112 K shows a more delocalized behavior, with BVS values of 2.79, 2.59, and 3.09. Were the two results interchanged in the publication? In ZUSJEC,[25] at 112 K the BVS values are 2.90, 2.97, and 2.69 and are very close to the BVS values at 298 K of 2.73, 2.86, and 2.67, although the authors suggest an increase in delocalization with an increase in temperature. Inspection of the cell parameters for ZUSJEC in Table 1 of ref 25 indicates that the *b* axis increases in length with a decrease in temperature, which is a most unusual change.

The BVS values for the tetranuclear iron clusters reported by Lippard's group reflect very nicely their postulated bonding. In LEFWUO,[26] the four Fe(II)−O atom pairs have BVS values of 2.20, 2.21, 2.22, and 2.18. However, in LEFXAV,[27] two of the Fe−O atom pairs have sums close to three, 2.88 and 2.61, while the remaining six are very close to two, 2.15, 2.16, 2.19,

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[13] DUDCIO is bis(12-crown-4-*O,O′,O″,O‴*)iron(II) hexafluorophosphate acetonitrile solvate. Meier, K.; Rihs, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 858.

[14] KENZAE is tetrakis(μ_2-oxo)tetrakis(*N,N′, N″*-trimethyl-1,4,7-triazacyclononane-*N,N′,N″*)dioxomolybdenum(VI)iron(II) sodium tetrakis(tetraphenylborate). Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch., B* **1990**, *45*, 619.

[15] The complex reported by Wildner and Giester (Wildner, M.; Giester, G. *Z. Kristallogr.* **1991**, *196*, 269) is not in the CSD file and was not included in the calculation of the various R_0 values.

[16] ZAXHEL is octakis[bis(ethylenedithio)tetrathiafulvalene]tetracontraoxododecatungsten(VI)iron(III) nonahydrate. Gomez-Garcia, C. J.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; Le Magueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau. C.; Delhaes, P. *Inorg. Chem.* **1995**, *34*, 4139.

[17] SEVWOF is (μ_3-oxo)pentakis(μ_2-propionato)diiron(III) manganese(II) nitrate. Zhang, H.; Yu, X. *Jiegou Huaxue* **1990**, *9*, 1; *Chem. Abstr.* **1991**, *114*, 177088h.

[18] HEDROX is (μ_3-oxo)hexakis(μ_2-benzoato-*O,O′*)tris(methanol)iron(III)]. Degang, F.; Guoxiong, W.; Wenxia, T.; Kaibei, Y. *Polyhedron* **1993**, *12*, 2459.

[19] OXFGLY is (μ_3-oxo)hexakis(μ_2-glycinato-*O,O′*)tris[aquairon(III)]. Thundathil, R. V.; Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 1818.

[20] FUFRON01 is (μ_3-oxo)hexakis(μ_2-trichloroacetato-*O,O′*)tris [(methanol)iron(III)]. Shilov, G. G.; Ponomarev, V. I.; Atovmyan, L. O. *Koord. Khim.* **1990**, *16*, 230.

[21] WEGGUK is (μ_3-oxo)hexakis(μ_2-cyanoacetato-*O,O′*)tris[aquairon(III)]. Nakamoto, T.; Katada, M.; Kawata, S.; Kitagawa, S.; Kikuchi, K.; Ikemoto, I.; Endo, K.; Sano, H. *Chem. Lett.* **1993**, 1463.

[22] Nakamoto, T.; Hanaya, M.; Katada, M.; Endo, K.; Kitagawa, S.; Sano, H. *Inorg. Chem.* **1997**, *36*, 4347.

[23] ZUSHUR is (μ_3-oxo)hexakis(μ_2-bromoacetato-*O,O′*)tris[aquairon(III)]. Sato, T.; Ambe, F.; Endo, K.; Katada, M.; Maeda, H.; Nakamoto, T.; Sano, H. *J. Am. Chem. Soc.* **1996**, *118*, 3450.

[24] ZUSJOM01 is (μ_3-oxo)hexakis(μ_2-chloroacetato-*O,O′*)tris[aquairon(III)]. Sato, T.; Ambe, F.; Endo, K.; Katada, M.; Maeda, H.; Nakamoto, T.; Sano, H. *J. Am. Chem. Soc.* **1996**, *118*, 3450.

[25] ZUSJEC is (μ_3-oxo)hexakis(μ_2-acetato-*O,O′*)tris[aquairon(III)]. Sato, T.; Ambe, F.; Endo, K.; Katada, M.; Maeda, H.; Nakamoto, T.; Sano, H. *J. Am. Chem. Soc.* **1996**, *118*, 3450.

[26] LEFWUO is tetrakis[(μ_3-methoxo)(μ_2-dibenzoylmethane)(methanol)iron(III)] toluene solvate. Taft, K. L.; Caneschi, A.; Pence, L. E.; Delfs, C. C.; Papaefthymiou, G. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 11753.

[27] LEFXAV is tetrakis[(μ_3-methoxo)(μ_2-benzoato-*O,O′*)tris(methanol)methoxytriiron(II)iron(III)] methanol solvate. Taft, K. L.; Caneschi, A.; Pence, L. E.; Delfs, C. C.; Papaefthymiou, G. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 11753.

2.17, 2.13, and 2.36, and reflect the formulation of one Fe(III) atom and three Fe(II) atoms in each of the two independent Fe_4 clusters. In summary, the BVS for iron clusters provides supporting evidence for postulated trapped or delocalized valence states.

Table 3 contains a summary of the Fe−O distances used in the BVS analysis as a function of oxidation state and coordination number. The average Fe−O distance increases with an increase in coordination number at a constant oxidation state, as expected. Similarly, the Fe−O distance decreases with increasing oxidation state at a constant coordination number, also as expected. However, the important point is that there is a large range of values at any fixed combination of oxidation state and coordination number. The large variation in the Fe−O distance is understandable in terms of the BVS. Ligand constraints can limit the range of Fe−O distances that are possible so that the other ligands must assume distances that are compatible with the BVS being equal to the oxidation state. The principle of the BVS being equal to the oxidation state of the metal ion is an important principle that must be satisfied at the expense of a constant bond radius. Under these conditions, the calculation of the BVS is much more meaningful than bond distance comparisons.

Conclusions and Summary

The oxidation-state-independent R_0 value of 1.745 can be used with eq 2 to calculate the oxidation state of iron in complexes containing only Fe−O bonds. A deviation of greater than 0.25 valence units from an integer value in a mononuclear complex is a good indication that there are problems with the crystal structure. In the case of polynuclear Fe clusters, the BVS affords a simple calculation that can lend support to postulated delocalization and/or valence state trapping. In the event that the BVS appears to be somewhat off, the oxidation state values of 1.713 for Fe(II) and 1.751 for Fe(III) can be used as a further check on the correctness of the structure.

Supporting Information Available: Listings of the BVS calculations for the 297 Fe complexes used in the analysis (15 pages). Ordering information is given on any current masthead page.

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