Articles

Bond Valence Sums in Coordination Chemistry Using Oxidation State Independent R_0 Values. A Simple Calculation of the Oxidation State of Titanium in Complexes Containing Ti−N, Ti−O, and Ti−Cl Bonds

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A simple method for determining the oxidation state of the Ti in complexes involving only N, O, or Cl donors using the bond valence sum, henceforth BVS, is proposed. New R_0 values of 1.906 for Ti−N, 1.790 for Ti−O, and 2.184 for Ti−Cl were determined from TiL_n complexes where L was N, O, or Cl and n varied from 4 to 7. These R_0 values were then used to calculate the BVS for 534 Ti complexes with coordination numbers of 4−7 and only N, O, or Cl as donor atoms. Examples where the BVS was a noninteger value or differed from the reported oxidation state are discussed.

Introduction

The bond valence sum, henceforth BVS, has not been applied routinely in coordination chemistry although it appears to be extremely useful. The basic concept that the valence of the jth atom or ion, z_j, can be defined in terms of the sum of the individual bond valences, s_{ij}, as shown in eq 1, can be traced to Pauling.[1] The valences of the individual bonds can be calculated from the observed bond lengths using eq 2, where R_{ij} is the observed bond length, R_0 is a constant dependent upon the nature of the ij pair, and $b = 0.37$. The calculation can be illustrated using R_0 values of 1.906 for Ti−N, 1.790 for Ti−O, and 2.184 for Ti−Cl and a five-coordinate Ti complex with bond lengths of Ti−N = 2.267 Å, Ti−O = 1.815, 1.817, and 1.800 Å, and Ti−Cl = 2.292 Å. Using eq 2 the individual bond valences are 0.377, 0.935, 0.930, 0.973, and 0.747 for a total valence of 3.962 compared to the value of 4.0 that was postulated. Two important points are the dependence of the BVS on the R_0 value used and the fact that almost all of the values currently available are oxidation state dependent. A more extensive discussion can be found in a recent review.[2]

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

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

The question is whether R_0 is dependent upon the oxidation state or only upon the nature of the two atoms. My interest has been in exploring the latter idea as applied to coordination compounds since the oxidation state could then be calculated without any assumptions. Several examples of the use of the BVS in coordination chemistry using oxidation state independent R_0 values were recently reported.[3,4] The majority of the other examples[5−7] have used R_0 values which depend on the oxidation state of the atom pairs. The present report considers the case of Ti with N, O, and Cl donor atoms as the first part of a program to assess whether the concept of oxidation state independent R_0 values is useful in coordination chemistry and whether the method is applicable to a range of coordination numbers, geometries, and oxidation states.

Table 1. Summary of BVS Calculations for Various Titanium Complexes[a]

CN	no.	R_0(Ti−N)	no.	R_0(Ti−O)	no.	R_0(Ti−Cl)
4	9	1.903	13	1.785		
5	5	1.903	22	1.794		
6	4	1.916	112	1.790	6	2.184
7			4	1.800		
all 18		1.906	151	1.790	6	2.184
Initial		1.934		1.814		2.186

[a] CN is the coordination number, and no. is the number of complexes used in determining that particular R_0 value. The starting values used to aid in assigning oxidation numbers are given as initial at the end of the table.

Experimental Section

The bond length data were from the June 1996 release of the Cambridge Structural Database (henceforth CSD) containing 160 091 entries.[8] For a given coordination number, n, only those entries containing only all N, all O, or all Cl atoms were retrieved, i.e., TiO_n etc. The R_0 which minimized the difference between the assigned valence and the valence calculated from the BVS was determined. The R_0 values determined in this way are given in Table 1 together with the initial R_0 values calculated using published parameters.[9] The next step was to consider the 534 Ti complexes where the donor atoms were limited to any combination of N, O, or Cl and to calculate the BVS for each entry. An analysis of the bond length data in the 534 Ti complexes

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(1) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.
(2) Urusov, V. S. *Acta Crystallogr., Sect. B* **1995**, *B51*, 641.
(3) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 122.
(4) Browning, K.; Abboud, K. A.; Palenik, G. J. *J. Chem. Crystallogr.* **1995**, *25*, 847.
(5) Eriksen, K. M.; Nielsen, K.; Fehrmann, R. J. *Inorg. Chem.* **1996**, *35*, 480.
(6) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102−4105 and references therein.
(7) Wang, X.; Liebau, F. *Acta Crystallogr., Sect. B* **1996**, *B52*, 7.
(8) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
(9) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226.

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Table 2. Summary of the Distances Used in the Analysis[a]

CN	atom	ox	no.	av	σ	min	max
4	O	3	13	1.897	0.094	1.806	2.089
5	O	3	15	1.960	0.130	1.767	2.162
6	O	3	122	2.042	0.087	1.809	2.221
7	O	3	49	2.095	0.036	2.025	2.198
4	O	4	81	1.781	0.038	1.664	1.862
5	O	4	171	1.870	0.119	1.613	2.186
6	O	4	1080	1.965	0.133	1.637	2.408
7	O	4	91	1.995	0.141	1.680	2.603
6	N	2	8	2.327	0.056	2.271	2.381
4	N	3	9	2.026	0.097	1.947	2.267
5	N	3	19	2.123	0.174	1.702	2.352
6	N	3	74	2.211	0.075	2.075	2.388
7	N	3	12	2.313	0.027	2.271	2.371
4	N	4	73	1.893	0.058	1.719	2.034
5	N	4	172	2.037	0.156	1.663	2.451
6	N	4	245	2.133	0.128	1.723	2.432
7	N	4	30	2.203	0.124	1.873	2.386
6	Cl	2	4	2.487	0.011	2.477	2.496
4	Cl	3	10	2.318	0.067	2.220	2.376
5	Cl	3	6	2.363	0.061	2.293	2.462
6	Cl	3	92	2.370	0.055	2.273	2.502
7	Cl	3	2	2.378	0.001	2.377	2.379
4	Cl	4	46	2.219	0.034	2.156	2.299
5	Cl	4	67	2.305	0.088	2.171	2.573
6	Cl	4	529	2.312	0.096	2.176	2.839
7	Cl	4	5	2.367	0.042	2.340	2.442

[a] CN is the coordination number; atom is the atom type; ox. is the Ti oxidation state of the Ti; and no. is the number of bonds used to compute the average bond length, av, and the calculated σ. Min is the minimum bond length found in the sample set, and max is the maximum bond length found in the set.

used in the study is given in Table 2. A complete listing of the compounds used is available as Supporting Information. The BVS was calculated using FORTRAN programs written by the author; they are available on request.

Results and Discussion

A difference between the assigned oxidation state and the bond valence sum can occur in two different ways: the BVS can differ significantly from an integer value, or the calculated BVS can differ from the assigned oxidation state. Examples of both deviations are present in this analysis of Ti compounds.

Of the 534 Ti complexes containing only N, O, or Cl donors for which the BVS was calculated, only 47 had values that differed by 0.3 or more from an integer value. Of the 47 there were 6 cases where the *R* value was greater than or equal to 0.089. Crystal structures with *R* values of about 0.09 are usually considered to be not well refined and therefore were not examined in detail. The question was whether there were features of the remaining 41 that caused the BVS not to have an integer value or whether the calculations were not accurate to more than about 10%. All 41 examples were not examined in detail since in many cases only a minimum of crystallographic data was reported or the original journal article was not readily available. However, in the cases that were examined in detail, a noninteger BVS sum usually indicated some problem with the crystal structure determination or possible steric effects in the molecule as will be illustrated by the following examples.

In the case of JADWIU,[10] the Ti was six coordinate with 4 Cl and a disordered O, Cl in the other two sites, and a BVS of 3.47 versus an expected 4.0. The CSD entry was flagged to indicate that the reported cell constants were in error. BAXFUB[11] with a BVS of 3.89 had been reported earlier and was an ordered structure that had 6 Cl atoms. In fact a comparison of the unit cells and positional parameters for JADWIU[10] and BAXFUB[11] indicated that they appeared to be identical. In JADWIU, the chlorine analysis, the thermal parameters for the disordered Cl and O atoms, the very sensitive nature of $TiCl_4$, and the synthetic route also support the hypothesis that the two structures are identical. The deviation of the BVS in the JADWIU case could have been considered a warning about problems with the structure.

Another example is that of YEKPIN,[12] which contained 3 independent Ti atoms in a trimeric unit. The BVS values were 3.47, 3.44, and 3.51 while the expected value was 4.0. Inspection of the published parameters revealed that the *U*(eq) for the 3 Ti atoms averaged 0.102 compared with 0.063 for the Cl atoms, which is unreasonable. In fact some of the carbon atoms had *U*(eq) values that were lower than those of the Ti atoms. The wR_2 was not given for this structure but was given for the other three structures in the paper. The structure solution is not trivial, and these observations suggest that this crystal structure has serious problems.

In PIXTEX[13] the BVS was 4.33 while 4.0 was the expected value. The authors state, "Although vibrational spectroscopy and the electrochemistry unambiguously establishes that these crystals also contain molecules of $[(Me_3tacn)Ti(O)(NCO)_2]$, this has not been detected by X-ray crystallography." In fact the authors suggest that "...a compositional disorder prevails" and do not discuss the "metrical details". In summary there are definitely problems with the structure as was indicated by the BVS.

An analysis of the 47 examples where the difference was greater than 0.3 indicated that 30 of the 47 had a BVS that was less than the expected value. A lower value could arise if the bond lengths were longer than expected due to steric effects. Steric effects have been invoked by others[14,15] to explain discrepancies in inorganic structures, and they appear to be operative in the case of YEXCAF[16] versus YEXCEJ.[16] The BVS values for YEXCAF were 4.00 and 4.07 for the two independent Ti atoms in the methyl complex but 3.80 for the bulkier isopropyl derivative in YEXCEJ. In CTMSIA,[17] WEDCUD,[18] and WEDDAK,[18] the Ti was four coordinate with bulky

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(10) JADWIU is tetrakis(ethyl acetate-*O*)magnesium(II)−bis(μ-chloro)-trichlorohydroxotitanium(IV). Giunchi, G.; Albizzati, E.; Malpezzi, L.; Gianetti, E. *Inorg. Chim. Acta* **1988**, *147*, 159.

(11) BAXFUB is tetrakis(ethyl acetate-*O*)magnesium(II)−bis(μ-chloro)-tetrachlorotitanium(IV). Bart, J. C. J.; Bassi, I. W.; Calcaterra, M.; Albizzati, E.; Giannini, U.; Parodi, S. *Z. Anorg. Allg. Chem.* **1981**, *482*, 121.

(12) YEKPIN is bis(μ_3-trimethylphosphine imido)tris((μ_2-trimethylphosphine imido)dichlorotitanium(IV)) tetraphenylborate. Rübenstahl, T.; Weller, F.; Dehnicke, K.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1741.

(13) PIXTEX is (1,4,7-trimethyl-1,4,7-triazacyclononane)bis(isocyanato)-peroxotitanium(IV). Jeske, P.; Haselhorst, G.; Weyhermüller, T.; Weighardt, K.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 2462.

(14) Brown, I. D. *J. Solid State Chem.* **1991**, *90*, 155.

(15) Withers, R. L.; Thompson, J. G.; Rae, A. D. *J. Solid State Chem.* **1991**, *94*, 404.

(16) YEXCAF is dichloro(*tert*-butylimido)(tetramethylethylenediamine)-titanium(IV), and YEXCEJ is dichloro(*tert*-butylimido)(diisopropylethylenediamine)titanium(IV). Lewkebandara, T. S.; Sheridan, P. H.; Heeg, M. J.; Rheigold, A. L.; Winter, C. H. *Inorg. Chem.* **1994**, *33*, 5879.

(17) CTMSIA is chlorotris(bis(trimethylsilyl)amido)titanium(IV). Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1991**, 2010.

(18) WEDCUD is bis(μ-(trimethylsilyl)imido)bis(chloro[bis(trimethylsilyl)amido]titanium(IV)), and WEDDAK is (μ_2-(trimethylsilyl)imido)-[chloro{bis(trimethylsilyl)imido}titanium(IV)](μ_2-2,2-dimethyl-1-(trimethylsilyl)-1-aza-3-azonia-2-silapropane-*N*,*N*,*N*′)[bis(trimethylsilyl)-imido]titanium(IV)]. OvchiAiroldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1991**, 2010.

trimethylsilylamine groups and the BVS values were 3.55, 3.88, and 3.41, respectively. A BVS less than 4.0 can thus be ascribed to steric effects.

The BVS can be larger than the expected value if there are large thermal motions in the coordinated atoms. Large thermal motions lead to apparent bond lengths that are shorter than expected. In KOXGUZ[19] the *B*(eq) values for the three isopropoxide groups attached to the Ti atom were relatively large, 10.0, 5.5, and 7.2. The BVS of 4.35 may be a reflection of the large thermal motions in the complex. The *B*(eq) values for the Cl atoms in YUXBIC[20] were about twice that of the Ti atom, and the BVS was 4.35.

Similarly, in LAWNAY[21] the BVS was 4.33 while 4.0 was the predicted value. The crystal was very large, 0.3 × 0.5 × 1.0 mm, and there was no indication that an absorption correction had been applied. The *B*(eq) values, in units of $\mathrm{pm}^2 \times 0.1$, for the three Cl atoms were 123, 147, and 87 compared to 64 for the Ti and 54 for the N attached to Ti. The *B*(eq) values for the three Cl atoms were among the largest in the structure, and only the *B*(eq) values for the C atoms of the trimethylsilyl group at 124, 147, and 123 were of comparable magnitude. Certainly, the distances in this molecule should be viewed with caution as suggested by the large BVS.

A problem occurs if the oxidation state found in the CSD file does not agree with the calculated BVS. Differences of this type can arise either from an error in the CSD file, the failure to locate a hydrogen atom, or some ambiguity in the oxidation state. The CSD contains over 160 000 entries, and errors, while rare, can occur. For example, JOHBAJ[22] had a BVS of 2.91, but Ti(II) was given in the CSD file; however, in the original paper the oxidation state was given as 3+.

There are a few examples where an ambiguity occurs for the oxidation state of the ligand and hence for the metal atom. In both JOLJOJ[23] and JOGZUA[24] the starting material was a Ti(II) complex, and the authors postulated an unusual diamagnetic, very "thermally robust" dinitrogen complex with a "rather long" N−N distance of 1.263 Å. The BVS values were 3.56 and 3.38 rather than the expected 2.0. The formulation of the oxidation state of the N_2 unit as either 0, −2, or −4 determines the oxidation state of the Ti. Although the authors assumed a neutral unit, the N−N distance of 1.289 Å in JOGZUA and of 1.263 Å in JOLJOJ would be in better agreement with an $(N{=}N)^{2-}$ formulation and a +3 oxidation state for the Ti. However, a −4 charge has been postulated for a somewhat similar Ta case[25] where the N−N distance was 1.282(6) Å, and in this case the Ti would be +4 and diamagnetic. A lower BVS might be anticipated because of the bulky silyl groups. Another possibility would be if oxidation had occurred and the N_2 unit were really an $(O_2)^{2-}$, giving a BVS of 2.98 for JOGZUA and 3.16 for JOLJOJ. The original reaction started with a Ti(II) species and produced the paramagnetic Ti(III) JOHBAJ[22] with no indication of what was reduced in this oxidation step. There was no chemical analysis reported in the note to substantiate the formulation as a dinitrogen complex. Finally, the thermal parameters which could give some indication of whether the bridge should be an N_2 rather than O_2 were not given. In the absence of additional evidence regarding the novel complexes JOLJOJ and JOGZUA, we suggest that the results of these two determinations be viewed with caution.

The ligand in KIMNOJ[26] could be neutral, −1, or −2. The authors assumed that the ligand was −1 and hence the Ti was +3. The BVS was 3.70, which suggested that the ligand was −2 and the Ti was +4. The starting material was $TiCl_4$, and the authors reported an NMR spectrum suggesting a diamagnetic Ti(IV). The slightly smaller BVS could result from steric considerations due to the *tert*-butyl groups (*vide supra*).

Metal complexes with bipyridyl are almost classic examples of the difficulties in assigning formal oxidation states. In FODXIF[27] the complex was postulated as a Ti(II) with two neutral bpy ligands by the authors, who also noted that bpy^- was possible and would result in a higher oxidation state for the Ti. The BVS values of 3.54 and 3.53 for the two independent Ti atoms suggest that a formulation involving the bpy^- might be more appropriate. The *R* value, 0.089, was relatively high, and further refinement "was in progress" but has not yet appeared.

The $Ti{-}OCH_3$ distance of 1.77 Å in BULXIP[28] is very short for a Ti(III)−O distance for CN = 5 as given in Table 2. The short bond could be rationalized if there were disorder in the $Ti{-}OCH_3$ group as has been observed in some Fe porphyrin complexes. The relatively high *R* value of 0.105 could be an indication that disorder exists in the structure. The resulting BVS of 3.30 would be reduced by a lengthening of the Ti−O bond.

The synthesis and structure of dichloroimidobis(triphenylphosphine oxide)titanium(IV) was reported, but there was very little evidence for the imido group.[29] There was no NH resonance in the NMR, the H was not located in the X-ray study, and the Ti−N distance was short. The reactions with triethylamine that indicated an NH group were carried out, but whether the X-ray sample was used for these experiments is unclear. The calculated BVS was 4.69 using the R_0 values in ref 9 or 4.44 using the newer values from this report, both of which seemed too large. However, assuming an O^{2-} group instead of NH^{2-}, the BVS was 4.06 or 3.89. The *U*(eq) of 0.037 for the "imido N" in the Supporting Information was smaller than that of the Ti (0.048), reasonable if the NH were really an O. Therefore, the possibility of an O^{2-} rather than NH^{2-} in the sample used for the X-ray analysis should be considered.

The various bond distances used in the analysis were sorted according to the donor atom, coordination number, and oxidation

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(19) KOXGUZ is (μ_2-3,3′-bis(dimethylbutylsilyl)binaphthyl-2,2′-diolato)-bis{tris(isopropoxy)titanium(IV)}. Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F.; Connolly, J. W. *Organometallics* **1992**, *11*, 1112.

(20) YUXBIC is dichlorobis(triphenylphosphaniminato-*N*)titanium. Rubenstahl, F.; Weller, F.; Wocadlo, S.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1995**, *621*, 953.

(21) LAWNAY has the formula $([Me_3Si]_2NPPh_2NPPh_2N)TiCl_3$ and was incorrectly named in the CSD file and not named in the original paper. Hasselbring, R.; Leichtweis, I.; Noltemeyer, M.; Roesky, H. W.; Schmidt, H.-G.; Herzog, A. Z. *Anorg. Allg. Chem.* **1993**, *619*, 1543.

(22) JOHBAJ is bis(tetramethylethylenediamine)lithium(I) dichlorodi(bis-{trimethylsilyl}amido)titanate(III). Beydoun, N.; Duchateau, R.; Gambarotta, S. *J. Chem. Soc., Chem. Commun.* **1992**, 244.

(23) JOLJOJ is (μ_2-diazo)bis(chlorobis(pyridine)(bis{trimethylsilyl}amido)-titanium) as given in the CSD file but was formulated in ref 22 as a dinitrogen, not a diazo species.

(24) JOGZUA is (μ_2-diazo)bis(chlorotetramethylethylenediamine((trimethylsilyl)amido)titanium) as given in the CSD file but was formulated as a dinitrogen, not a diazo species. Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986.

(25) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 218.

(26) KIMNOJ is (μ_2-dichloro)bis(chloro[glyoxal bis{*tert*-butylimine}]-titanium) in the CSD file and dichloroglyoxal bis(*tert*-butylimine)-titanium in the following: tom Dieck, H.; Rieger, H. J.; Fendesak, G. *Inorg. Chim. Acta* **1990**, *177*, 191.

(27) FODXIF is bis(2,2′-bipyridyl)bis(2,6-bis{isopropyl}phenoxo)titanium. Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720.

(28) BULXIP is methoxy(tetraphenylporphyrinato)titanium(III). Boreham, C. J.; Buisson, G.; Duee, E.; Jordanov, J.; Latour, J.-M.; Marchon, J.-C. *Inorg. Chim. Acta* **1983**, *70*, 77.

(29) McKarns, P. J.; Yap, G. P. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1996**, *35*, 5968.

state of the Ti and are given in Table 2. We see that the average bond distance increases with coordination number when the donor and oxidation state are held constant. The average value also is smaller for the higher oxidation states. While these trends are expected, an analysis of this type for Ti has not been published to my knowledge. The range of bond distances for a given donor, coordination number, and oxidation state was surprisingly large. The variation represents the donor ability of different types of donor groups, indicating that a comparison of, for example, Ti−O bonds without specifying the type of O donor atom is not justified.

Conclusions and Recommendations

The BVS is a relatively simple calculation if the appropriate R_0 values are available. For the Ti case with N, O, or Cl as donor atoms we have determined R_0 values that can be used to calculate the oxidation state of the Ti atom with no prior assumptions.

The deviation of the BVS from an integer value frequently indicates problems with the reported crystal structure as was illustrated in the case of JADWIU,[10] YEKPIN,[12] and PIXTEX.[13]

When the BVS is much lower than the expected value, the existence of steric constraints is a possibility. The examples of YEXCEJ,[16] CTMSIA,[17] WEDCUD,[18] and WEDDAK[18] were given to illustrate steric effects on the BVS.

A large noninteger BVS can arise from large thermal motion in the bonded groups or disorder, which can give rise to apparently short bonds. KOXGUZ,[19] LAWNAY,[21] and BULXIP[28] illustrate libration and disorder problems.

Finally, the BVS can be used in cases where the ligand oxidation state is ambiguous. The BVS gives the oxidation state of the metal and therefore, by inference, the ligand. JOLJOJ,[23] JOGZUA,[24] KIMNOJ,[26] and FODXIF[27] were presented as examples to illustrate how useful the BVS can be in these cases.

In summary the BVS is a rather simple calculation that can be carried out with any hand calculator having natural log functions and that should be very useful to chemists in general and structural chemists in particular. The BVS can provide a very useful guide in assessing or understanding the reported structure. Deviations of the BVS from a noninteger value would suggest a reexamination of the structural details.

A serious lacuna exists in the current literature because of an increasing number of papers published in which the authors neither name their compound nor give the proposed oxidation state for the metal ion. The absence of these data places the onus on the reader to determine the missing information. In studying the various compounds used in preparing this report there were numerous occasions where the oxidation state was not easily determined from the data given.

Another disturbing trend is the increasing unavailability of all of the crystallographic data. The B(eq) values are a good indication of the quality of the structure determination but are not retained in the CSD. In addition the various metal ligand bond distances are frequently summarized and not given in full, placing the onus on the reader to recover the full details, if that is at all possible. The large number of crystal structures that are being carried out will increase the pressure to publish less and less of the details, making an assessment even more difficult.

Supporting Information Available: Listings of the BVS calculations for the 534 Ti complexes used in the analysis (14 pages). Ordering information is given on any current masthead page.

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