

# Consistent approaches to van der Waals radii for the metallic elements

Sheng-Zhi Hu<sup>\*1</sup>, Zhao-Hui Zhou<sup>1</sup> and B. E. Robertson<sup>II</sup>

<sup>I</sup> Department of Chemistry, Institute of Physical Chemistry, Xiamen University, Xiamen, China 361005

<sup>II</sup> Department of Physics, University of Regina, Regina, Canada S4S 0A2

Received January 3, 2009; accepted March 23, 2009

*van der Waals radius / Metallic element /  
Average atomic volume / Single covalent radius /  
Bond valence parameter*

**Abstract.** Due to the paucity of data on non-bonding interactions for metal atoms, no complete tabulation is available for crystallographic van der Waals radii for metallic elements. In this work several sets of van der Waals radii for metal atoms are derived indirectly. Unique data resources used for the derivation are (i) average volumes of elements in crystals, (ii) single covalent radii, (iii) Allinger's van der Waals radii, as well as (iv) bond valence parameters for *metal-oxygen* bonds. The van der Waals radii for metal atoms deduced from these various approaches are basically comparable with each other, but are strikingly different from those from Bondi's system of van der Waals radii. A complete set of new values for metallic elements up to Am, derived from bond valence parameters, are recommended.

## 1. Introduction

The earliest work on atomic radii for intermolecular distances was presented in 1932 by Magat [1] and Mack [2], but it was Pauling who first introduced the term 'van der Waals radius' to science in 1939 [3], fully seventy years ago. Pauling's pioneering work on crystallographic van der Waals radii has since been used frequently in crystallography and structural chemistry. Bondi later reported additional van der Waals radii for 19 non-metallic and 19 metallic elements in 1964 and 1966 respectively [4]. Unlike the non-metallic elements, however, there are many metallic elements for which a van der Waals radius has not yet been well-established. Moreover, Mingos *et al.* were the first to claim that Bondi's radii for metal atoms were too small by a systematic deviation [5], and even attempted to correct them with a linear equation. Successively, Zefirov [6] and then Batsanov [7] questioned the methods used by Bondi to estimate the radii based on various types of data, such as gas-kinetic collision cross sec-

tions, critical densities, and properties in the liquid state, along with the crystallographic data available during the nineteen-sixties. It was argued that Bondi's van der Waals radii did not constitute a consistent approach based on a unitary data resource.

On the other hand, Pauling had derived van der Waals radii based on the close contact distances in a series of crystal structures [3]. These crystallographic van der Waals radii (hereafter  $R_{vdw}$ ) are different from Allinger's van der Waals radii [8], which were deduced from an energetically neutral distance at which the attractive and repulsive forces are equal. They are also different from the gas-kinetic van der Waals radii deduced from the distance for minimum energy interaction [6(b)]. Methodologically, Bondi's van der Waals radii belong to none of these three van der Waals radius systems.

Unlike the non-metallic atoms, most of the metal atoms do not appear on the periphery of a molecular packing of metal-organic compounds in the crystalline state. Therefore, weak intermolecular *metal...metal* contact distances cannot be determined directly and estimation of the  $R_{vdw}$  for a metal atom has remained a challenge for decades. Nevertheless, the situation has changed gradually over the last decade because it has become possible to derive the  $R_{vdw}$  by certain indirect methods. More specifically:

- Zefirov has proposed provisional values of  $R_{vdw}$  for the Group I–III metals by assuming that the absolute difference between the values derived by Allinger and  $R_{vdw}$  is about  $0.33 \pm 0.2 \text{ \AA}$  [9], and that these values derived from the Allinger's radii were better than those estimated from the so-called spherical domain radii for many metal atoms, including the Group I–III elements;
- Batsanov has used the estimation by Pauling [3(a)] that the single covalent radius and  $R_{vdw}$  of an atom have a nearly constant difference with a value of  $0.80 \text{ \AA}$  [10], and applied intra-molecular contact-distance data to derive the  $R_{vdw}$  values for most of the metallic elements;
- Datta *et al.* have calculated  $R_{vdw}$  values using the bond valence parameters, either derived empirically or calculated theoretically, for d elements with considerable success [11]; and

\* Correspondence author (e-mail: szhu@xmu.edu.cn)

- (d) We have applied the spherical radii of the average atomic volumes in crystals in which the *f* elements were involved, to determine  $R_{\text{vdw}}$  for all metallic elements [12].

In order to establish a reliable  $R_{\text{vdw}}$  system for all the metallic elements in the Periodic Table, all of the indirect and consistent approaches mentioned above are revisited in this work. Highlighted is an extremely simple approach using only the empirical bond valence parameters for *metal–oxygen* bonds instead of a complicated calculations for the mean value of ten *metal* ··· *X* (*X* = F, Cl, Br, I, O, S, Se, Te, N, P) bonds to derive the  $R_{\text{vdw}}$ . Finally, certain problems related to the application of Bondi's radii for metal atoms are illustrated by some interesting examples.

## 2. Computation methods and data resources

A consistent approach toward the  $R_{\text{vdw}}$  refers to a specific method using a unique data resource to obtain the van der Waals radii for all of the metallic elements in the Periodic Table. It is our view that four data resources can be used independently for the present purposes.

### 2.1 Average volume of the elements in crystals

Dirichlet's polyhedra are a method of partitioning the space in a crystal into polyhedra, each surrounding its constituent atoms and ions [13]. The values of spherical domain radii  $R_{\text{sd}}$ , are calculated to be the radius of a sphere with a volume equal to that of the polyhedral volume. The  $R_{\text{sd}}$  may yield the  $R_{\text{vdw}}$  data for the metal atoms or ions at the center of the polyhedron. Though the  $R_{\text{sd}}$  values agree well with the  $R_{\text{vdw}}$  of some non-metallic atoms, it is doubtful whether the  $R_{\text{sd}}$  can serve as a  $R_{\text{vdw}}$  for metal atoms such as the elements of Group I–III [9] and the lanthanides [14].

The failure in this derivation for metal atoms might be attributed to the non-close contact between the central metal and the ligand atoms in these polyhedra. Alternatively, the average volume of elements, statistically derived from the analysis of the Cambridge Structural Database (CSD) [15], is a method of partitioning space to obtain atomic size in crystals. Instead of the volume of the Voronoi-Dirichlet's polyhedra, the average volume could be used to determine the spherical domain radii to be considered for use as the  $R_{\text{vdw}}$  [12].

The results are encouraging. For example, 1.08 Å is obtained for the  $R_{\text{vdw}}$  of H, close to the value of 1.10 Å proposed by Pauling [3(b)]. Those for lanthanides, ranging from 2.2 ~ 2.4 Å, are also acceptable, and are roughly 0.7 Å larger than their covalent radii [10(b)]. However, these spherical domain radii should be considered as only approximately equal to the values of  $R_{\text{vdw}}$  for metal atoms. They are useful as a first approximation in the derivation of  $R_{\text{vdw}}$  [16].

### 2.2 Single covalent radii

Pauling originally proposed the single covalent radii of metal atoms, and summarized that the  $R_{\text{vdw}}$  of non-metals

could be taken as equal to these radii by adding a constant 0.80 Å [3(a)] [17]. Bondi later suggested that the constant should be 0.76 Å but did not provide any rationalization [4(a)]. Batsanov then set forward the first  $R_{\text{vdw}}$  system which covered most of the metal atoms, using covalent radius plus 0.80 Å and his own covalent radii data [18].

Batsanov has confirmed that the  $R_{\text{vdw}}$  and covalent radii of an atom differed by 0.7 to 0.8 Å because of the effect of variations in the coordination number [19]. In fact, this constant can be estimated using the relationship between the bond order of homopolar bonds and their bond length as first proposed by Pauling [17],

$$\Delta = R(1) - R(n) = 0.300 \ln n \quad (1)$$

where  $n$  is the bond order and is equal to the ratio of the valence to the coordination number, and  $\Delta$  is the homopolar bond length increment caused by the increase in the coordination number. Lengthening the single covalent bond length by increasing coordination number from 1 to 12, the equivalent of the shortest non-bonded distance, will take the bond order from 1 down to  $1/12$ , giving  $\Delta = -0.75$  Å.

$\Delta = -0.77$  Å is obtained after a further increase in the coordination number to 13. We prefer the constant  $-0.76$  Å which is a mean value derived by extensive use of Pauling's formula (1). Incidentally, this important formula has been presented incorrectly in the literature with logarithms to the base 10 [17, 19].

### 2.3 Allinger's van der Waals radii

Allinger himself has noted that the van der Waals radii used in molecular mechanics are roughly 30% larger than those used by crystallographers. Zefirov even attempted to derive the  $R_{\text{vdw}}$  for the Group I–III metal atoms by reducing Allinger's radii by a factor of 8 to 29% [9]. After due consideration, we conclude that Allinger's estimation of the van der Waals radii used in molecular mechanics is 30% too large. We speculate that this problem may arise because the reference data may be from Bondi's system. Therefore, a unique multiplicative reducing factor of 0.866 (*i.e.*, roughly 15%, not 30%) is a better approach to the reduction of Allinger's van der Waals radii to the  $R_{\text{vdw}}$ . The  $R_{\text{vdw}}$  determined this way are not only basically consistent with those presented by Zefirov for group I–III metals, but also can be accessible for all metal atoms with this unique factor.

### 2.4 Bond valence parameters

Pauling's formula (1) can be applied not only to homopolar bonds, for example to the accurate prediction of the length of the quadruple C≡C bond at 1.128 Å [20], but also to heteropolar bonds, for which the commonly used expression is

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

where  $s_{ij}$  is the bond valence of the metal atom  $M_i$  bonded to a electronegative atom  $X_j$  with the experimental bond length  $r_{ij}$ , and  $R_0$  and  $B$  are the bond valence parameters dependent of the nature of the  $ij$  pair [21]. Generally,

these parameters are fitted to ensure that the sums of the bond valences around all the atoms in a large number of well-determined crystal structures are the same as their valences [21].

The  $R_0$  value can be viewed as a bond length of unit valence, and  $B = 0.37 \text{ \AA}$  has been assumed to be a ‘universal’ constant although this is not always accepted [22]. Obviously, the  $r_{ij}$  value will increase from  $R_0$  to the sum of the  $R_{\text{vdw}}$  of the  $ij$  pair when the  $s_{ij}$  decreases from 1 to a value closing to 0. Datta *et al.* have taken an appropriate value of  $s_{ij} = 0.01$  v.u. to successfully deduce the  $R_{\text{vdw}}$  for the  $d$  elements [11].

It is noted that the van der Waals interaction energy of  $1 \sim 10$  kJ/mol is roughly two orders of magnitude less than that for normal chemical bonding. We will assume this value for  $s_{ij}$  in order to extend the study of  $R_{\text{vdw}}$  to all metal atoms. On the other hand, we will greatly simplify Datta’s calculations by using the  $R_0$  values only for one M–O bond instead of an  $R_0$  value averaged over ten M–X ( $X = \text{F, Cl, Br, I, O, S, Se, Te, N, P}$ ) bonds [11]. The merit of our approach is not only that reliable  $R_0$  values for most empirical M–O bonds are accessible via the internet [23], and which are believed to be superior to all values calculated using the rules of Brown and Altermatt [24], but also one need not be concerned that many of the bonds, such as Cu(I)–F, Cu(II)–I, Tl(III)–I, and Fe(V)–P *et al.* do not objectively exist at all [11]. Furthermore, the linear correlation between metal oxidation state and  $R_0$  for M–O bonds can be utilized [25]. Consequently, the amount of calculation can be greatly reduced without loss of accuracy.

From Eq. (2) with  $B = 0.37 \text{ \AA}$  and the  $R_{\text{vdw}}$  of  $1.40 \text{ \AA}$  for O atoms [3], a linear relationship is obtained between  $R_{\text{vdw}}$  and  $R_0$  with  $B = 0.37 \text{ \AA}$  for the metal atom:

$$R_{\text{vdw}} = R_0 + 0.304 \quad (3)$$

Interestingly, both the single covalent radii and the unit valence bond length  $R_0$  are linked to the  $R_{\text{vdw}}$  with differences of only a constant of  $0.76 \text{ \AA}$  and  $0.304 \text{ \AA}$ , respectively. Thus both simple approaches to  $R_{\text{vdw}}$  may be developed along with that derived from the average atomic volume in crystals as an approximate “back of the envelope” method [16].

At this stage, an overall comparison among the derivations discussed above is appropriate, and should lead to values for  $R_{\text{vdw}}$  suitable for recommendation.

### 3. Results and discussion

#### 3.1 $R_{\text{vdw}}$ for s–d–p elements

The results for  $R_{\text{vdw}}$  obtained by the various approaches discussed earlier, and the data sets recommended by Zefirov [9], Batsanov [10] and Datta *et al.* [11] along with Bondi’s and Allinger’s values for s–d–p metal atoms are listed in Table 1. The values of  $R_{\text{vdw}}$  for the  $f$  elements as independently derived by the aforementioned consistent methods are listed in Table 2.

The approach based on the average volume of elements in crystals has been used to deduce the  $R_{\text{vdw}}$  values from

H ( $1.08 \text{ \AA}$ , close to the value of  $1.10 \text{ \AA}$  proposed by Pauling [3(b)]), through to U ( $2.40 \text{ \AA}$ ) consistently for the first time to our knowledge [10(b)] [12]. However, this is a first level of approximation, and the data are not accurate for some elements, such as for the alkali metals and for the lanthanides. For the former, the values deduced are even smaller than those of Bondi, and for the latter, the well-known lanthanide contraction is not present, though the range of  $2.2 \sim 2.4 \text{ \AA}$  is quite acceptable: see Table 2.

The  $R_{\text{vdw}}$  for the alkali metals are significantly modified by the other three approaches; see Table 1, and the  $R_{\text{vdw}}$  values derived by these different approaches are, in general, comparable with each other.

By adding  $0.76 \text{ \AA}$  to single covalent radii to derive the corresponding  $R_{\text{vdw}}$  implies that the sums of van der Waals radii are about  $1.5 \text{ \AA}$  longer than the sums of the corresponding single covalent radii. In the other words, the difference of  $1.0 \text{ \AA}$  between these two sums estimated earlier seems to be too small [26]. This important conclusion is strongly supported by the studies of the histograms of Sb–O and Bi–O distances using the bond length data from the Cambridge Structural Database (CSD) [27]; see Fig. 1.

With regard to the approach based on Allinger’s van der Waals radii, the absolute difference between the  $R_{\text{vdw}}$  and Allinger’s data is  $0.34(2) \text{ \AA}$ , which is somewhat close to the results provided by Zefirov [9], but much improved both in accuracy and in the number of metal atoms included. As is well known, Allinger’s radii are too large compared with the  $R_{\text{vdw}}$  derived using the foregoing consistent approaches in this study, see Table 1. By contrast, we also see that Bondi’s radii are generally too small to be compared in any indirect way.

Bondi himself had tried to modify the  $R_{\text{vdw}}$  values of Zn, Cd, Hg [4(b)], for example, which are still at least  $0.5 \text{ \AA}$  smaller than what we expect. Before pointing out the problems encountered when applying Bondi’s values for metal atoms, let us have a close look at the simplified derivation of the  $R_{\text{vdw}}$  based on bond valence parameters.

Figure 2 shows the examples selected for comparison between the results obtained by Datta *et al.* and those obtained in this study. It can be seen from Figs. 2(a) and 2(b) that in the same oxidation state range, the  $R_{\text{vdw}}$  obtained for many elements are similar. This includes most metals, such as Mo, W, V, Cu and Fe *et al.* However in cases in which the range of oxidation states covered by the various methods was quite different, better agreement of the  $R_{\text{vdw}}$  could not be expected; see Figs. 2(c) and 2(d). In Fig. 2(c), the  $R_0$  values for Ru–O bonds for Ru<sup>3+</sup> to Ru<sup>7+</sup> were retrieved from the database [23], except the value of  $1.714 \text{ \AA}$  for Ru(II)–O which was fitted by us. In Fig. 3(d), the  $R_0$  values for Ir–O bonds for Ir<sup>3+</sup> to Ir<sup>6+</sup>, which are  $1.786, 1.870, 1.963$  and  $2.039 \text{ \AA}$  respectively, are fitted by us except for the value  $1.870 \text{ \AA}$  for Ir(IV)–O bonds which was retrieved from the database [23].

It is noted that a linear correlation between metal oxidation state and empirical bond valence parameters fitted from the data of CSD for M–O bonds is clearly exhibited in these examples. Based on these linear relationships the average  $R_0$  values can be easily obtained, and the related  $R_{\text{vdw}}$  values can be calculated using Eq. (3). On the other hand,

**Table 1.** van der Waals radii (Å) of metal atoms.

a: Derived from single covalent radii in Ref. [8];

b: Derived from Allinger's van der Waals radii in Ref. [8];

c: Derived from bond valence parameters in Ref. [23] except where noted otherwise.

Element	Bondi [4]	Allinger [8]	Zefirov [9]	Batsanov [10]	Datta [11]	Hu [12]	This work a	This work b	This work c
Li	1.82	2.55	2.2	2.2		1.75	1.99	2.21	<b>2.14</b>
Na	2.27	2.70	2.3	2.4		1.84	2.33	2.34	<b>2.38</b>
K	2.75	3.09	2.7	2.8		2.05	2.79	2.68	<b>2.52</b>
Rb		3.25	2.8	2.9		2.16	2.92	2.81	<b>2.61</b>
Cs		3.44	2.9	3.0		2.22	3.11	2.98	<b>2.75</b>
Cu	1.4	2.26	1.9	2.0	1.92	1.86	1.96	1.96	<b>1.96</b>
Ag	1.72	2.43	2.0	2.1	2.10	2.03	2.10	2.10	<b>2.11</b>
Au	1.66	2.43	2.0	2.1	2.10	2.17	2.10	2.10	<b>2.14</b>
Be		2.23	1.9	1.9		2.05	1.64	1.93	<b>1.69</b>
Mg	1.73	2.43	2.0	2.2		2.05	1.93	2.10	<b>2.00</b>
Ca		2.81	2.4	2.4		2.21	2.50	2.43	<b>2.27</b>
Sr		3.00	2.6	2.55		2.24	2.68	2.60	<b>2.42</b>
Ba		3.07	2.6	2.7		2.51	2.74	2.66	<b>2.59</b>
Zn	1.39	2.29	1.9	2.1	1.98	2.10	2.01	1.98	<b>2.01</b>
Cd	1.62	2.50	2.1	2.2	2.17	2.30	2.17	2.17	<b>2.18<sup>d</sup></b>
Hg	1.70	2.53	2.0	2.05	2.24	2.09	2.20	2.19	<b>2.23</b>
Sc		2.61	2.2	2.3	2.12	2.16	2.20	2.26	<b>2.15</b>
Y		2.71	2.3	2.4	2.29	2.19	2.38	2.35	<b>2.32</b>
La		2.78	2.3	2.5	2.45	2.40	2.45	2.41	<b>2.43</b>
B		2.15	1.8	1.8		1.47	1.64	1.86	<b>1.68</b>
Al		2.36	2.0	2.1		2.11	2.01	2.04	<b>1.92</b>
Ga	1.87	2.46	2.1	2.1		2.08	2.01	2.13	<b>2.03</b>
In	1.93	2.64	2.2	2.2		2.36	2.26	2.29	<b>2.21</b>
Tl	1.96	2.59	2.2	2.2		2.35	2.31	2.24	<b>2.27</b>
Ti		2.39		2.15	2.07	1.87	2.08	2.07	<b>2.11</b>
Zr		2.54		2.3	2.19	1.86	2.21	2.20	<b>2.23</b>
Hf		2.53		2.25	2.19	2.12	2.20	2.19	<b>2.23</b>
Si	2.10	2.29		2.1		2.07	1.93	1.98	<b>1.93</b>
Ge		2.44		2.1		2.15	1.98	2.11	<b>2.05</b>
Sn	2.17	2.59		2.25		2.33	2.16	2.24	<b>2.23</b>
Pb	2.02	2.74		2.3		2.32	2.30	2.37	<b>2.37</b>
V		2.29		2.05	2.06	1.79	1.98	1.98	<b>2.07</b>
Nb		2.43		2.15	2.17	2.07	2.10	2.10	<b>2.18</b>
Ta		2.43		2.2	2.18	2.17	2.10	2.10	<b>2.22</b>
As	1.85	2.36		2.05		2.06	1.97	2.04	<b>2.08</b>
Sb		2.52		2.2		2.25	2.17	2.18	<b>2.24<sup>e</sup></b>
Bi		2.66		2.3		2.43	2.28	2.30	<b>2.38</b>
Cr		2.25		2.05	2.06	1.89	1.93	1.95	<b>2.06</b>
Mo		2.39		2.1	2.16	2.09	2.05	2.07	<b>2.17</b>
W		2.39		2.1	2.18	2.10	2.06	2.07	<b>2.18</b>
Mn		2.24		2.05	2.04	1.97	1.93	1.94	<b>2.05</b>
Tc		2.36		2.05	2.16	2.09		2.04	<b>2.16</b>
Re		2.37		2.05	2.16	2.17	2.04	2.05	<b>2.16</b>
Fe		2.23		2.0	2.02	1.94	1.92	1.93	<b>2.04</b>
Co		2.23		2.0	1.91	1.92	1.92	1.93	<b>2.00</b>
Ni	1.63	2.22		2.0	1.98	1.84	1.91	1.92	<b>1.97</b>
Ru		2.34		2.05	2.17	2.07	2.00	2.03	<b>2.13</b>
Rh		2.34		2.0	2.04	1.95	2.01	2.03	<b>2.10</b>
Pd	1.63	2.37		2.05	2.09	2.03	2.04	2.05	<b>2.10</b>
Os		2.35		2.0	2.17	2.16	2.02	2.04	<b>2.16</b>
Ir		2.36		2.0	2.09	2.02	2.02	2.04	<b>2.13</b>
Pt	1.72	2.39		2.05	2.09	2.09	2.05	2.07	<b>2.13</b>
Po						2.29	2.29	2.24	<b>2.49</b>
At						2.36		2.17	
Fr						2.56		3.15	
Ra						2.43		2.83	
Th				2.4		2.37	2.43	2.37	<b>2.45</b>
U	1.86			2.3		2.40	2.38	2.18	<b>2.41</b>

d:  $R_0$  of 1.875 with  $B = 0.37$  Å for Cd(II)–O bonds was used in the calculations, see Palenik, G. J.: Can.: J. Chem. **84** (2006) 99;e:  $R_0$  values 1.955/1.912 Å with  $B = 0.37$  Å for Sb(III)/Sb(V)–O bonds were applied, see Palenik, R. C.; Abboud, K. A.; Palenik, G. J.: Inorg. Chim. Acta. **358** (2005) 1034.

**Table 2.** van der Waals radii (Å) of the lanthanide and actinide elements.

a: Derived from single covalent radii in Ref. [8];

b: Derived from Allinger's van der Waals radii in Ref. [8];

c: Derived from bond valence parameters in Ref. [30];

d: Derived from single bond radii reported in a booklet: Makarov, E. S.: Crystal Chemistry of Simple Compounds of Uranium, Thorium, Plutonium and Neptunium. Consultants Bureau, Inc., NY 1959;

e: Derived from bond valence parameters of this work.

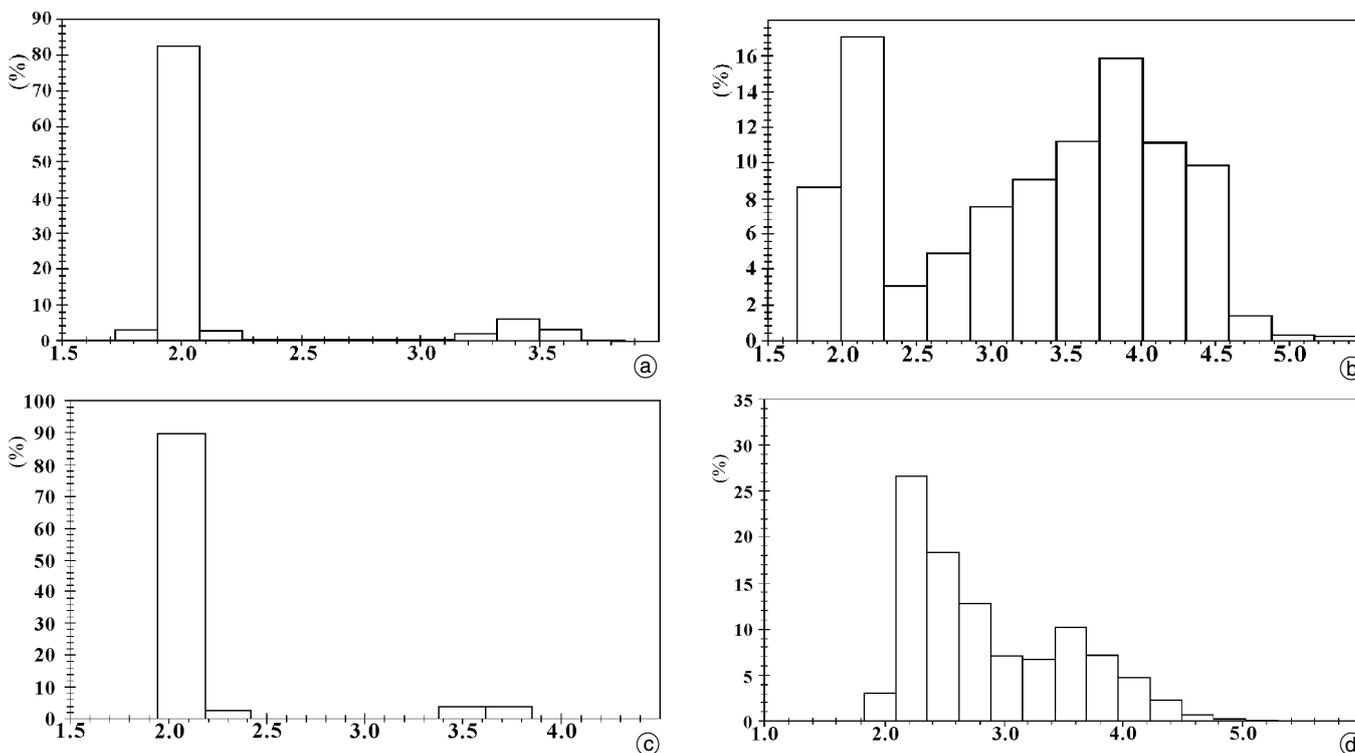
Element	Hu [12]	This work a	This work b	This work c	Element	Hu [12]	This work d	This work b	This work e
La	2.40	2.45	2.41	<b>2.43</b>	Ac	2.60		2.67	<b>2.47</b>
Ce	2.35	2.44	2.37	<b>2.42</b>	Th	2.37	2.43	2.37	<b>2.45</b>
Pr	2.39	2.43	2.36	<b>2.40</b>	Pa	2.43	2.40	2.29	<b>2.43</b>
Nd	2.29	2.42	2.36	<b>2.39</b>	U	2.40	2.38	2.18	<b>2.41</b>
Pm	2.36 <sup>f</sup>	2.40	2.36	<b>2.38</b>	Np	2.21	2.36	2.18	<b>2.39</b>
Sm	2.29	2.39	2.35	<b>2.36</b>	Pu	2.56 <sup>f</sup>	2.34	2.18	<b>2.37</b>
Eu	2.33	2.38 <sup>g</sup>	2.35 <sup>g</sup>	<b>2.35</b>	Am	2.56 <sup>f</sup>	2.33		<b>2.35</b>
Gd	2.37	2.37	2.35	<b>2.34</b>	Cm	2.56 <sup>f</sup>			
Tb	2.21	2.36	2.34	<b>2.33</b>	Bk	2.56 <sup>f</sup>			
Dy	2.29	2.35	2.33	<b>2.31</b>	Cf	2.56 <sup>f</sup>			
Ho	2.16	2.34	2.31	<b>2.30</b>	Es	2.56 <sup>f</sup>			
Er	2.35	2.33	2.31	<b>2.29</b>	Fm	2.56 <sup>f</sup>			
Tm	2.27	2.32	2.31	<b>2.27</b>	Md				
Yb	2.42	2.32 <sup>g</sup>	2.30 <sup>g</sup>	<b>2.26</b>	No				
Lu	2.21	2.32	2.29	<b>2.24</b>	Lr				

f: Average atomic volume retrieved from the data reported in Mighell, A. D.; Hubbard, C. R.; Stalick, J. K.; Santoro, A.; Snyder, R. L.; Holomany, M.; Scidel, J.; Lederman, S.: (1987). National Bureau of Standards, Gaithersburg, MD 20899, USA;

g: Derived with the aid of extrapolation.

the bond parameters calculated theoretically should be used with caution in quantitative work [21] and we propose that it is almost impossible to extend the estimation of the van der Waals radii to the *f*-block elements using theoretical

bond valence parameters. Because the oxidation states of Ru and Ir both range from 1+ to 6+ or beyond, and the common one is 4+, we believe that approaches based on the 4+ oxidation state should be closest to their  $R_{vdw}$  values.

**Fig. 1.** Distribution of interatomic distances (Å) of Sb/Bi-O according to the CSD data. (a) Sb(V)-O; (b) Sb(III)-O; (c) Bi(V)-O; (d) Bi(III)-O.

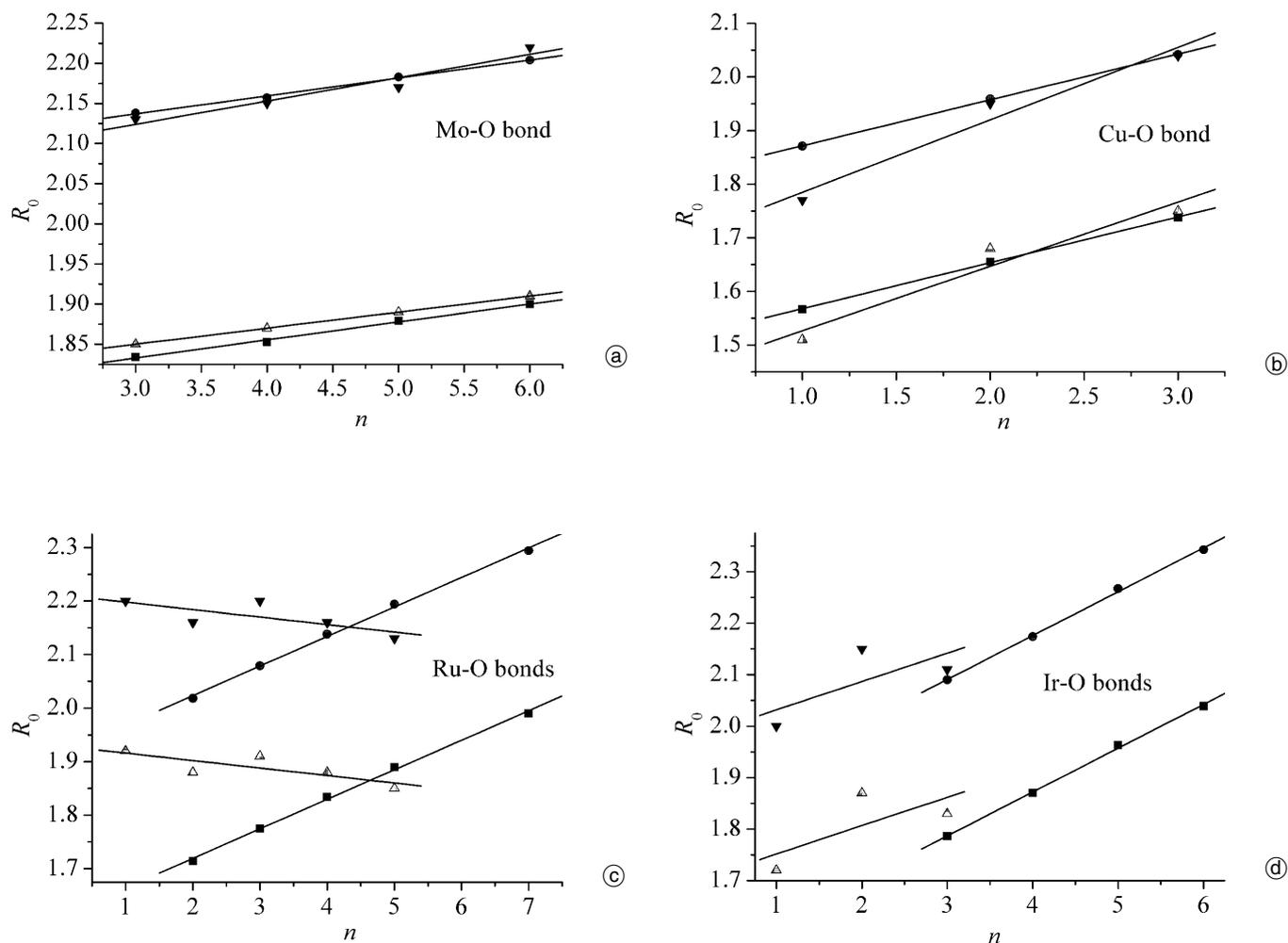


Fig. 2. Oxidation state  $n$  versus  $R_0$  for M–O bonds and  $R_{vdw}$  of M (M: Mo, Cu, Ru, Ir) in Å.

- :  $R_0$  for M–O bonds fitted from crystal data;
- :  $R_{vdw}$  for M derived from  $R_0$  by adding 0.304 Å;
- △:  $R_0$  for M–O bonds reported by Datta *et al.* in [9];
- ▼:  $R_{vdw}$  of M averaged from  $R_0$  for M–X bonds in [9]

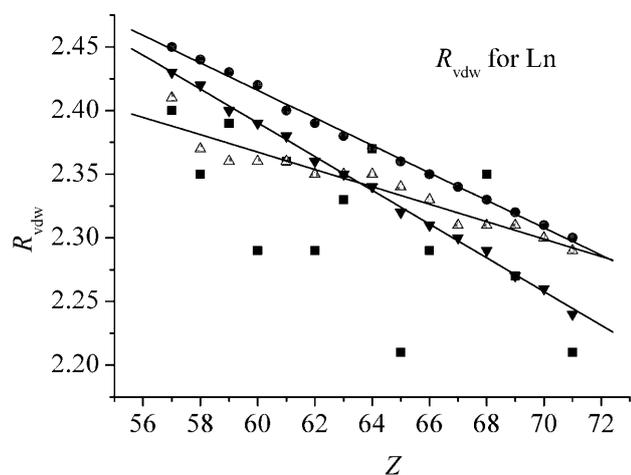


Fig. 3. Linear relationship between atomic number  $Z$  and  $R_{vdw}$  (Å) of the lanthanides.

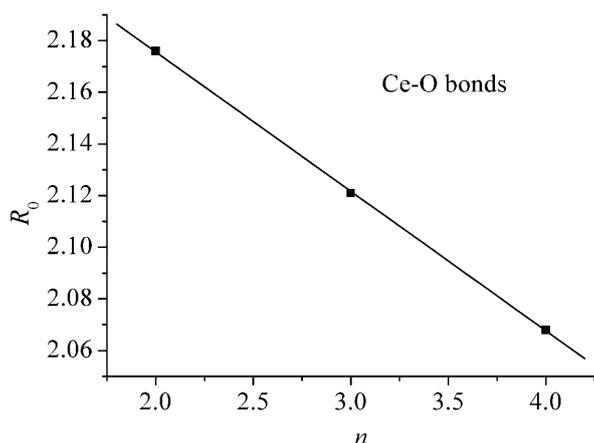
- : from average atomic volumes;
- : from single covalent radii;
- △: from Allinger's parameters;
- ▼: from  $R_0$  for Ln(III)-O bonds.

The derivation of  $R_{vdw}$  for Os is similar to that for Ru, and yields a value for  $R_{vdw}$ , close to those determined previously by Datta *et al.* [11] and by ourselves, in spite of the fact that the slope of the linear relationship between  $R_0$  and the oxidation state has the opposite sign and that the two sets of data cover different oxidation states.

### 3.2 $R_{vdw}$ for f elements

The  $R_{vdw}$  of 1.86 Å for the U atom proposed by Bondi [4(a)] is probably the only  $R_{vdw}$  value for f elements reported in the literature, textbooks and online databases [28] until relatively recently. The full presentation of the  $R_{vdw}$  values for f elements was not available until values estimated indirectly appeared in 2003 [12].

In this work we extend the derivation to include all f elements using alternative indirect methods, see Table 2. As expected, Fig. 3 shows that the famous lanthanide contraction does indeed emerge in these approaches except for those derived from the average atomic volume of the lanthanides. Among the results shown, we prefer, the  $R_{vdw}$



**Fig. 4.** Linear relationship between  $R_0$  (Å) and oxidation state  $n$  for Ce–O bonds.

derived from  $R_0$  values for the Ln–O bonds, and the  $R_0$  values used in that derivation will be explained in detail.

The  $R_{\text{vdw}}$  values must be independent of the oxidation state of a metal atom, and the chemistry of the lanthanides is dominated by trivalency. Ce(IV), Sm(II), Eu(II) and Yb(II) are important exceptions. Assuming a linear correlation between  $R_0$  and oxidation state in the range from 2+ to 4+, then the  $R_{\text{vdw}}$  values derived only from the  $R_0$  for Ln(III)–O bonds will consequently lead to the best approach. This reasonable assumption is supported by the linear relationship between  $R_0$  with  $B = 0.37$  Å and oxidation state for Ce–O bonds; see Fig. 4.

A straight line has been fitted to the  $R_0$  of 2.121(13) Å for Ce(III)–O and 2.068(12) Å for Ce(IV)–O bonds [29]. The  $R_0$  of 1.746 Å for Ce(II)–O bonds is obtained by extrapolation through the linear equation for  $R_0$  and atomic number  $Z$  below.

$$R_0^{\text{Ln(II)}} = 3.073(4) - 0.01547(6) Z \quad (4)$$

Equation (4) is fitted using the  $R_0$  values for Sm(II)–O, Eu(II)–O and Yb(II)–O bonds of 2.114(21), 2.098(21) and 1.990(20) Å, respectively, using the bond length data in the CSD.

The  $R_0$  values for Ln(III)–O have already been fitted with  $B = 0.37$  Å [30] to give

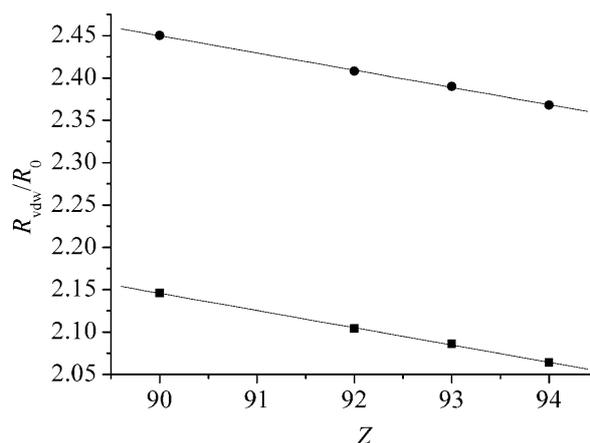
$$R_0^{\text{Ln(III)}} = 2.879 - 0.0132 Z \quad (5)$$

Similarly, the  $R_0$  values for Ln(III)–O bonds were fitted independently later [31] to give

$$R_0^{\text{Ln(III)}} = 2.871(18) - 0.0131(13) Z \quad (5')$$

It is not surprising that Eqs. (5) and (5') both would deduce exactly the same  $R_{\text{vdw}}$  values as those provided according to Eq. (3), see Table 2.

On the other hand, derivation of the  $R_{\text{vdw}}$  for actinides (An) would be expected to be somewhat complicated relative to that of the lanthanides. One of the reasons is that complex compounds with high oxidation state are more the norm for 5f elements than their 4f counterparts, especially for the light actinides [32]. In addition, there is no information available for the heavy 5f elements from the



**Fig. 5.** Linear relationship between atomic number  $Z$  and  $R_0/R_{\text{vdw}}$  (Å) of the actinides.

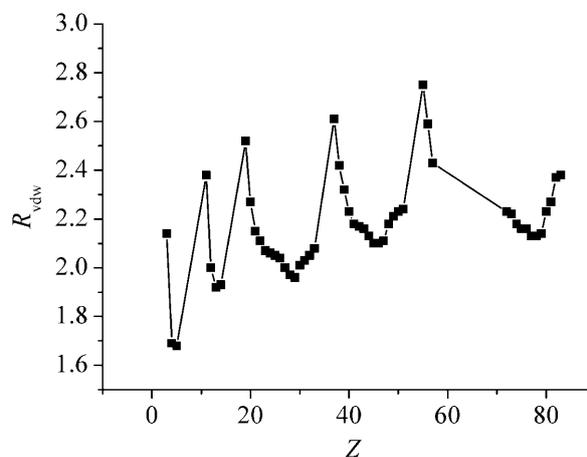
■:  $R_0$  for An(IV)–O bonds fitted from crystal data;  
●:  $R_{\text{vdw}}$  for An derived from  $R_0$  by adding 0.304 Å

CSD to date. Therefore, we will focus here on the light actinides, and the  $R_0$  values for An(IV)–O bonds will be considered later.

Though the oxidation state of U ranges from 2+ to 7+, only the  $R_0$  values for U(III)–O to U(VI)–O bonds can be fitted from the bond-length data from the CSD. The linear correlation between  $R_0$  and oxidation state  $n$  using the values 2.122, 2.099, 2.068 and 2.030 Å for the oxidation states from 3+ to 6+ respectively can be well established. In addition,, we are able to fit the  $R_0$  values with  $B = 0.37$  Å of 2.146, 2.086 and 2.064 Å for Th(IV)–, Np(IV)– and Pu(IV)–O bonds respectively from the CSD, see Fig. 5, which can be described by Eq. (6). All of the  $R_{\text{vdw}}$  values derived here are listed in Table 2. Detailed information concerning the fitting of bond valence parameters for M–O bonds using CSD data in this work will be published elsewhere.

$$R_0^{\text{An(IV)}} = 3.962(126) - 0.0202(14) Z \quad (6)$$

Figure 6 shows that the  $R_{\text{vdw}}$  data set contains the expected periodicity, and only the  $R_{\text{vdw}}$  data for lanthanides in Table 2 in boldface bridges the large gap between Ba



**Fig. 6.** Periodicity of van der Waals radii derived from the values of  $R_0$  (Å) for M–O bonds.

and Hf properly. Thus we believe that the derivation of the van der Waals radii for all metal atoms has been accomplished.

### 3.3 Current application issues

Given that the validity of the  $R_{\text{vdw}}$  derived indirectly are dependent on both the correctness of the calculation methods and the reliability of the original data resources, we prefer the  $R_{\text{vdw}}$  data set deduced from the bond valence parameters to the others, which are listed in the last column of Tables 1 and 2 with boldface, and the one deduced from the Allinger's van der Waals radii is most likely to have the lesser reliability among the values derived from these indirect approaches on  $R_{\text{vdw}}$  for metals though they are considered to be comparable with each other as a whole.

It is obvious from Table 1 that, Bondi's system for metal atoms gives results that extremely underestimate the  $R_{\text{vdw}}$  values compared with our recommended data, as well as the values presented by other systems, except for Allinger's radii. To emphasize the serious problems that might be caused by application of Bondi's values, let us repay a visit to the values of  $R_{\text{vdw}}$  for the Hg atom as presented in the literature.

After the values of 1.55 [4(a)] and 1.70 Å [4(b)] were established by Bondi, a series of values 1.73 Å [33], 1.75 Å [34], 2.0 Å [9], 2.05 Å [10], 2.09 Å [12] and 2.24 Å [11] has been proposed over time. The value of 2.23 Å is recommended in this study, see Table 1, which is roughly 0.5 Å larger than the value first given by Bondi. The value based purely on a theoretical calculation, 1.75 Å [34] seemed at the time to be supported by the former empirical value, 1.73 Å [33]. However, that value is too small, as shown in the histogram of Hg–N distances taken from the CCD data [35], as a consequence of the  $R_{\text{vdw}}$  of 1.50 Å for the N atom set forward by Pauling [3], see Fig. 7.

It is worth mentioning that this histogram, including that presented in Fig. 1 is a crystallographic court of last resort.

If the  $R_{\text{vdw}}$  values for Hg offered by Bondi and others, at approximately 1.7 Å, were applied inadvertently to define secondary bonding, the mercuriophilic interaction with Hg···Hg distances 3.7–4.0 Å in mercury bis-acety-

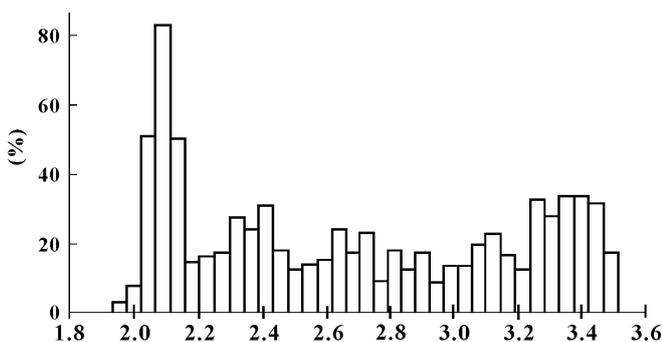


Fig. 7. Distribution of interatomic distances (Å) of Hg–N according to the CSD data.

lides would, unfortunately, not be included as a contact [36].

In addition, by using Bondi's radii for metal atoms, one would be lead to quite plausible conclusions such as "appreciable Ni···O interactions at distances almost equal to the sum of the van der Waals radii for the two atoms" see Li *et al.* [37], or simply to not comment on weak interactions with long Ag···Ag distances beyond the sum of Bondi's  $R_{\text{vdw}}$  for the Ag atom [38]. Obviously, without seriously taking into account these weak interactions, neither the coordination modes nor the coordination polyhedral forms of the metal atoms could be described properly.

Bondi's system is still finding use in recently published textbooks and handbooks, as well as in databases accessible on the internet [28], in which the only f element presented is U, and with the underestimated  $R_{\text{vdw}}$  value of 1.86 Å. Not surprisingly, this value is comparable with its empirical atom radius 1.75 Å, which is even shorter than its covalent radius of 1.96 Å as has been published recently [28]. In our study, however, a value of 2.41 Å is proposed, which is a change of 0.55 Å and is supporting by the actinide contraction, see Table 2. Incidentally, the new covalent radius 1.96 Å [39] is 0.32 Å longer than that which we used in this study.

Unfortunately, we could not use these modified radii to deduce the  $R_{\text{vdw}}$ . This is one of the reasons why we prefer the  $R_{\text{vdw}}$  values derived from bond valence parameters over the other approaches, including that from the covalent radii.

The situation for U is an example of the problems arising from the use of the van der Waals radii proposed by Bondi [4] and that would not be practical to discuss all of them here. Furthermore only 19 metal atoms were considered. Without reliable  $R_{\text{vdw}}$  data, the "less than the sum of van der Waals radii" criterion will surely lead to major errors in the search for secondary bonding in crystallography and structural chemistry [40]. We have attempted to address the obvious need.

## 4. Conclusions

Consistent approaches toward the estimation of crystallographic van der Waals radii for the metallic elements covering the Periodic Table are presented, which are comparable to each other. Specifically recommended is the data set derived simply from the empirical bond valence parameters for metal-oxygen bonds. This recommended data set can be used in crystallography and structural chemistry, which may be further improved as the bond valence parameters updated in future.

*Acknowledgments.* The authors would like to thank G. Heale and T. Allgood of CCDC for assistance with regard many questions concerning the CSD. Various helpful recommendations from the reviewers is gratefully acknowledged. We are also indebted to Professor Khi-Rui Tsai (also known as Qi-Rui Cai) of Xiamen University for stimulating interest in this challenging study, which is dedicated to him on the occasion of his 95th birthday.

## References

- [1] Magat, M.: Über die "Wirkungsradien" gebundener Atome und den Orthoeffekt beim Dipolmoment. *Z. Phys. Chem. (Münich)*. **16** (1932) 1–18.
- [2] Mack, E.: The spacing of non-polar molecules in crystal lattices: The atomic domain of Hydrogen. *J. Am. Chem. Soc.* **54** (1932) 2141–2165.
- [3] (a) Pauling, L.: The nature of the chemical bond. NY: Cornell University Press, 1939.  
(b) Pauling, L.; Pauling, P.: Chemistry, San Francisco: W. H. Freeman, Company 1975.
- [4] (a) Bondi, A.: van der Waals volumes and radii. *J. Phys. Chem.* **68** (1964) 441–451.  
(b) Bondi, A.: van Waals volumes and radii of metals in covalent compounds. *J. Phy. Chem.* **70** (1966) 306–307.
- [5] Mingos, D. M. P.; Andrew, L. R.: Size and shape characteristics of inorganic molecules and ions and their relevance to molecular packing problems. *Dalton Trans.* (1991) 3419–3425.
- [6] (a) Zefirov, Y. V.: Comparative analysis of systems of van der Waals radii. *Crystallogr. Rep.* **42** (1997) 111–116.  
(b) Zefirov, Y.V.: van der Waals radii and current problems of their application. *Russ. J. Inorg. Chem.* **46** (2001) 568–572.
- [7] Batsanov, S. S.: Estimation of the van der Waals radii of elements with the use of the Morse equation. *Russ. J. Gen. Chem.* **68** (1998) 495–500.
- [8] Allinger, N. L.; Zhou, X.; Bergsma, J.: Molecular mechanics parameters. *J. Mol. Struct. (Theochem.)* **312** (1994) 69–83.
- [9] Zefirov, Y. V.: van der Waals atomic radii of group I–III metals. *Russ. J. Inorg. Chem.* **45** (2000) 1552–1554.
- [10] (a) Batsanov, S. S.: van der Waals radii of elements. *Inorg. Mater.* **37** (2001) 871–885, and the references therein.  
(b) Batsanov, S.S.: Experimental foundations of structural chemistry. Moscow: Moscow University Press 2008.
- [11] Nag, S.; Banerjee, J.; Datta, D.: Estimation of the van der Waals radii of the d-block elements using the concept of bond valence. *New J. Chem.* **31** (2007) 832–834.
- [12] Hu, S. Z.; Zhou, Z. H.; Tsai, K. R.: Average van der Waals radii of atoms in crystals. *Acta Phys.–Chim. Sin.* **19** (2003) 1073–1077.
- [13] Vainshtein, B. K.: Modern Crystallography I. Symmetry of crystals, methods of structural crystallography. NY: Springer Verlag 1981.
- [14] Vologzhanina, A. V.; Pushkin, D. V.; Serezhkin, V. N.: LnO<sub>n</sub> coordination polyhedra (Ln = La–Lu) in crystal structures. *Acta Cryst.* **B62** (2006) 754–760.
- [15] Hofmann, D. W. M.: Fast estimation of crystal densities. *Acta Cryst.* **B58** (2002) 489–493.
- [16] Alkorta, I.; Rozas, I.; Elguero, J.; Foces-Foces, C.; Cano, F. H.: A statistical survey of the Cambridge Structural Database concerning density and packing. *J. Mol. Struct.* **382** (1996) 205–213.
- [17] Pauling, L.: Atomic radii and interatomic distances in metals. *J. Am. Chem. Soc.* **69** (1947) 542–553.
- [18] Batsanov, S. S.: The atomic radii of the elements. *Russ J. Inorg. Chem.* **36** (1991) 1694–1705.
- [19] Batsanov, S. S.: Relationship between the covalent and van der Waals radii of elements. *Russ. J. Inorg. Chem.* **46** (2001) 1374–1375.
- [20] Schleyer, P. von R.; Maslak, P.; Chandrasekhar, J.: Is a C≡C quadruple bond possible? *Tetrahedron Lett.* **34** (1993) 6387–6390.
- [21] Brown, I. D.: The Chemical bond in Inorganic Chemistry. The bond valence model. NY: Oxford University Press 2002.
- [22] Adams, S.: Relationship between bond valence and bond softness of alkali halides and chalcogenides. *Acta Cryst.* **B57** (2001) 278–287.
- [23] Brown, I. D.: Accumulated Table of Bond Valence Parameters: [www.ccp14.ac.uk/ccp/web-mirrors/i\\_d\\_brown/](http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown/).
- [24] Brown, I. D.; Altermatt, D.: Bond–valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Cryst* **B41** (1985) 244–247.
- [25] Hu, S. Z.; Zhou, Z. H.: The correlation between metal oxidation state and bond valence parameters for M–O bonds (M = V, Fe and Cu). A simple method to search for the metal oxidation-state independent parameter pairs. *Z. Kristallogr.* **219** (2004) 614–620.
- [26] Richardson, M. F.; Wulfsberg, G.; Marlow, R.; Zaghonni, S.; McCorkle, D.; Shadid, K.; Gagliardi, Jr., J.; Farris, B.: Coordination of ortho chlorines in nickel and zinc 4- substitute 2, 6-dichlorophenolates. *Inorg. Chem.* **32** (1993) 1913–1919.
- [27] Hu, S. Z.; Chen, M.D.; Robertson, B.E.: Study on the secondary bonding and coordination polyhedral in crystal of antimony (III) complexionate family. *Acta Phys.–Chim. Sin.* **21** (2005) 646–652.
- [28] <http://www.webelements.com/uranium/atom-sizes.html/>
- [29] Roulhac, P. L.; Palenik, G. J.: Bond valence sums in coordination chemistry. The calculation of the oxidation state of cerium in complexes containing cerium bonded only to oxygen. *Inorg. Chem.* **42** (2003) 118–121.
- [30] Chen, M. D.; Hu, S. Z.: Study on the bond valence parameters related to lanthanoid. *Acta Phy–Chim. Sin.* **18** (2002) 1104–1109.
- [31] (a) Trzesowska, A.; Kruszynski, R.; Bartczak, T. J.: New bond–valence parameters for lanthanides. *Acta Cryst.* **B60** (2004) 174–178.  
(b) Trzesowska, A.; Kruszynski, R.; Bartczak, T. J.: Bond–valence parameters of lanthanides. *Acta Cryst.* **B62** (2006) 745–753.
- [32] Greenwood, N. N.; Earnshaw, A.: Chemistry of the elements. Oxford: Pergamon Press 1984.
- [33] Canty, A. J.; Deacon, G B.: The van der Waals radius of mercury. *Inorg. Chim. Acta* **45** (1980) L225–L227.
- [34] Pyykkö, P.; Straka, M.: Ab initio studies of the dimmers (HgH<sub>2</sub>)<sub>2</sub> and (HgMe<sub>2</sub>)<sub>2</sub>. Metallophilic attraction and van der Waals radii of mercury. *Phys. Chem. Chem. Phys.* **2** (2000) 2489–2493.
- [35] Kuz'mina, L. G.: Secondary bonds and their role in chemistry. *Russ. J. Coord. Chem.* **25** (1999) 599–617.
- [36] Faville, S. J.; Henderson, W.; Mathieson, T. J.; Nicolson, B. K.: Solid–state aggregation of mercury bis-acetylides, Hg(C=CR)<sub>2</sub>, R = Ph, SiMe<sub>3</sub>. *J. Organomet. Chem.* **580** (1999) 363–369.
- [37] Li, X. Z.; He, J. H.; Liao, D. Z.: Appreciable Ni···O interaction at distances almost equal to the sum of the van der Waals radii of the two atoms. *Inorg. Chem. Commun.* **8** (2005) 939–942.
- [38] Zhao, L.; Zhao, X. L.; Mak, T. C. W.: Assembly of infinite silver(I) columns, chains, and bridged aggregates with supramolecular synthon bearing substituted phenylethylenes. *Chem. Eur. J.* **13** (2007) 5927–5936.
- [39] Cordero, B.; Gómez, V.; Platero-Prats, A.E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S.: Covalent radii revisited. *Dalton Trans.* (2008) 2832–2838.
- [40] Schiemenz, G. P.: The sum of van der Waals radii – A pitfall in the search for bonding. *Z. Naturforsch.* **62b** (2007) 235–243.