Covalent radii revisited†‡

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A new set of covalent atomic radii has been deduced from crystallographic data for most of the elements with atomic numbers up to 96. The proposed radii show a well behaved periodic dependence that allows us to interpolate a few radii for elements for which structural data is lacking, notably the noble gases. The proposed set of radii therefore fills most of the gaps and solves some inconsistencies in currently used covalent radii. The transition metal and lanthanide contractions as well as the differences in covalent atomic radii between low spin and high spin configurations in transition metals are illustrated by the proposed radii set.

Introduction

The atomic radius is not—and cannot be—an intrinsic property of an element. At least for a chemist, who is interested in atoms within molecules rather than as isolated entities, because the electron density cloud associated with an atomic nucleus is modified in different ways, both in shape and in size, by the different atoms bonded to it. Probably the most elegant and unequivocal definition of the shape of an atom is provided by Bader's *atoms in molecules* theory:[1] the space enclosed within a zero flux surface of the electron density around the nucleus. But in a molecule such a shape is hardly spherical enough to allow us to define an atomic radius. Even if we approximate its shape to a sphere and define an average radius, it is clear that the size depends strongly on the bonds that the atom is forming to its neighbours. Therefore, there is little hope of defining a theoretically sound atomic radius that is valid for a given element in a wide variety of molecules. Yet, the concept of attaching an approximate size to the atoms of a given element is deeply rooted in chemistry since Bragg's proposal that interatomic distances in crystal structures can be considered as sums of atomic radii.[2] The idea was complemented by Pauling's metallic radii,[3] van der Waals radii proposed by Bondi,[4] Slater's covalent radii[5] and ionic radii proposed by Shannon and Prewitt.[6,7] For more detailed discussions and bibliography on atomic radii the reader is referred to the classical book of Pauling,[8] the more recent books of Mingos,[9] Alcock[10] and Butler and Harrod,[11] and a recent review

by Batsanov.[12] A good illustration of the intrinsic uncertainty associated with the empirical definition of an atomic radius for an element is provided by the large differences between ionic, covalent and metallic radii for the same element. For instance, the Shannon and Prewitt cationic radius of an element[7] is typically at least 0.5 Å shorter than its covalent radius, while the opposite situation occurs with the anionic radii, showing how strongly the effective radius of an atom depends on its electronegativity relative to that of the atom to which it is bonded.

What do we need atomic radii for? They should provide a rough idea of the steric bulk of diverse molecular fragments and allow for a semiquantitative analysis of kinetic data in the search for steric effects. Different reactivity of the early and late lanthanides can be associated with the differences in atomic radii.[13] Covalent radii are also used in crystallographic software to indicate the existence of chemical bonds and the subsequent establishment of molecular structures, even if there are always cases in which deciding whether there is or is not a chemical bond between two atoms is 'quicksand territory'. Finally, covalent radii are used in crystallographic software to provide reasonable ball and stick three-dimensional representations of molecules.

In spite of the widespread use of covalent radii in structural chemistry, there are many elements for which a covalent radius has not been established. Furthermore, the most commonly used radii, from the Cambridge Structural Database (CSD), do not show any clear periodic trend and even present some inconsistencies within a transition series or within a periodic group. In other instances, the radii are too short in comparison with experimental bond distances. Consider as an example the Ba–N bond distances: 98% of the more than 600 such bond distances collected in the CSD are at least 0.6 Å longer than the sum of the radii for Ba and N (Fig. 1). Similar results can be found for the Ba–O bond distances as well as for other alkaline and alkaline earth elements. But for atomic radii to be a useful tool they must be able to give expected bond distances within one or two tenths of an ångström of the mean experimental values. The very definition of elemental radii in the CSD[14] indicates that the radii adopted are considered as provisional: "The covalent radii have been defined over the years to minimise the need for editorial changes for specific structures. Elements not yet encountered in the CSD are assigned a radius

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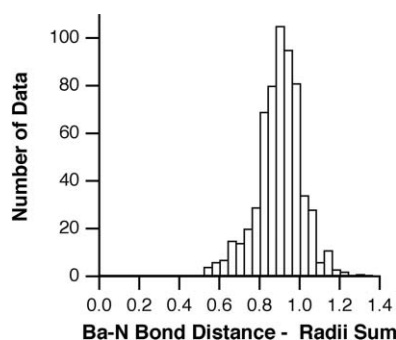

Fig. 1 Distribution of the difference between the experimental Ba–N bond distances and the sum of the CSD covalent atomic radii.

of 1.50 Å." The CSD team is well aware of these limitations, and makes use of the set of covalent radii with a wide tolerance margin, combined with a series of tests and internal software to sensibly decide on the existence of bonding between each pair of atoms in a structure.

In recent years we have addressed this problem for first row transition metals by carrying out systematic searches in the CSD and establishing a new collection of empirical covalent radii for those elements.[15] Those radii seemed to follow a sensible trend and allowed us to better handle the delicate question of whether there is a chemical bond between two transition metal atoms in M_2X_2 rhombuses in bridged dinuclear complexes with two X bridging atoms. With these precedents, we planned a set of systematic studies of crystallographic data that could provide us with a consistent set of empirical covalent radii, taking advantage of the exponential growth of the structural information available in structural databases, whose results are presented in this paper.

Methodology

There is no single element that forms a significant number of structurally characterized bonds to all elements of the periodic table. For that reason we have defined covalent radii from experimental bond distances to N, C or O, according to criteria discussed below. We therefore start by defining the radii for these three elements.

The covalent radius for nitrogen was obtained from N–N bond distances in substituted hydrazines (only H or C atoms bonded to N) with three-coordinated nitrogen atoms, excluding all structures with an R factor larger than 10% or presenting disorder or errors. The resulting value, 0.706(13) Å, is the average of 2200 crystallographically independent data and was used throughout with three decimal figures for calculating other radii from N–element bond distances to minimize rounding-off errors. It must be kept in mind, though, that the third decimal figure is not significant and the radii collected in Table 2 are shown with only two decimals. The use of a more restrictive criterion for the structural data ($R \leq$ 5%) did not result in a significant change in the atomic radius or in the standard deviation of the sample. Conversely, by allowing any coordination number of the N atoms we obtained practically the same results, 0.708(12) Å, but now representing 3046 independent bond lengths. From here on, all the estimated standard deviations (e.s.d.) given in parentheses together with the radii are e.s.d.s of the sample.

To obtain a covalent radius for carbon we searched for Csp^3–Csp^3 single bonds, adopting criteria similar to those used for nitrogen, only we could in this case restrict the agreement factor to 5% and limit the search to purely organic compounds, resulting in a radius of 0.762(11) Å for a sample of 10 000 structural data.[16] Bond distances to carbon are affected by differences in hybridization, as discussed by Alcock,[10] and covalent radii for Csp^2 and Csp atoms using the same criteria have been found to be 0.727(20) and 0.689(6) Å, respectively. Even if one might expect pathological cases, such as cyclopropanes or cyclobutanes, to affect the deduced carbon radius, a search restricted to acyclic C–C bonds gives practically the same covalent radius, 0.764(10) Å. To test the effect of choosing carbon or nitrogen to deduce covalent radii for other elements, we obtained the covalent radius of carbon also from C–N bonds with similar criteria and found a value of 0.754(16) Å, indicating that the choice of the reference atom affects the derived radii by only about one hundreth of an ångström, well within one standard deviation. The covalent radius for O was derived from a sample of 10 000 acyclic C–O bond distances, in a search limited to purely organic compounds with two-coordinate oxygen and four-coordinate carbon atoms with $R \leq 5\%$, and the value obtained was 0.676(28) Å.

Before adopting the covalent radii proposed here for our reference elements, C, N and O, we must compare them with those previously used. The radii deduced by us for these elements are nearly coincident with those proposed by Alcock[10] (Table 1), and show a linear dependence on the atomic number. The covalent radius for carbon given by other authors is nearly coincident with the one deduced by us, but those for nitrogen and oxygen present a more pronounced variation, with a significantly larger radius for oxygen, while the CSD radii for these three elements have the same value (0.68 Å).

A large variety of amines act as Lewis bases toward a number of acids, including transition metals, rare earths and main group metallic elements, offering a large number of structurally characterized metal–nitrogen bonds. Besides, such bonds have a higher degree of covalency than the corresponding metal–oxygen or metal–halogen bonds. In addition, nitrogen also forms covalent bonds with practically all non-metallic elements. In total, the version of the CSD used for this study holds 37 410 crystal structures with 131 837 crystallographically independent N-element bonds for 80 elements, disregarding the ubiquitous elements carbon and hydrogen. For that reason, the covalent radii for most elements were deduced from N–element bond distances, restricting the searches to three- or four-coordinate nitrogen atoms. For hydrogen, an additional constraint imposed was that the structural data came from a neutron diffraction experiment. The exceptions are some main group elements (including the metals of the Zn group), for which the N–element bond distances

Table 1 Comparison of the reference covalent radii with those proposed by other authors (all values in Å, e.s.d.s in parentheses)

Author	C	N	O	Ref.
This work	0.762(11)	0.706(13)	0.661(19)	
Alcock	0.767	0.702	0.659	10
Mingos	0.77	0.74	0.72	9
Butler and Harrod	0.77	0.75	0.73	11
Wells	0.77	0.74	0.74	17

either did not provide a sufficiently large data set or showed too much dispersion. In those cases we deduced the corresponding radii from E–C distances, where E is an element of Group 12, 13, 14, 15 (except N), 16 or 17, or from E–O bond distances for E an alkaline or alkaline earth metal, Xe, Pu or Am. It is worth noting that the covalent radius for F deduced here, 0.57(3) Å, is practically coincident with that proposed by Gillespie and Robinson from the analysis of a variety of covalent fluoro compounds (0.54 Å).[18]

Bond length data were obtained from version 5.28 of the CSD[19] (400 977 entries) plus two 2007 updates (25 175 entries). Except when otherwise specified, searches were restricted to structures with no disorder, no errors and an agreement factor R of at most 10%. For obtaining the covalent radii of those elements for which the number of structures was too small, one or more of those constraints was removed. For elements insufficiently or not represented at all in the CSD, some structural data could be found in Karlsruhe's inorganic database (November 2006 version of the ICSD[20] with 93 720 entries). As a general criterion, we searched for covalent radii that may represent a given element in its typical oxidation states and coordination numbers. Therefore, we exchange accuracy for generality, accepting that the uncertainty associated with these two factors is embedded into the estimated standard deviation. Nevertheless, several tests have been made to quantify the importance of both coordination number and oxidation state, especially in transition metals. A more detailed discussion of the effects that coordination number, oxidation state, bond order and other factors have on bond distances (hence on derived radii) can be found in the review of Batsanov.[12]

Our choice of one of our three reference elements (C, N and O) to deduce each radius might have an influence on its numerical value that must also be evaluated. In general, the shape of the periodic dependence of the covalent radii (see Fig. 2) is not significantly altered (see ESI‡), and we comment here on the main differences found between our chosen radii and the alternative choices. For Si, P and S, the alternative radii deduced from bond distances to N are about one tenth of an ångström shorter. In the case of the alkaline and alkaline earth metals, the choice of N as a reference instead of O would result in somewhat larger radii for K and Rb. Taking C as reference would result in significantly larger radii for these elements. However, the periodic dependence of the radii would not be qualitatively affected, since different reference elements change only the height of the maxima in Fig. 2, but not their positions. For transition metals, if we take carbon as the reference element, the resulting radii are in general slightly smaller than those deduced from M–N bonds, with significant differences (of up to 0.3 Å) especially for the early transition metals (Groups 13–15). For lanthanides, the use of C as the reference element gives also smaller radii, but the values obtained show an erratic dependence on the atomic number. The small increase in the covalent radii of Hg and Cd relative to their preceding elements that appears when we use C as the reference element (Fig. 2) is found also if N is used as reference instead, even if more pronounced. Tl, Pb and Bi give much longer radii when deduced from M–N bonds than from M–C bonds, and also give a much larger e.s.d., indicating that those M–N bonds are rather ionic and have correspondingly shallower potential energy minima. Finally, Th and Pa would give smaller radii if C was taken as a reference element for them instead of N.

A further test of the effect of the choice of N or C as reference elements for deducing the covalent radius of a given element corresponds to the case of Ru. For this metal, the radius deduced from Ru–N bond lengths is 1.45(7) while from Ru–Cl distances we obtain 1.40(5) Å, which differ by less than a standard deviation. If Ru–C bond distances are used instead, we obtain a bimodal distribution corresponding to radii of 1.10 and 1.30 Å, approximately. However, if the C atom is restricted to be sp^3 hybridized, we obtain again a similar value, 1.40(7) Å, while the shorter Ru–C distances are seen to correspond to Ru–C≡X groups, which are likely to incorporate significant mutiple Ru–C bond character.

In the case of copper, to exclude the long distances associated with the Jahn–Teller effect present in Cu(II) compounds, only Cu–N distances corresponding to Cu atoms with coordination numbers of four or less were considered. Similarly, to rule out long distances associated with hypervalent compounds, the search
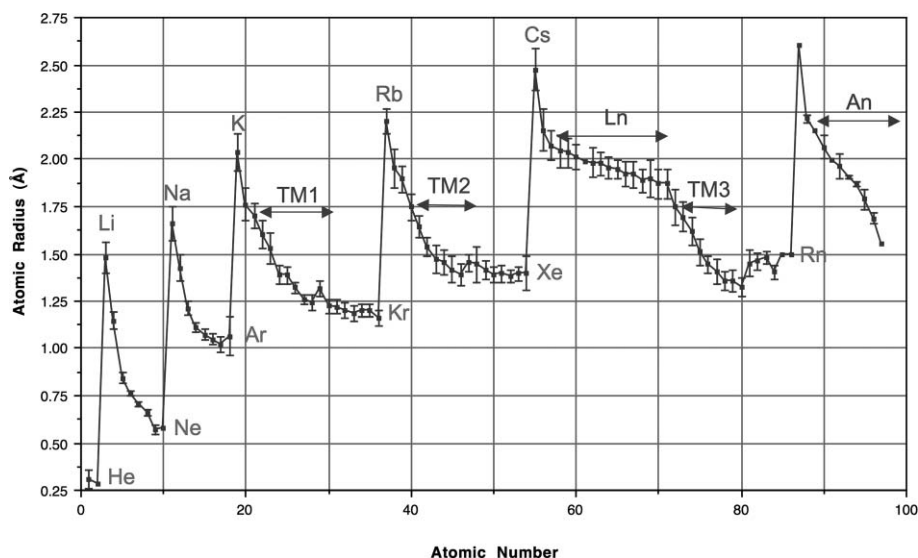

Fig. 2 Proposed covalent radii as a function of the atomic number. The vertical bars correspond to the estimated standard deviation. The labels TM1, TM2 and TM3 indicate the position of the first, second and third transition series, respectively; Ln indicates the lanthanides and An the actinides.

for all non-transition elements (including Zn, Ag and Au) was restricted to coordination numbers 2, 3 or 4. In the same vein, for main group elements, we restricted coordination numbers to the typical values (*i.e.*, 2 for S, 3 for P or 4 for Si), but allowed for higher coordination numbers, up to four, to include those compounds in which the corresponding atom is acting as a two-, four- or six-electron donor.

Specific problems we have to deal with appear for the first transition series metals. One is the variability of coordination number. Hence, for consistency, we have considered only bond distances in six-coordinate complexes, except for the case of copper commented above. As for the effect of the oxidation states, in most cases the covalent radii are quite insensitive to the oxidation state. Thus, the radii for Fe(II) and Fe(III) in either the low (l.s.) or high spin (h.s.) forms differ by at most 0.01 Å, and also changes of at most 0.03 Å result for V in oxidation states between +2 and +5. In the case of Mo, oxidation states +3 and +4 have the same radii within one e.s.d., while oxidation states +5 and +6 have radii 0.1 Å longer, a fact that seems to be associated with the presence of oxo ligands with significant Mo=O multiple bond character in the highest oxidation state. We find also that the radius of Co(II) is significantly larger than that of Co(III), but this is due to the fact that the former is dominated by high spin complexes and the latter by low spin ones (see below). In the case of Mn we find also significant differences (0.2 Å) between oxidation states +2 and +5, attributable in part more to the presence of high- and low-spin compounds than to differences in oxidation state. In this case, however, it is not easy to perform an automatic search for each oxidation state independently, since the higher oxidation states appear most often in mixed valence compounds.

For some elements for which structural data are scarce we were forced to use specific approaches to deduce sensible covalent radii. Hence, a challenging case is constituted by the family of noble gases. For Ar and Kr we used the noble gas–noble metal bond distances in the gas phase reported by Gerry and coworkers.[21] Although the data available for Xe compounds are significantly larger, its radius is highly sensitive to its oxidation state. We therefore disregarded the high oxidation states for which highly ionic bonds are expected and took only data from compounds in the formal oxidation state +2. From more than one hundred Xe–E distances (E = N, O, F) we deduced a radius of 1.40(9) Å (all data from the ICSD). As expected, data from compounds with higher oxidation states result in smaller values of the Xe radius. It must be stressed that the radii proposed here based on structural data are nearly coincident with those based on extrapolated electronegativity.[22] For He, Ne and Rn we could only extrapolate covalent radii values from the neighboring elements in the periodic system.

The covalent radius proposed for Ac, deduced from Ac–H distances in AcH₂ (2.15 Å),[23] fits nicely into the periodic trend and is not significantly different from that obtained from Ac–O bond distances in Ac₂O₃ (1.94 Å).[24] In AcCl₃ and AcBr₃, the Ac atoms present tricapped trigonal prismatic coordination spheres with three short bonds that would lead to a radius of 1.58 or 1.55 Å, respectively, but the average of nine Ac–X bonds gives a radius of 2.15 or 2.13 Å, consistent with that deduced from Ac–H bond distances. A covalent radius of 2.00 Å for Pa has been deduced from bond distances in PaH₃.[25] A radius 0.1 to 0.2 Å shorter would result from Pa–Cl and Pa–Br bond distances in

the corresponding halides,[26] much shorter than those of its two neighboring elements Th and U, although it must be noted that those bond distances vary some 0.3 Å within the same compound. The radius of Ra has been deduced from RaF₂,[27] RaS and RaSe.[28] For Pu, the only Pu–N distances available come from the structure of the [Pu(NCMe)₉]³⁺ cation,[29] but the average of 1.87(1) Å fits nicely into the trend shown by other actinides, and can be retained as representative, subject to revision when structural data on more compounds become available. A radius for Pu derived from Pu–O distances gives a somewhat smaller value (1.76 Å) but with a too large dispersion (e.s.d. = 0.11 Å). For a few elements (Pm, At and Fr) guess values of covalent radii have been obtained by interpolation or extrapolation from neighboring elements and from the general trends.

Results and discussion

The covalent atomic radii proposed are collected in Table 2 and the periodic trends can be best appreciated in Fig. 2. The first clear feature is the presence of peaks that indicate that the largest element of each period is the alkaline metal, while the smallest ones are the halogen and the noble gas. Within each period, there is a sharp decrease of the covalent radii from the alkaline to the Group 13 element, while the changes from Group 13 to Group 18 are much less pronounced (Fig. 3). In fact, differences in size between these elements are significant only for the second period (from B to Ne), while in the next periods the atomic radii for the corresponding elements are roughly constant. The exception to this behavior corresponds to the elements of the sixth period, for which there is an increase in radii from Hg (Z = 80) to Po (Z = 84). These are precisely elements for which the atomic radii could not be very well established due to the scarce number of structural data and the variability of their coordination number. Hence, the uncertainty in their radii is transferred to our extrapolated values for At and Rn. This situation was already spotted by Slater when much less structural data were available. He noticed that for elements from mercury to polonium it is very difficult on the basis of empirical evidence to assign a unique radius from the crystal structures.[5] For a comparison of the similarities and differences between the theoretical radii for isolated atoms and the empirical radii deduced from bond distances presented here, the reader is referred to a recent paper by Ghosh and Biswas[30] and references therein.
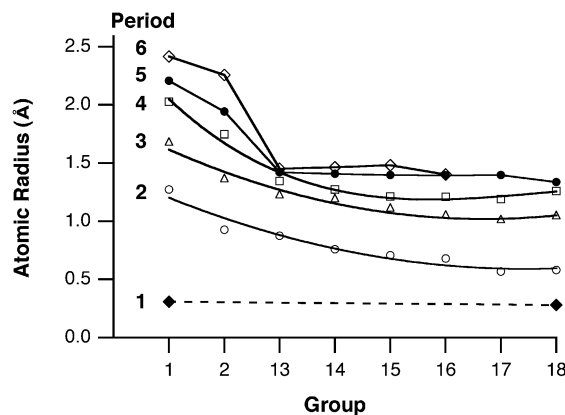

Fig. 3 Evolution of the covalent radii along the periods for main group elements.

Table 2 Proposed covalent radii (Å), estimated standard deviation and number of bond distances analyzed

Table 2 *(Contd.)*

Z	Element	r	e.s.d.	n
1	H	0.31	5	129
2	He	0.28		
3	Li	1.28	7	5789
4	Be	0.96	3	310
5	B	0.84	3	1770
6	Csp^3	0.76	1	10 000
	Csp^2	0.73	2	10 000
	Csp	0.69	1	171
7	N	0.71	1	2200
8	O	0.66	2	10 000
9	F	0.57	3	10 000
10	Ne	0.58		
11	Na	1.66	9	1629
12	Mg	1.41	7	3234
13	Al	1.21	4	3206
14	Si	1.11	2	10 000
15	P	1.07	3	10 000
16	S	1.05	3	10 000
17	Cl	1.02	4	1987
18	Ar	1.06	10	9
19	K	2.03	12	435
20	Ca	1.76	10	2647
21	Sc	1.70	7	32
22	Ti	1.60	8	231
23	V	1.53	8	389
24	Cr	1.39	5	916
25	Mn l.s.	1.39	5	321
	h.s.	1.61	8	929
26	Fe l.s.	1.32	3	336
	h.s.	1.52	6	1540
27	Co l.s.	1.26	3	5733
	h.s.	1.50	7	780
28	Ni	1.24	4	1030
29	Cu	1.32	4	1149
30	Zn	1.22	4	443
31	Ga	1.22	3	1330
32	Ge	1.20	4	1013
33	As	1.19	4	2015
34	Se	1.20	4	1717
35	Br	1.20	3	2140
36	Kr	1.16	4	5
37	Rb	2.20	9	23
38	Sr	1.95	10	1500
39	Y	1.90	7	30
40	Zr	1.75	7	93
41	Nb	1.64	6	18
42	Mo	1.54	5	97
43	Tc	1.47	7	96
44	Ru	1.46	7	1032
45	Rh	1.42	7	458
46	Pd	1.39	6	1892
47	Ag	1.45	5	1728
48	Cd	1.44	9	19
49	In	1.42	5	546
50	Sn	1.39	4	2999
51	Sb	1.39	5	609
52	Te	1.38	4	692
53	I	1.39	3	451
54	Xe	1.40	9	2
55	Cs	2.44	11	24
56	Ba	2.15	11	3076
57	La	2.07	8	190
58	Ce	2.04	9	47
59	Pr	2.03	7	58
60	Nd	2.01	6	96
61	Pm	1.99		
62	Sm	1.98	8	53
63	Eu	1.98	6	167
64	Gd	1.96	6	178
65	Tb	1.94	5	55
66	Dy	1.92	7	59
67	Ho	1.92	7	48
68	Er	1.89	6	66
69	Tm	1.90	10	15
70	Yb	1.87	8	122
71	Lu	1.87	8	61
72	Hf	1.75	10	53
73	Ta	1.70	8	88
74	W	1.62	7	219
75	Re	1.51	7	476
76	Os	1.44	4	99
77	Ir	1.41	6	131
78	Pt	1.36	5	1768
79	Au	1.36	6	114
80	Hg	1.32	5	137
81	Tl	1.45	7	291
82	Pb	1.46	5	112
83	Bi	1.48	4	51
84	Po	1.40	4	4
85	At	1.50		
86	Rn	1.50		
87	Fr	2.60		
88	Ra	2.21	2	3
89	Ac	2.15		1
90	Th	2.06	6	11
91	Pa	2.00		1
92	U	1.96	7	57
93	Np	1.90	1	22
94	Pu	1.87	1	9
95	Am	1.80	6	11
96	Cm	1.69	3	16

For the transition metals, plotted independently in Fig. 4, we observe a clear decrease in the radius along the first transition series. The deviation of the copper radius from the general trend must be attributed to the plasticity of its coordination sphere that gives several coordination numbers and may even incorporate weakly bonded ligands. We must recall that the slightly large radius of Cu cannot be attributed to the presence of Jahn–Teller distortions in Cu(II) compounds, since we have explicitly excluded five- and six-coordinate compounds to disregard such weak bonds. We must notice also that changes in covalent radii on going from Group 11 to Group 12 elements are biased by the change of reference bonded atom from nitrogen to carbon and we will not attempt to discuss such variations, which might not be significant. The radii for the second transition series elements show an evolution along the period practically parallel to those of the first transition series, with values roughly 0.1 Å longer than for the corresponding first row metal. The third transition series elements present radii that are practically coincident with the second series ones, with the exception of La. Such a behavior is well known and is attributed to the lanthanide contraction.[9] It is worth mentioning that for the later transition elements there seems to be a crossover of the two curves and the size of Au becomes smaller than that of Ag, a fact that was already pointed out by Schmidbaur and coworkers.[31] A similar inversion of the atomic size is apparent for Cd and Hg in Fig. 4.

A feature that must be considered for first row transition elements is the significant difference in bond distances that the same metal presents in its high- and low-spin compounds. Hence, for such metals it is practical to associate a different radius for
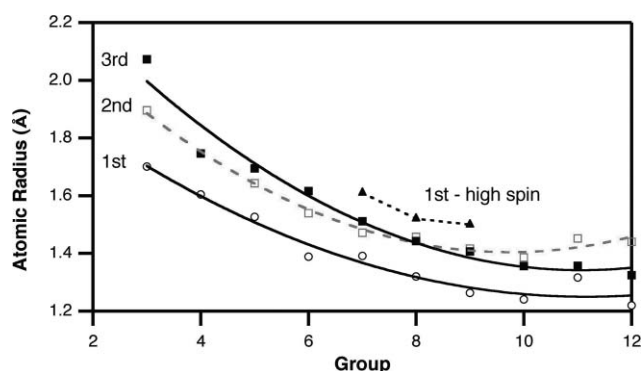
Fig. 4 Evolution of the covalent radii along the transition series.

each of the two spin states. This can be easily done from structural data because the M–N bond distances for Mn, Fe and Co show bimodal distributions (Fig. 5), from which we can associate the maximum at shorter distances to the low spin and that at longer distances to the high spin complexes. In the case of Co, even if the distribution of bond distances is dominated by short ones attributable to the most abundant low spin Co(III) compounds, a small peak at larger values, probably corresponding to high spin Co(II) complexes, allowed us to also assign a high spin radius to this element. The corresponding radii deduced from M–C bond distances give only one maximum for each metal that is roughly coincident with the shorter one deduced from M–N distances, thus confirming that the attribution of the lower peak to low spin complexes is a sensible approach, since we expect C-donor ligands to favor a low spin ground state. A look at Fig. 4 shows that the low spin radii nicely follow the same trend as other transition metals with only one spin state. It is also remarkable that the high spin radii are significantly larger than those of the third transition series metals, and that they also decrease monotonically with the atomic number.
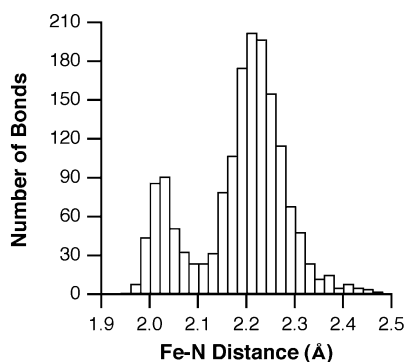

Fig. 5 Bimodal distribution of the Fe–N bond distances in six-coordinate iron compounds. The maximum at short distances is assigned to low spin complexes and the one at longer distances to high spin ones, regardless of the oxidation state.

While the elements of most main groups show a monotonic increase in their covalent radii down the Group (Fig. 6), elements of Groups 13 and 14 present a discontinuity between the second and third periods, *i.e.*, from Al to Ga and from Si to Ge. Such discontinuities should be attributed to the increased nuclear charge of the heavier elements of these couples, not fully screened by the valence 3d electrons. Such an effect, termed *transition series*
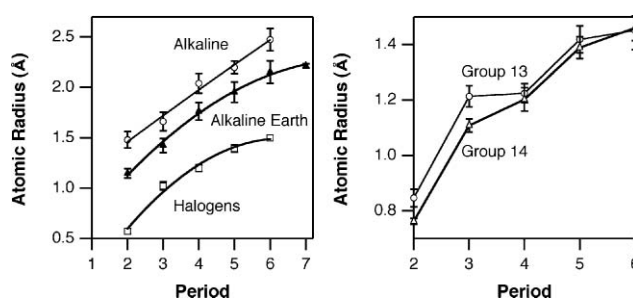

Fig. 6 Evolution of the covalent radii down the main groups. Group 16 elements and noble gases, not shown for clarity, are practically coincident with the halogens.

contraction,[9] is similar to the lanthanide contraction responsible for the nearly identical radii of Zr and Hf.

In summary, the set of atomic covalent radii proposed has been deduced for most elements with atomic numbers up to 96 from the analysis of more than 228 000 experimental bond distances to N, C or O atoms. Such covalent radii offer a wider and more consistent view of the periodic trends than those currently in use. The average standard deviation of the radii is 0.06 Å with a maximum of 0.12 Å (for K). Only six elements have a covalent radius with a standard deviation of 0.10 Å or larger (Ca, Hf, Tm, Ar, Sr, Cs, Ba and K). Taking again the example of Fig. 1, we compare now the Ba–N distances with the sum of the atomic radii proposed here and find the distribution shown in Fig. 7, with an average deviation of 0.10 Å and a maximum deviation of 0.53 Å, even if the radius for Ba has not been deduced from Ba–N but from Ba–O distances.
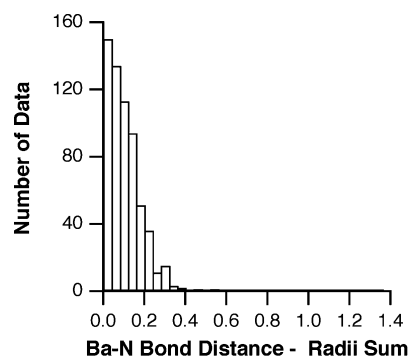

Fig. 7 Distribution of the difference between the experimental Ba–N bond distances and the sum of the covalent radii proposed here (absolute values), to be compared with Fig. 1.

All the radii are at least 0.5 Å shorter than the van der Waals radii[4] and are very similar to Pauling's metallic radii for those elements for which the latter are defined. As a test of the general applicability of the present set of covalent radii, we have randomly chosen 160 different bond types not involving the reference elements (C, N and O) and compared the resulting 172 000 experimental bond distances with the corresponding radii sums. The results (ESI‡) show that 96% of the bond types have average bond distances that fall within three standard deviations of the radii sum, while 84% are found within two standard deviations. As an additional check, radii have been deduced for elements of periodic Groups 14 to 17 from element–element bond lengths in $Me_nE–EMe_n$ and related compounds ($n = 3, 2, 1$ and 0 for Groups 14, 15, 16 and 17, respectively) in the Mogul knowledge base.[32]

The agreement is excellent (data and plot provided as ESI‡), but the radii proposed here are representative of a much wider set of structural data corresponding to a variety of bonds to different elements, and still their standard deviations are in general smaller.

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