What Factors Determine Cation Coordination Numbers?

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Abstract

Over 14 000 coordination environments of 100 different cations retrieved from the Inorganic Crystal Structure Database have been analyzed. For comparison predicted coordination numbers (PCN's) have been calculated using ionic radius ratios. The observed coordination numbers are generally smaller than or equal to the PCN's and their range, for most cations, can be predicted from a knowledge of the Lewis-base strengths of available anions and the requirement that these strengths be close to the Lewis-acid strength of the cation. The occurrence of smaller coordination numbers is associated with strongly directed bonds (electronic effects) and is found for main-group elements in low oxidation states and for closed-d-shell cations of Groups 11, 12 and 13. An analysis of the results shows that to use ionic radii to predict both coordination numbers and interatomic distances it is necessary to use cation and anion radii that both vary in the same way with the cation coordination number (N). The value found for the oxygen radius is $1 \cdot 12 + 0 \cdot 23 \ln(N-2)$ Å. The average observed coordination number is used to calculate cation Lewis-acid strengths which are shown to correlate with electronegativity.

1. Introduction

In the simplest model of chemical bonding, the ionic model, the coordination number of a cation is determined only by the number of anions that can be fitted around it. The model has been made quantitative (Pauling, 1960) by treating the ions as hard spheres and assigning to each a radius. In cases where the chemical bonding is primarily covalent the bonding environment is determined by the availability of suitable bonding orbitals. Such bonds may show directional effects but in any case the coordination number should not exceed that predicted by the ionic model since this model represents the physical limit for packing ligands around the central metal. How well do the observed coordination numbers agree with these predictions and can one use them to monitor the transition from ionic to covalent bonding?

In order to answer this question, coordination environments ranging from nearly purely ionic to nearly purely covalent around a large number of cations have been examined. Although a wide range of bond types is included, all can be described as Lewis-acid–Lewis-base bonds so it is convenient to refer to the Lewis acid as a *cation* and the Lewis base as an *anion* even when the bonding is clearly covalent. Such labels should not be taken to imply that the results are restricted only to those situations which can be discussed in terms of the ionic model. The result of the examination of over 14 000 coordination environments involving nearly 100 different cations is presented in the form of a series of cation coordination number distributions, one for each cation–anion pair.

In § 2 the experimental procedures are described and § 3 discusses the results in terms of the Pauling (1960) ionic radius model, the bond-valence model (Brown, 1981) and VSEPR model (Gillespie, 1972) (§ 3.1). In § 3.2 the observed coordination numbers are used to propose a set of Lewis-acid strengths for cations and in § 3.3 the implications of the results for the concept of ionic radius are discussed.

2. Experimental procedure

All entries in the 1983 release of the Inorganic Crystal Structure Database (ICSD) (Bergerhoff, Hundt, Seivers & Brown, 1983) were passed through the program *SINDBAD* as described by Altermatt & Brown (1985). This program calculates all the acid–base bonds in a structure and stores them in a BONDFILE. At this stage structures were selected from among those in the database by eliminating those that: (i) contain bonds that are not recognized by the program as acid–base bonds (*e.g.* those in polysulfur compounds and carbonyl complexes), (ii) were so poorly determined that the bonding patterns could not be reliably established by *SINDBAD* or (iii) contained errors in the data stored in the database. A considerable number of structures were excluded by (iii) as the 1983 release of ICSD had not been fully checked for internal consistency.*

The BONDFILE was searched for all cations whose environments (i) contain only one kind of anion and (ii)

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* A number of structures have been determined or refined more than once and in this early release some structure determinations were inadvertently included twice. These factors occur randomly and are unlikely to introduce a statistical bias into the analysis.

contain no disorder. The resulting list was sorted by cation type, anion type and cation coordination number. The assignment of coordination numbers in inorganic crystal structures is usually a matter of individual judgement, although there have been a number of attempts to devise systematic definitions (Brunner, 1977; Carter, 1978; O'Keeffe, 1979; Hoppe, 1979). In the present study the criteria used in *SINDBAD* (Altermatt & Brown, 1985) ensure that a uniform definition of coordination number is applied to all cations. The number of examples of each coordination number for each ion pair is given in Table *S*1.* For most anions other than oxygen the size of the sample tends to be small and, in order to improve the sample size, the anions were grouped where no statistical difference in the coordination number distribution could be detected. In most cases the smaller anions from Period 2 (F and O) were placed in one group and the larger, those from Periods 3–5 (Cl, Br, I and S), were placed in a second group. For the alkali metals it was necessary to group the univalent anions (F, Cl, Br and I) in the first group and divalent anions (O and S) in the second.† For each cation–anion group the average cation coordination number (AOCN, 'average observed coordination number'), its standard uncertainty, and the standard deviation of the coordination number distribution are given in Table 1.

It is important to keep in mind the structures that are not included in these tables. Since only the Inorganic Crystal Structure Database was searched no organic compounds are included in the list. This excludes such compounds as $[N(CH_3)_4]_2ZnBr_4$. In addition all compounds with mixed ligands, all compounds for which, for one reason or another, *SINDBAD* did not calculate a meaningful arrangement of bonds, and all coordination spheres that contained any kind of disorder were excluded. Despite these shortcomings the distribution of coordination numbers probably corresponds reasonably well to the distribution expected from a random sample of stable compounds containing bonds between the respective cation and anion although one must be careful not to over interpret the numerical results.

Nord & Kierkegaard (1984) have recently surveyed the coordination numbers observed for a variety of divalent metals bonded to oxygen. Although, for the cations concerned, their sample was somewhat larger than the present one, they accepted the coordination number assignments of the original authors. Values of

the AOCN's calculated from the data given in their Table XIV are shown in brackets in Table 1. The present values agree with theirs within three estimated standard uncertainties except for Cu where the assignment of coordination numbers is more subjective. In this case *SINDBAD* calculates coordination numbers smaller on average than those assigned by the original authors.

3. Discussion

3.1. *Prediction of coordination numbers*

For simple binary ionic compounds Pauling (1960) has shown that the coordination number can usually be predicted using the ratio of the cation and anion radii derived from a semi-empirical model. He points out that the radius ratio is usually equal to or larger than the ideal radius ratio for the observed coordination number (see Pauling, 1960; Tables 13-16 to 13-18). The radius ratio can therefore be used to calculate a 'predicted coordination number' (PCN). Although an observed coordination number is necessarily an integer there is no need to restrict the PCN's to integral values since they are to be compared with non-integral AOCN's. By interpolating between the radius ratios for the integral coordination numbers, 0·155 (CN = 3), 0·224 (CN = 4), 0·414 (CN = 6), 0·645 (CN = 8) and 1·0 (CN = 12), the non-integral PCN's given in Table 1 were found. The radii used were determined according to the procedures given in *Appendix* I.

In the following discussion attention will be focused on coordination between cations and oxygen since only for these environments is a large number of data available. The results should, with suitable allowances for the differences in numerical values, be applicable to other ligands.

While Table 1 shows that the PCN is a reasonable predictor of the AOCN for the majority of cations, it does not account for the wide range of coordination numbers that some cations adopt in different compounds. For example, Zn has a PCN of 6·7 but is known to occur with all coordination numbers from 3 to 6. What factors determine which coordination number will be found in a particular compound? The question does not have a simple answer but one of the important determinants is the Lewis-base strength of the anion. A strong Lewis base will form stronger bonds to the Zn ion, thus lowering its coordination number. A quantitative measure of the Lewis-base strength (S_b) of an anion is given by the strength of the bonds it forms, namely its formal charge divided by the coordination number (see *Appendix* II for details of how the Lewis-base strengths are calculated). Accordingly four-coordination would be expected around Zn when the base strength of the ligand anion is 0·5 v.u. (valence units) (*e.g.* O^{2-}) and six-coordination when it is 0·33 v.u. (*e.g.* $P_2O_7^{3-}$, H_2O) based on the notion that

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* Table *S*1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51079 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Since under suitable conditions. Tl[I] behaves like an alkali metal it might be argued that its anions should be grouped by charge. Tl[I] is included in the tables both ways since the arrangement by charge is better than that by size. In[I] should be similar but the data are too sparse.

Table 1. *Average observed coordination numbers (AOCN's) and predicted coordination numbers (PCN's)*

AOCN's are not given for samples of less than 10. Standard uncertainties are not given when only one coordination number is observed. Values in square brackets are from Nord & Kierkegaard (1984).

	Cation radius (Å)	Univalent anions			Divalent anions			
		AOCN	PCN	Std dev. (%)	AOCN	PCN(O^{2-})	AOCN/PCN	Std dev. (%)
Li	0·60	5·3 (4)	*	17	4·87 (5)	6·1	0·80	21
Na	0·95	6·7 (1)	*	18	6·4 (1)	8·4	0·76	31
K	1·33	9·0 (2)	*	32	7·9 (1)	11·0	0·73	28
Rb	1·48	9·8 (3)	*	26	8·0 (1)	12·6	0·63	29
Cs	1·69	10·4 (2)	*	20	8·8 (2)	14·4	0·61	27
Tl^I	1·49	8·3 (2)	*	23	6·9 (2)	12·3	0·55	30

* Will depend on the anion.

	Cation radius (Å)	Anions of Period 2 (O, F)				Anions of Periods 3–5 (Cl, S, Br, I)			
		AOCN	PCN	AOCN/PCN	Std dev. (%)	AOCN	PCN	AOCN/PCN	Std dev. (%)
Main-group elements in highest oxidation state									
Be	0·31	3·99 (2)	3·8	1·05	8				
Mg	0·65	5·98 (5) [5·93]	6·4	0·94	13	6·0	5·3	1·13	0
Ca	0·99	7·31 (5) [7·48]	8·7	0·84	16	6·7 (4)	6·8	0·99	13
Sr	1·13	8·57 (15)	9·8	0·88	24	7·4 (3)	7·2	1·03	9
Ba	1·35	10·24 (11)	11·6	0·88	20	8·0 (1)	8·5	0·94	16
B	0·20	3·46 (2)	2·9	1·21	14				
Al	0·50	5·27 (4)	5·4	0·98	18	4·1 (1)	4·3	0·95	11
Ga^{III}	0·62	4·62 (11)	6·1	0·75	20	4·0	5·1	0·78	0
In^{III}	0·81	5·98 (6)	7·4	0·81	8	5·5 (1)	6·1	0·90	15
Tl^{III}	0·95	6·1 (3)	8·4	0·73	20		6·6		
C	0·15	2·96 (1)	2·7	1·11	4	3·2 (2)	2·4	1·33	9
Si	0·41	4·02 (1)	4·6	0·87	4	4·0	3·9	1·03	0
Ge	0·53	4·51 (6)	5·6	0·80	19	3·83 (6)	4·5	0·84	10
Sn^{IV}	0·71	5·86 (9)	6·7	0·88	10	5·1 (2)	5·5	0·93	20
Pb^{IV}	0·84	5·73 (10)	7·6	0·75	8		6·0		
N	0·11	3·00 (2)	2·4	1·25	6		2·4		
P	0·34	4·01 (1)	4·2	0·95	3	4·2 (1)	3·4	1·24	14
As^V	0·47	4·41 (8)	5·1	0·86	18		4·2		
Sb^V	0·62	6·05 (5)	6·1	0·99	8	5·1 (2)	5·1	1·00	19
S	0·29	4·0	3·7	1·08	0				
Se^{VI}	0·42	4·0	4·6	0·87	0				
Te^{VI}	0·56	6·0	5·8	1·03	0				
Cl^{VII}	0·26	4·0	3·4	1·18	0				
I^{VII}	0·50	5·6 (3)	5·4	1·04	17				
Low-valence states of main-group elements									
In^I	1·32					6·7 (3)	8·2	0·82	16
Tl^I	1·49	7·4 (4)	12·3	0·61	34	7·7 (2)	9·3	0·83	35
Sn^{II}	0·86	4·4 (3)	7·7	0·57	41	5·5 (3)	6·2	0·89	20
Pb^{II}	1·12	6·9 (2)	9·8	0·70	39	6·73 (8)	7·3	0·92	13
As^{III}	0·65	3·07 (3)	6·3	0·49	8	3·19 (6)	5·2	0·62	15
Sb^{III}	0·83	4·8 (2)	7·6	0·63	26	4·74 (9)	6·1	0·75	20
Bi^{III}	0·95	6·2 (2)	8·5	0·73	23	6·0 (2)	6·6	'0·91	17
S^{IV}	0·39	3·4 (1)	4·4	0·77	15		3·2		
Se^{IV}	0·56	3·3 (1)	5·6	0·59	24		4·6		9
Te^{IV}	0·73	4·1 (1)	6·9	0·59	22	5·8 (3)	5·6	1·04	24
I^V	0·67	3·8 (2)	6·4	0·59	25				
Transition elements									
Cu^I	0·72	2·2 (2)	6·8	0·32	41	3·50 (5)	5·7	0·61	14
Ag^I	1·10	5·1 (4)	9·7	0·53	39	4·4 (2)	7·3	0·62	23
Cr^{II}	0·80^s		7·3			5·9 (1)	6·0	0·98	8
Mn^{II}	0·80	5·98 (4) [5·94]	7·4	0·82	11	5·7 (1)	6·0	0·95	12
Fe^{II}	0·74	5·89 (5) [5·85]	7·0	0·84	11	5·4 (2)	5·6	0·96	17
Co^{II}	0·70	5·70 (8) [5·84]	6·7	0·85	14	4·8 (2)	5·4	0·89	21
Ni^{II}	0·66	5·90 (9) [5·89]	6·4	0·92	9				
Cu^{II}	0·69	5·10 (5) [5·44]	6·6	0·77	16	4·7 (2)	5·3	0·89	21
Zn^{II}	0·71	4·98 (7) [4·90]	6·7	0·75	19	4·0	5·5	0·73	0
Pd^{II}	0·86^s	4·4 (2)	7·7	0·57	18	4·0	6·3	0·63	0
Cd^{II}	0·91	6·14 (7) [6·26]	8·2	0·74	13	4·6 (2)	6·5	0·71	22
Pt^{II}	0·80^s		5·8			4·0	6·0	0·67	0
Hg^{II}	0·98	5·5 (2)	8·7	0·63	35	4·0 (2)	6·7	0·60	25
Sc^{III}	0·71	6·18 (8)	6·7	1·02	9	6·0	5·5	1·09	0
V^{III}	0·60	6·0	6·0	1·02	0		4·8		
Cr^{III}	0·58	6·0	5·8	1·03	0	6·0	4·8	1·25	0
Mn^{III}	0·62	5·78 (6)	6·0	0·97	9		4·8		
Fe^{III}	0·62	5·69 (4)	6·0	0·95	12	4·4 (2)	5·1	0·86	18
Co^{III}	0·54^s	5·91 (9)	5·7	1·04	5				

Table 1 (cont.)

	Cation radius (Å)	Anions of Period 2 (O, F)				Anions of Periods 3–5 (Cl, S, Br, I)			
		AOCN	PCN	AOCN/PCN	Std dev. (%)	AOCN	PCN	AOCN/PCN	Std dev. (%)
Y^{III}	0·88	7·0 (1)	8·0	0·88	17		6·1		
Rh^{III}	0·66^s	6·0	6·5	0·92	0		5·1		
La^{III}	1·03	8·5 (2)	9·1	0·93	18	7·8 (2)	7·0	1·11	8
Ti^{IV}	0·57	5·96 (2)	5·7	1·05	5	5·9 (1)	4·9	1·20	8
V^{IV}	0·53	5·6 (1)	5·4	1·04	11		4·5		
Mn^{IV}	0·50	6·0	5·2	1·15	0		4·3		
Zr^{IV}	0·68	6·72 (9)	6·5	1·03	13	6·2 (2)	6·0	1·03	9
Pt^{IV}	0·63	6·0	6·1	0·98	0		5·0		
V^V	0·47	4·62 (8)	5·0	0·92	18		4·2		
Nb^V	0·58	6·07 (2)	5·8	1·05	5		4·7		
Ru^V	0·55^s	6·0	5·7	1·05	0		4·6		
Ta^V	0·59	6·08 (3)	5·8	1·05	6		4·8		
Re^V	0·58^s	6·0	6·0	1·00	0		4·7		
Cr^{VI}	0·39	4·0	4·4	0·91	0				
Mo^{VI}	0·51	4·88 (7)	5·2	0·94	20				
W^{VI}	0·52	5·6 (7)	5·3	1·06	14				
Re^{VII}	0·53^s	4·6 (2)	5·6	0·82	20				

S = radii from Shannon (1976).

the sum of the valences of the bonds that each Zn atom forms is equal to its oxidation state (Brown, 1978). The success of this prediction can be judged from Fig. 1 which shows how the coordination numbers of Rb and Zn vary as a function of the anion base strength (S_b). A similar correlation is shown for Tl^I in Fig. 3 of Brown & Faggiani (1980). Dent-Glasser (1981) has also shown that the occurrence of four- and six-coordination around Al is related to the base strength of the anion.

The range of coordination numbers observed can be predicted using the valence-matching principle (Brown, 1981) which states that for stable compounds the Lewis-base strength of the anion should equal the
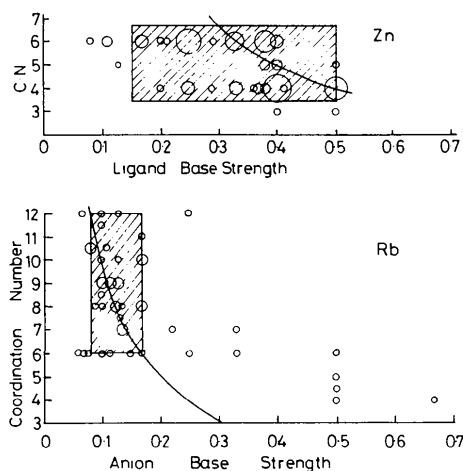

Fig. 1. The observed coordination numbers, as a function of anion base strength, shown as circles whose area is proportional to the number of examples. Top figure: Zn oxides and fluorides; lower figure: Rb oxides. The line indicates the coordination numbers expected if the bond valences were equal to the anion base strengths. The shaded boxes indicate the predictions discussed in the text.

similarly defined Lewis-acid strength (S_a) of the cation (S_a = formal cation charge/coordination number) since both are estimates of the strength of the bond between them. In practice some degree of mismatch between S_a and S_b is allowed and, for a given cation, compounds are found to exist with anions whose base strength lies anywhere in the range $0·5 S_a < S_b < 2·0 S_a$. Choosing

$$S_a = V/\text{PCN},\tag{1}$$

where V is the cation oxidation number, and assuming that the strength of the bonds formed by the cation is exactly equal to S_b, then the range of coordination numbers (N) that would be expected would be $0·5\text{PCN} < N < 2·0\text{PCN}$. If we also assume that the PCN, which represents the maximum number of ligands than can surround a cation, is an upper limit on the value of N, the effective range is reduced to $0·5\text{PCN} < N < \text{PCN}$. These regions are shown shaded in Fig. 1. Further restrictions arise because in inorganic compounds one finds few bases with $S_b < 0·08(\text{ClO}_4^-)$ or $S_b > 0·50(\text{O}^{2-})$. This provides an upper limit of 12-coordination for univalent cations, and lower limits of four for divalent cations, six for trivalent cations etc. Fig. 2 shows how well these predictions (the horizontal lines) agree with the observed ranges (circles) for mono-, di- and trivalent cations. The absence of weak bases is seen to be the factor limiting the coordination numbers of the larger univalent cations (especially Cs) and this accounts for the low value of its AOCN (8·8) compared to its PCN (14·4). At the opposite extreme the small cations with high formal charge (e.g. B) are limited by having a PCN which only permits the formation of bonds stronger than 0·5 v.u. This effectively restricts them to bonding to the simple anions (e.g. O, F) which can form bonds considerably in excess of their nominal base strengths (see Appendix II). In

some cases such small highly charged cations show coordination numbers greater than their PCN (e.g. four for B); the strain introduced in such cases being in part reduced by the resulting bonds being closer to the anion base strength.

The coordination number ranges predicted using these arguments agree with the numbers observed for many of the main-group elements in their normal oxidation states (Fig. 2, see especially the alkaline earths) though there are a few outliers (notably Ga). For rubidium (see Fig. 1), coordination numbers below the lower limit of six occur only with very strong bases. Most, if not all, of these compounds are extremely moisture sensitive and require special handling (see for example Klassen & Hoppe, 1982)* as is predicted by the valence-matching principle for compounds in which the Lewis base is much stronger than the Lewis acid (Brown, 1981).

For main-group elements in lower oxidation states the observed coordination numbers extend to values lower than 0.5 PCN and the AOCN's are much lower than would be expected from the radii. An examination of the coordination environments in these cases shows that low coordination numbers are invariably associated with stereoactivity of the valence lone-pair electrons. Tl^I offers a dramatic illustration of this effect. With a PCN of 12.3 one would expect Tl^I to behave as a weak Lewis acid ($S_a = 1/12 \cdot 3 = 0.08$ v.u.) similar to Rb and to show coordination numbers no smaller than

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* Most of these compounds have been reported only by Professor Hoppe and his colleagues. They illustrate the distortions that can be introduced into a statistical survey of this kind by the efforts of one laboratory that specializes in an unusual field of chemistry.

six. In part it does show this behaviour but, unlike Rb, it forms stable low-coordination compounds with quite strong bases [e.g. $Tl^{III}O_3^{3-}$ ($S_b = 0.5$) and BO_3^{3-} ($S_b = 0.33$)]. In these cases the bonding is well described by the valence-shell electron-pair repulsion (VSEPR) model (Gillespie, 1972) with the lone-pair electrons occupying one of the four tetrahedral ligand positions to give the configuration MX_3E [in the notation of Gillespie (1972)]. Fig. 3 shows how the coordination sphere around Tl^I varies as a function of anion base strength. In this figure, the non-centro-symmetric distortion* of the environment is shown on the vertical axis, the numbers indicate the observed coordination number with the polygons indicating (by the numbers of their sides) the number of strong bonds. For bases stronger than 0.27 v.u., the bonding is fully directed (MX_3E). For weaker bases the effect is variable but shows a tendency for the coordination number to rise and the distortion to diminish as the base strength is reduced.

Electronic effects of a different kind are observed for elements in Groups 11, 12 and 13† with filled d shells, particularly Cu^I and Hg^{II} where linear two-coordination is found and Ga where four-coordination is the norm. As in the case of the main-group elements in low oxidation states, the electronic effects, where expressed, dominate for the smaller cations but size effects are equally important for the larger cations. Other electronic effects, such as the Jahn–Teller distortions around Cu^{II} (Orgel, 1960), also result in directed bonds but do not lead to unusual coordination numbers.

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* This distortion is calculated in the following way. The Tl—O bond lengths (R) are converted to bond valences (S) using the equation $S = \exp(2 \cdot 226 - R/0 \cdot 37)$. The bond valence is treated as a vector pointing in the direction of the bond and the distortion is the magnitude of the vector sum of these quantities around the Tl ion.

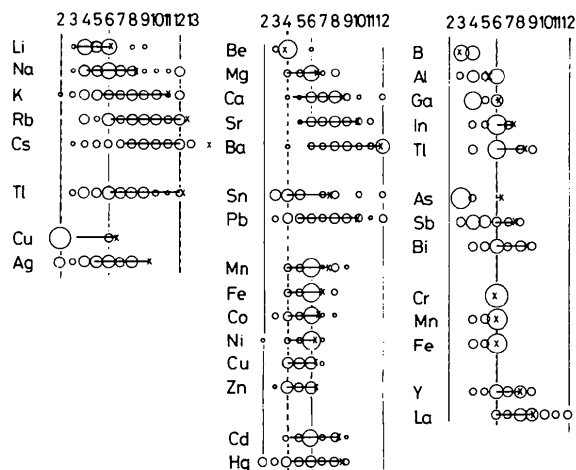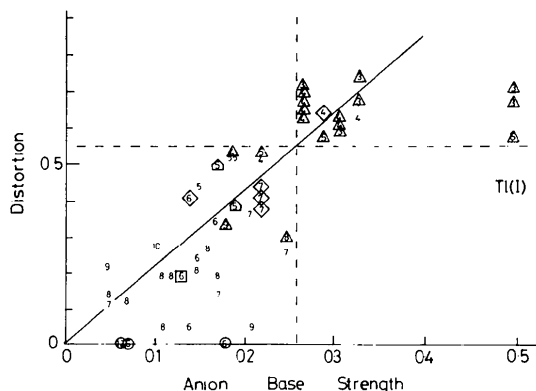† The recently proposed renumbering of the long groups of the Periodic Table from 1–18 is used in this paper.

Fig. 2. Coordination numbers (horizontal) around univalent, divalent and trivalent cations. The area of each circle corresponds to the number of examples observed (normalized to the same total for each cation). The PCN is indicated by ×, the predicted ranges are indicated by the horizontal lines. The vertical broken lines indicate the limits imposed by the restricted range of bases available in nature.

Fig. 3. Environments found around Tl^I. Numbers indicate the coordination numbers, the polygons (by the number of their sides) indicate the number of strong bonds where identifiable. Circles indicate an isotropic environment. The distortion measures the stereoactivity of the lone pair (see footnote * above).

3.2. Cation acid strengths

In the previous section the Lewis-acid strength of the cation was taken to be the oxidation state divided by the PCN. This represents an idealized acid strength that would be expected if the packing of ligands around the cation were the only factor determining the coordination number. As the above discussion shows, several other factors are also involved and these generally tend to lower the coordination number (increase the acid strength). When applying the valence-matching principle in real crystals it is better to use an acid strength calculated by substituting the AOCN for the PCN in (1). These values of S_a are listed in Table 2. The spread of observed coordination numbers around the AOCN (as indicated by the standard deviations in Table 1) is a measure of the ability of a given cation to bond to anions of different Lewis-base strengths. For example, Cr^{III} is both observed and predicted from the above discussion to have a tightly defined $S_a = 0.5$ v.u. with no spread (standard deviation = 0%). As^{III} is also observed to have a small spread with $S_a = 1.0$ v.u. (standard deviation = 8%), though the reason in this case lies in the energetically favourable MX_3E configuration involving a stereoactive electron pair. By contrast, Tl^I shows a wide range of Lewis-acid strengths ($S_a = 0.14$, standard deviation = 30%); in the presence of strong bases it has an effective $S_a = 0.33$ v.u. (MX_3E configuration) but in the presence of weak bases it has $S_a = 0.1$ v.u. (configuration determined by crystal packing) indicating that there is little energetic difference between the lone electron pair being in an s or in an sp^3 orbital.

The average Lewis-acid strengths given in Table 2 can be seen to increase with the electronegativity. The correlation between the two quantities is shown in Fig. 4 using the Zhang (1982) electronegativities that are specific to oxidation state. The line corresponds to the equation

$$\chi = 1.18S_a + 0.771 \qquad (2)$$

which can be rewritten as

$$\chi' = 4.90S_a \qquad (3)$$

where $\chi' (= Z^*/r^2)$ is the quantity referred to by Allred & Rochow (1958) as the absolute electronegativity.

3.3. Bond distances and ionic radii

Ionic radii were originally introduced as a way of rationalizing and predicting interatomic distances. In determining these radii it is necessary to choose one radius arbitrarily; the rest can then be determined by subtracting this radius from the appropriate observed interatomic distances. By convention the radius of oxygen is taken to be 1.40 Å since this represents half the O—O distance found in many crystals. Such a model implies that the ions behave as hard spheres, and

Table 2. *Average Lewis-acid strengths based on AOCN's*

Standard uncertainties, where available, are given in parentheses.

	Univalent anion	Divalent anion
Li	0.188 (14)	0.205 (2)
Na	0.148 (2)	0.156 (2)
K	0.112 (3)	0.126 (2)
Rb	0.102 (3)	0.124 (3)
Cs	0.094 (2)	0.113 (3)
Tl^I	0.120 (3)	0.146 (5)

	Anion of Period 2	Anion of Periods 3–5
Main-group cations		
Be	0.501 (3)	
Mg	0.334 (3)	0.33
Ca	0.274 (2)	0.30 (2)
Sr	0.233 (4)	0.27 (1)
Ba	0.195 (2)	0.249 (4)
B	0.87 (1)	
Al	0.57 (1)	0.73 (1)
Ga	0.65 (2)	0.75
In^{III}	0.50 (1)	0.54 (1)
In^I		0.15 (1)
Tl^{III}	0.49 (2)	0.62 (6)
Tl^I	0.14 (1)	0.13 (1)
C	1.35 (1)	1.26 (9)
Si	1.00 (1)	1.00
Ge	0.89 (1)	1.04 (2)
Sn^{IV}	0.68 (1)	0.79 (3)
Sn^{II}	0.45 (3)	0.36 (2)
Pb^{IV}	0.70 (1)	
Pb^{II}	0.29 (1)	0.30 (1)
N	1.67 (1)	
P	1.247 (2)	1.19 (3)
As^V	1.13 (2)	
As^{III}	0.98 (1)	0.94 (2)
Sb^V	0.83 (1)	0.98 (4)
Sb^{III}	0.62 (2)	0.65 (1)
Bi^{III}	0.48 (1)	0.50 (1)
S	1.5	
Se^{VI}	1.5	
Se^{IV}	1.20 (6)	
Te^{VI}	1.0	
Te^{IV}	0.98 (2)	0.68 (4)
Cl^{VII}	1.75	
I^{VII}	1.2 (3)	
I^V	1.3 (1)	
Transition-metal cations		
Sc^{III}	0.49 (1)	0.50
Y^{III}	0.43 (3)	0.47 (3)
La^{III}	0.35 (1)	0.38 (1)
Ti^{IV}	0.67 (1)	0.68 (2)
Zr^{IV}	0.60 (1)	0.65 (2)
V^V	1.08 (2)	
V^{IV}	0.71 (1)	
V^{II}	0.50	
Nb^V	0.823 (2)	
Ta^V	0.822 (5)	
Cr^{VI}	1.50	
Cr^{III}	0.50	
Mo^{VI}	1.23 (2)	
W^{VI}	1.07 (1)	
Mn^{VI}	1.00	
Mn^{III}	0.52 (1)	
Mn^{II}	0.344 (2)	0.35 (1)
Re^{VII}	1.51 (6)	
Re^V	0.83	
Fe^{III}	0.527 (4)	0.68 (3)
Fe^{II}	0.340 (2)	0.36 (2)
Ru^V	0.83	
Co^{III}	0.51 (1)	
Co^{II}	0.351 (4)	0.42 (2)
Rh^{III}	0.50	
Ni^{II}	0.339 (3)	0.37 (3)
Pd^{II}	0.46 (2)	0.50
Pt^{IV}	0.67	0.69 (3)
Pt^{II}		0.50

Table 2 (cont.)

	Anion of Period 2	Anion of Periods 3–5
Cu^{II}	0·392 (4)	0·42 (2)
Cu^{I}	0·45 (5)	0·29 (1)
Ag^{I}	0·20 (1)	0·23 (1)
Au^{I}		0·31 (8)
Zn^{II}	0·402 (5)	0·50
Cd^{II}	0·326 (3)	0·43 (2)
Hg^{II}	0·36 (2)	0·50 (2)

its success is shown by the ability of the PCN's (derived from these radii) to predict maximum coordination numbers.

It is less successful in predicting bond distances when the cation coordination number is not six and corrections (see Pauling, 1960; Tables 13-14) have been proposed for the cation radii that recognise that the cations are not perfectly hard. Shannon & Prewitt (1969) and Shannon (1976) have tabulated empirical 'effective ionic radii' that also depend on coordination number. However, these corrected cation radii are much less successful in predicting coordination number.

An alternative way of analyzing the variation of bond length with coordination number (N) is to use bond valences (S) calculated from the cation oxidation state (V) (Brown, 1978). For a regular coordination environment

$$S = V/N \qquad (4)$$

and S can then be used to calculate a bond distance (R) using

$$R = R_0 - 0·37\ln S \qquad (5)$$

with R_0 for the appropriate cation–anion pair taken from Brown & Altermatt (1985). The O—O separation within the polyhedron can then be calculated (at least for regular coordination spheres) from the geometry. It is not necessary for N to be an integer in these equations and a notional value for the O—O distance can also be found for non-integral values of N by interpolating between the values of O—O/M—O calculated for high-symmetry coordination spheres around the cation M.

O—O and M—O distances calculated in this manner using the AOCN are indicated by the element symbols in Fig. 5. These represent distances that are expected in a typical environment around the cation. Distances calculated using the PCN (not individually shown) all lie close to the broken line. However, if the rigid-sphere model were true, all the points in Fig. 5 should lie on the vertical line corresponding to O—O = 2·8 Å. The large deviations of the points from this line indicate that the rigid-sphere model is quite inappropriate for predicting both O—O and M—O distances however successful it may be in predicting coordination numbers. The cation and anion radii are both clearly functions of the coordination number but, as the above analysis of the PCN's (based on six-coordinate radii) shows, their ratios are not. It
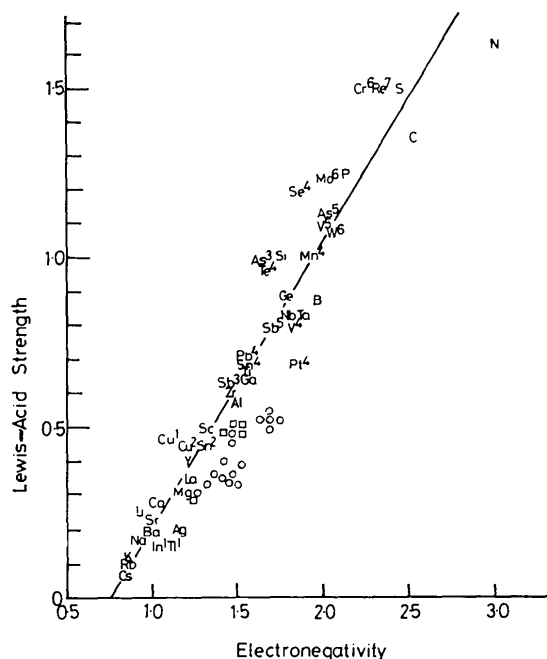

Fig. 4. Lewis-acid strength (Table 2) as a function of electronegativity (Zhang, 1982). Circles represent transition metals, squares nontransition metals. The line represents equation (2).
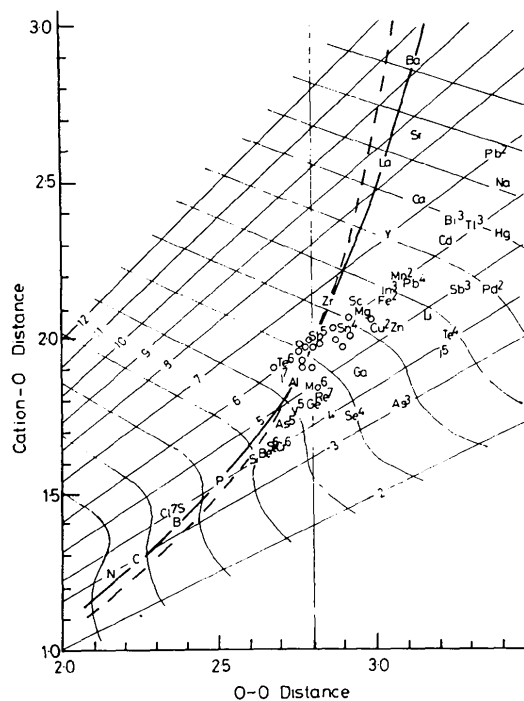

Fig. 5. Calculated M—O versus O—O distances expected for cations with coordination numbers = AOCN. Circles represent transition metals. Corresponding quantities calculated using the PCN lie close to the broken line. The solid curve corresponds to equation (6). The diagonal lines directed to the top right correspond to lines of constant coordination number (as indicated) and those directed to the top left correspond to the paths followed by cations as their coordination numbers are changed.

follows that both the anion and the cation radii must vary in the same way with the cation coordination number. The relationship between the oxygen radius (r_o) and the cation coordination number (N) can be determined from the solid line in Fig. 5 which represents a fit to the AOCN's for those cations where electronic effects are apparently not determinant. This line corresponds to the empirical equation

$$r_o = 1\cdot12 + 0\cdot23\ln(N-2)\ \text{Å}. \qquad (6)$$

Since $r_m/r_o = x$ is essentially independent of N as indicated by the success of the PCN's calculated from six-coordinate radius ratios, the radius of the cation (r_m) is given by

$$r_m = x[1\cdot12 + 0\cdot23\ln(N-2)]\ \text{Å}. \qquad (7)$$

4. Conclusions

The coordination numbers (PCN's) predicted by Pauling's ionic (six-coordinate bonding) radii represent the maximum coordination numbers that are permitted by the packing of ligands around a cation without strain. Other things being equal, the PCN represents an ideal value which can be used to calculate an idealized Lewis-acid strength for the cation $(S_a = $ oxidation number/PCN). Lower coordination numbers can occur when the Lewis-base strength (S_b) of the ligand is greater than S_a, the lower limit being restricted by either the valence-matching principle or the lack of suitably strong bases in nature. High coordination numbers are similarly restricted by the value of the PCN or the lack of suitably weak bases. Exceptions are observed for small cations with high oxidation number where the strain resulting from a coordination number greater than the PCN is offset by the strain released when the bonding around the ligand is closer to the anion base strength.

The frequent occurrence around some cations of coordination numbers smaller than these limits indicates the presence of electronic effects influencing the crystal chemistry of the ion, but apart from this group (main-group elements in low oxidation states and full-d-shell cations from groups 11, 12 and 13), the arguments presented above, based on ionic sizes and valence matching, can account for the major variability observed in cation coordination numbers and can be used to predict the coordination numbers likely to be found in many individual compounds.

The average observed coordination numbers (AOCN's) can be used to calculate cation Lewis-acid strengths that are linearly related to the absolute electronegativity indicating that the factors that affect the coordination number are also responsible for variations in the electronegativity.

The results also show that ionic radii can be used to predict both $M-O$ and $O-O$ interatomic distances but

only if corrections for cation coordination are made to both cation and anion radii.

APPENDIX I
Determination of bonding radii used in this study

The term 'ionic radius' is widely used for radii compatable with the crystal radii given in Table 13-3. of Pauling (1960) but the term 'bonding radius' is used here since these radii are designed to reproduce the observed bond lengths in both ionic and covalent structures where the cation is six-coordinate.

For main-group elements in their highest oxidation state the bonding radii used in this study are the semi-empirical crystal radii given in Table 13-3 of Pauling (1960). Radii given by Pauling for other cations are derived empirically and, since much more accurate bond distances are now available, new cation radii have been obtained by subtracting the O-bonding radius (1·40 Å) from the six-coordinate cation–O distances calculated using equations (4) and (5) with the AOCN set equal to 6 (Shannon, 1976). In a few cases where bond-valence parameters were not available the six-coordinate effective ionic radii of Shannon (1976) have been used. The resultant bonding radii, which correspond in all cases to six-coordination, are shown in Table 1.

Since the anions were grouped, it was necessary to use average anion radii. For anions of the first Period (F, O) the anion radius was taken to be 1·40 Å, for the others (Cl, Br, S and I) 1·94 Å was used.

As indicated in the text these radii give good predictions of coordination number and of cation–oxygen distances around six-coordinated cations. The soft-sphere radii discussed in §3.3 must be used in other cases.

APPENDIX II
Calculations of the base strengths of anions

For simple anions the base strength is the oxidation number divided by the coordination number, taken as four for anions in Period 2 and six for other Periods. However, the base strength actually displayed by such simple anions can vary over a wide range depending on the acid strength of the counterion.

Complex ions, those that consist of one or more cations surrounded by simple anions, have base strengths that have a more limited range of values. We assume that the complex anion in a given compound includes all the cations having a higher Lewis-acid

Table 3. *Base strengths of some complex anions*

Anion stoichiometry	Coordination number of A			
	2	3	4	6
$A^{III}O_3^-$	0·17	0·25	0·25	0·50
$A^{II}O_2^{2-}$	0·33	0·40	0·50	1·00
$A^VO_3^-$	—	0·11	0·14	0·17
$A^{IV}O_3^{2-}$	—	0·22	0·28	0·33
$A^{III}O_3^{3-}$	—	0·33	0·38	0·50
$A^{VII}O_4^-$	—	—	0·08	0·12
$A^{VI}O_4^{2-}$	—	—	0·17	0·25
$A^VO_4^{3-}$	—	—	0·25	0·30
$A^{VI}O_6^{6-}$	—	—	—	0·33
$A_2^VO_5^{2-}$	—	—	0·22	—
$A_2^{III}O_5^{4-}$	—	0·31	0·44	0·57
$A_2^{VI}O_7^{2-}$	—	—	0·11	0·18
$A_2^VO_7^{4-}$	—	—	0·22	0·36
$A_2^{IV}O_7^{6-}$	—	—	0·32	0·55
$HA^{VI}O_4^-$	—	—	0·12	—
$HA^{VI}O_4^{2-}$	—	—	0·22	—
$H_2A^VO_4^-$	—	—	0·18	—

strength than the cation being studied *e.g.* when considering the effect of the anion base strength on Zn in NaZn(PO₄) the anion would be taken as $(PO_4)^{3-}$ since P is a stronger Lewis acid than Zn but when considering the influence on Na the anion would be taken as $[Zn(PO_4)]^-$. The base strength is calculated by dividing the net charge on the anion by the number of bonds it forms (coordination number). For complex anions the net charge is easily computed but the coordination number can only strictly be determined by examining the structure. However, a notional coordination number can be computed *a priori* as follows: it is assumed that each O (or F) atom forms a total of four bonds (including the bonds formed within the complex anion). The net coordination number of the complex is found by subtracting from this total the number of bonds that are used to coordinate the (strong) cations within the complex, *i.e.*

$$S_b = (n_m V_m + n_o V_o)/(n_o N_o - n_m N_m)$$

where V is an oxidation number (note $V_o < 0$), N is a coordination number and n is the number of atoms of that type in the complex. The subscript m refers to the strong Lewis acid incorporated in the anion and o to the O or F atom. N_m is equal to the actual coordination number of m in the complex (where known) or its AOCN. As above, N_o is taken as four. However if two of the bonds formed by O are strong (say greater than 0·8 v.u.) then N_o will be three and for each O that is protonated the formal charge of the complex is increased by 0·2 because of the formation of an external H bond. Some typical base strengths are shown in Table 3.

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Etude Cristallographique de Défauts Ponctuels et des Mécanismes de Diffusion Possibles pour les Alcalins dans les Iodures Mixtes d'Argent et d'Alcalin M: $M\mathrm{Ag}_4\mathrm{I}_5$ et $M_2\mathrm{AgI}_3$. Etude Théorique

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Abstract

The mobility of alkali cations K⁺ or Rb⁺ in the $M_2\mathrm{AgI}_3$ and $M\mathrm{Ag}_4\mathrm{I}_5$ compounds (M = K, Rb) is studied from a structural point of view. The occurrences of vacancies or interstitial defects are evaluated. The diffusion paths and therefore the possible diffusion mechanisms are described. A comparison between the two structural