

sesquichloride over a range of temperature from 650 to 860°. The tantalum container when opened was found to be apparently completely filled with long fibers of Sc_2Cl_3 which were only a few microns in diameter and resembled polyglass string. The principal amount of product occurs inside this cocoon-like shell on the metal as a hard crust with a dark brown to golden appearance. This is actually a very dense "forest" of thin fibers which grow normal to the metal surface, the individual "trunks" ($\sim 100\text{-}\mu$ diameter, 1–4 mm long) actually being composed of bundles which fray into smaller fibers ($\sim 3\text{--}10\ \mu$) when cut or rubbed. (The assembly also resembles the fibers in a cigarette filter.) The product is single phase to the microscope and to X-rays and is clearly isostructural with the sesquibromide, with lattice spacings about 6% smaller (see Experimental Section). The Sc_2Cl_3 melts peritectically at $877.0 \pm 0.2^\circ$, about 3° lower than the sesquibromide. The recombination reaction between ScCl_3 and the finely powdered metal produced on melting is evidently quite rapid as judged from the fact that the eutectic is not observed on cooling a decomposed 0.5-g sample from 877° to the expected 803° at $0.7^\circ \text{ min}^{-1}$. The transition is of course found on faster cooling.

The technique of premelting metal into 0.25-in. tantalum tubes prior to equilibration with liquid ScCl_3 was used in the previous chloride study³ in order to avoid problems of metal suspension which otherwise produced high and erratic solubilities, particularly above 900° . However this same technique also obscured the formation of Sc_2Cl_3 below 877° since the hard, thin layer of product formed on the limited surface readily blocked further reaction. The compositions determined³ below 880° were actually those of the Sc_2Cl_3 -saturated melt; the diffraction pattern of the sesquichloride is not evident in the powder pattern of such quenched samples. Nonetheless, the cooling curves were inadequately interpreted since some clearly showed the peritectic transition supercooled about 20° .

The only other element which forms a high-melting sesquihalide as the lowest phase is gadolinium,⁹ and, interestingly, the crystal habit of the two scandium sesquihalides greatly resembles that already known for Gd_2Cl_3 , where a remark-

able metal chain structure has been determined.¹⁵ The scandium phases would appear thermodynamically to be considerably more stable than Gd_2Cl_3 , however, melting almost 250° higher and notably less incongruently. The slight paramagnetism found for Sc_2Br_3 is not in conflict since such a small effect would be undetected in the large susceptibility background of the $4f^7$ metal cores observed for Gd_2Cl_3 .¹⁶ It is interesting to note that both elements form evidently metallic iodides, namely, ScI_2 ,¹⁵ and GdI_2 ,⁹ another constitution which doubtlessly also requires substantial orbital extension for the differentiating electrons. No further evidence is available at present concerning the possible structural similarities of the scandium and gadolinium compounds. Predictions^{17,18} of dihalide stability notwithstanding, scandium remains the only 3d element lacking a simple dihalide in the solid state. Of course the metal-reduced melt does contain substantial amounts of Sc^{2+} according to cryoscopic evidence, up to about 69 mol % ScX_2 in ScX_3 if this is the sole product, and so the solid dihalides may not be very far from stability. The alternate solid phases actually found for scandium do appear a good deal more interesting, however.

Registry No. Sc_2Cl_3 , 12-432-552; ScBr_3 , 13465-59-3; $(\text{NH}_4)_3\text{ScCl}_6$, 38136-16-2; ScCl_3 , 10361-84-9; Sc_2Br_3 , 12-431-582; NH_4Br , 12124-97-9; Sc_2O_3 , 12060-08-1.

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Ionic Radii for Spherical Potential Ions. I

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Experimental ionic radii (r_c) are available for several cations from X-ray density maps. Ionic radii for other cations with a rare gas configuration are derived from an empirical relation between r_c and the intermetallic distance of the corresponding metal. These are termed radii for spherical potential ions (SPI) and receive theoretical justification from the calculations of Paschalis and Weiss showing contraction of anions and expansion of cations in spherical potential wells of opposite sign. Expansion of cations in crystals is small and definite values of cation radii can be established. However, variable radii are proposed for anions to take into account the relatively large contraction of anions in the field of cations.

Introduction

The use of ionic radii and covalent radii¹ (which are ex-

tremely crude representations) along with sophisticated quantum mechanical calculations using accurate wave functions for electrons is one of the anachronisms of present day chemistry and physics.

Fajans² has long emphasized the deviations from additivity of internuclear distances in crystals and has shown, *e.g.*, that

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(1) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

an ion like Ag^+ appears larger than Na^+ in combination with F^- (which is strongly polarizing but has low polarizability), of the same size in perchlorates, and increasingly smaller with the highly polarizable Cl^- , Br^- , and I^- anions. The use of arbitrary ionic radii in the face of such demonstrations probably continued because no clearly defined radii were available. However, for a number of years there have been available electron density diagrams from careful X-ray diffraction experiments³ which show minima in electron density between anions and cations in the compounds NaCl , KCl , LiF , CaF_2 , MgO , CuCl , CuBr , and NiO . The radii (\AA) indicated by the minimum in electron density³ are as follows: Li^+ , 0.92; Na^+ , 1.18; K^+ , 1.45; Mg^{2+} , 1.02; Ca^{2+} , 1.26; Cu^+ , 1.10; Ni^{2+} , 0.94; Cl^- , 1.70 in KCl , 1.64 in NaCl ; 1.25 in CuCl ;⁴ Br^- , 1.36 in CuBr ;⁴ O^{2-} , 1.09 in MgO , 1.15 in NiO ;⁴ F^- , 1.09 in LiF , 1.10 in CaF_2 . These have been presented in textbooks⁴⁻⁶ as X-ray density map radii, and the rather large differences between these radii and the usual crystal radii (or ionic radii) and covalent radii have been noted.

Fajans⁷ has pointed out that the ratio of the X-ray density map radii of Na^+ and Cl^- (1.4) is much lower than that of Pauling's¹ calculated radii (1.885) and considered X-ray density map radii as idealized representations of ions which in reality interpenetrate and deform each other. Sanderson⁸ has used X-ray density map radii in discussing ionic properties, and these radii have been compared⁹ to those calculated by Fumi and Tosi using the Born-Mayer model of ionic solids. The most complete discussion of the complexities involved in determining empirical ionic radii from interionic distance in crystals is that of Shannon and Prewitt¹⁰ who reached some of the same conclusions as those of this paper.

It has been pointed out by a referee that electron density maps are not convincing evidence of the presence of Na^+ and Cl^- in solid NaCl since the electron density obtained by placing Na^0 and Cl^0 at the corresponding positions would give a comparable electron density map. The point of view taken in this paper is that other evidence establishes the presence of Na^+ and Cl^- in solid NaCl . Then the known radial electron distribution of free Na^+ and Cl^- coupled with the results of Paschalis and Weiss (see below) make it possible to interpret the minimum in electron density as the boundary of Na^+ and Cl^- .

A recent study of ion core sizes in metals¹¹ showed that there was the following relation between the above ionic radii from X-ray density maps (r_c) and interatomic distance (a) in the metals

$$r_c = ka/2 \quad (1)$$

where k is constant for a similar type of ion and is 0.64 for alkali metal and alkaline earth metal ions. It is proposed in

(2) K. Fajans, *Naturwissenschaften*, 11, 165 (1923); *Z. Kristallogr., Kristallgeometrie, Kristalphys., Kristalchem.*, 61, 18 (1925); K. Fajans and H. Grimm, *Z. Phys.*, 2, 299 (1920); K. Fajans, *Ceram. Age*, 54, 288 (1949).

(3) H. Witte and E. Wolfel, *Rev. Mod. Phys.*, 30, 51 (1958).

(4) M. C. Day, Jr., and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold, New York, N. Y., 1969.

(5) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 2, McGraw-Hill, New York, N. Y., 1965, p 107.

(6) K. B. Harvey and G. B. Porter, "Introduction to Physical Inorganic Chemistry," Addison-Wesley, Reading, Mass., 1963.

(7) K. Fajans, "Quanticule Theory of Chemical Binding," State Technical Publishing House, Warsaw, 1961.

(8) R. T. Sanderson, "Chemical Bonds and Bond Energy," Academic Press, New York, N. Y., 1971.

(9) D. F. C. Morris, *Struct. Bonding (Berlin)*, 4, 63 (1968).

(10) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1968).

(11) O. Johnson, *J. Res. Inst. Catal., Hokkaido Univ.*, 20, 95 (1972).

this paper to show that the positive ion core dimension in a metal is the same as for the corresponding rare gas cation in a crystal where the ions are in a spherically symmetrical environment and then to derive a consistent set of ion core (cation) radii and to develop the concept of a variable radius for anions. The more complex d^{10} cations and transition metal cations will be treated in a subsequent paper.

Relation of Cation Radii to Intermetallic Distance

The radii determined for several ions from the electron density minima were given above. The electron density maps³ show spherical ionic symmetry in NaCl , KCl , MgO , and Al metal. Using the minimum in density to define ionic radii the electron density map gives 10.05 electrons around Na^+ and 17.7 electrons around Cl^- . The largest deviations from spherical symmetry are for LiF and CaF_2 . The X-ray density map radius has been determined for K^+ and Br^- in KBr by Meisalo and Inkinen.¹² Their choice of $r_{\text{K}^+} = 1.57$ was made on the basis of decline to the same average electron density for anion and cation and is larger than observed in KCl by Witte and Wolfel.³ A radius of 1.41 \AA , which the authors listed as equally reasonable, gives an integrated total electron count of 18.19 around K^+ . The corresponding radius for Br^- would be 1.89 \AA . These uncertainties show the difficulties involved in accurate experimental determination of X-ray density radii. For aluminum metal the electron density drops to approximately 0.2 e/\AA^3 in a large region between ion cores and reaches this value at 0.9 \AA from the center of the ion core. Extrapolation of the electron density-distance curve from the region 0.5-0.8 \AA gives 0.92 \AA as the dimension of the ion core.¹¹

The ionic radii from X-ray electron density are given in Table I along with their ratio to half the interatomic distance in the metals. These radii represent the minimum in electron density between anion and cation; although the electron density does not go to zero at the minimum, these dimensions give the expected number of electrons around each ion and thus conform very closely to ideal ionic radii.

Although there are a limited number of experimental data, the k value of 0.64 for rare gas cations seems reasonable. Since Li^+ (and also Be^{2+}) differs from the other cations in only having a 1s shell, a smaller k (0.61) is not unexpected. Higher values of k are observed for Cu^+ (0.86) and Ni^{2+} (0.75) and probably result from the large effect of the poorer screening^{13,14} of the nuclear charge by d electrons for Ni^{2+} and Cu^+ .

The description of cations and anions in ionic crystals is customary and although most treatments of metals include ion cores and conduction electrons, the interstitial electron model¹⁵ explicitly treats the metal ion core as identical with the cation in ionic compounds. The electron density map for aluminum³ indicates an Al^{3+} radius of 0.92 \AA . The use of appropriate values for O^{2-} and F^- radii (see below) in conjunction with interionic distances in Al_2O_3 and AlF_3 indicate approximately the same radius for Al^{3+} in these compounds.

If one assumes that eq 1 applies to all metals where ion cores are in a spherically symmetric field, ion core radii can be derived for all such positive ion cores. The assumption that cations have a constant radii in the presence of different

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(15) O. Johnson, *Bull. Chem. Soc. Jap.*, 45, 1599, 1607 (1972).

Table I. Ratios of Positive Ion Core Radius and Intermetallic Distance^a

Metal	r_c , Å	$a/2$, Å	$r_c/(a/2)$
Li	0.92	1.52	0.61
Na	1.18	1.86	0.635
K	1.45	2.26	0.64
Mg	1.02	1.60	0.64
Ca	1.26	1.97	0.64
Al	0.92	1.43	0.64

^a r_c is the ion core radius or cation radius; a is the intermetallic distance.

anions is also implied in fixing cation radii. Values of k can be checked for cations in periodic groups for which X-ray density radii are not available from interionic distances, e.g., in their fluorides, by assuming an appropriate value for the fluoride ion radius. The values of ionic radii derived in this way for cations are given in Table II. They represent cation radii or ion core radii in a spherically symmetrical field of anions or the field of electrons in a metal, respectively. It is proposed that they be referred to as radii for spherical potential ions (SPI). Paschalis and Weiss¹⁶ (see below) have used the term spherical potential ion in a theoretical treatment of ions in crystals where a spherically symmetric potential around a given ion was used to simulate the environment of ions in crystals.

Values are given for cations up to M^{6+} although it should be realized that cations like V^{5+} and Cr^{6+} are usually found in anion groups such as MO_4 along with a different cation. They do occur in mixed oxides such as perovskites, e.g., $NaNbO_3$, in a symmetrical environment of anions and cations.

Theoretical Basis for Cation Radii

From an extensive series of refractometric investigations, Fajans and coworkers¹⁷ have concluded that there is a contraction of electronic shells of anions in the presence of cations and an expansion of the electronic shells of cations, especially for large or polarizable cations, in the presence of small anions. The resulting effects were large for anions and small for cations. Similar conclusions were reached from a study of systematic deviations from additivity of interionic distances in crystals. Recently, Paschalis and Weiss¹⁶ reported some results of quantum mechanical calculations which showed that there was a contraction of anions when they were placed in a spherical potential well of cations of equal charge at a distance r_0 and an expansion of cations when in the field of anions under comparable circumstances. They used Hartree-Fock-Roothaan wave functions for the free ions, and the spherical potential well model has constant potential up to a distance of r_0 with the potential declining as a function of $1/r$ at distances greater than r_0 . These calculations showed an expansion of cations (as shown by an increase in radial electron distribution over that of the free ion at a given r_0) and a considerably larger contraction of anions (a decrease in radial electron density). A larger effect for anions is in agreement with the conclusions of Fajans. Calculations by Paschalis and Weiss of the related increase in polarizability of cations and decrease for anions showed in general a 10-fold greater effect for anions. The relative expansion and contraction of Ca^{2+} and Cl^- in $CaCl_2$ were approximately 3 and 25% as shown by calculated radial distribution of electrons. Similar conclusions about anion

Table II. Ionic Radii (SPI) in Å, Calculated from Eq 1 [$r_c = ka/2$, Rare Gas Cations ($k = 0.64$)]^a

Li ⁺	Be ²⁺	B ³⁺			
0.92	0.69	(0.6) ^b			
Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺		
1.18	1.02	0.92	(0.8) ^c		
K ⁺	Ca ²⁺	Sc ³⁺	Ti ⁴⁺	V ⁵⁺	Cr ⁶⁺
1.45	1.26	1.06	0.94	0.84	0.80
Rb ⁺	Sr ²⁺	Y ³⁺	Zr ⁴⁺	Nb ⁵⁺	Mo ⁶⁺
1.56	1.38	1.14	1.02	0.92	0.87
Cs ⁺	Ba ²⁺	Lu ³⁺ ^d	Hf ⁴⁺	Ta ⁵⁺	W ⁶⁺
1.68	1.40	1.12	1.04	0.95	0.88

^a $k = 0.61$ for Li^+ and Be^{2+} . ^b Estimated. ^c Estimated radius in nonbonding direction from *Z. Phys. Chem. (Frankfurt am Main)*, 21, 143 (1959). ^d La^{3+} taken as the first rare earth cation; $r_c = 1.20$ for La^{3+} .

contraction and cation expansion were reached by Petrashen, *et al.*¹⁸

The calculations of Paschalis and Weiss show that when a free cation is placed in the spherical potential well of opposite charge, the expansion depends on r_0 , the dimension of the well. For the present purposes we need to compare the distance and potential of electrons in metal to those of anions in compounds. In relation to the metal interatomic distance (a), both the M^+-A^- distance and the M^+-e^- (center of e^- density) are $0.6-0.7a$. The potentials for a cation correspond to a change from monovalent anions to 1 electron in the corresponding metal or from divalent anions to 2 electrons in metals, etc. The interstitial electron model¹⁵ gives metal electron densities outside ion cores of $0.03 e/\text{Å}^3$ for Na, $0.11 e/\text{Å}^3$ for Mg, and $0.23 e/\text{Å}^3$ for Al. This is the same range of electron densities observed at the minimum electron density between ions in X-ray electron density diagrams.

The change from free Ca^{2+} to Ca^{2+} in a potential well with a radius of 1.87 Å gave a calculated expansion of only about 3%. A very much smaller change is expected between Ca^{2+} (in metal) and Ca^{2+} (in chloride). Data for Al^{3+} , given above, indicated no difference of ion core in metal and ionic crystal. Data given by Fajans¹⁹ to show expansion of the electronic shell of Rb and Cs by F^- indicated an effect on interionic distance for these rather polarizable ions of about 1%. The lattice energies of metals and corresponding halides also indicate approximately the same negative field around cations in a metal and ionic crystal. Alkali metals (halides) have lattice energies between 100 and 250 kcal/mol. Be and Al metals have lattice energies of 915 and 1311 kcal/mol, and their chlorides have energies of 719 and 1304 kcal/mol, respectively. Thus, although these considerations show changes in dimensions of ions are to be expected in different potential fields, it is a good approximation to use the same ion core radius in a metal and in a compound of the same cation if the cation is also in a spherically symmetrical field there.

Intermetallic distances provide a source for data to use in eq 1 to obtain ion core radii for most cations. The r_c values obtained in this way were given in Table II. In general they are considerably larger than the customary ionic radii. It is of interest that there is quite close agreement for alkali metal cations of the present set of radii and those calculated by Tosi and Fumi²⁰ with the Born-Mayer model.

On the other hand, there is no similar source of radii for anions. The anion radii are obtained by subtraction of

(18) M. I. Petrashen, L. V. Abarenkov, and N. N. Kristofel, *Opt. Spectrosc. (USSR)*, 9, 276 (1960).

(19) K. Fajans, *J. Chem. Phys.*, 9, 281, 378 (1941).

(20) M. P. Tosi and F. G. Fumi, *J. Phys. Chem. Solids*, 25, 45 (1964).

(16) E. Paschalis and A. Weiss, *Theor. Chim. Acta*, 13, 381 (1969).

(17) See, e.g., K. Fajans, *Z. Elektrochem.*, 34, 502 (1928).

cation radii from interionic distances in compounds. A set of radii were obtained by Gourary and Adrian²¹ by this method, but their cation radii include average effects of anion contraction and are thus too high for Rb and Cs. The more complicated behavior for anions is discussed in the next section.

Variable Anion Radii

Large variations in anion radii in the positive field of different cations are expected from the discussion in section 3, and large variations were experimentally observed for Cl^- by the X-ray diffraction experiments. The following procedure was used to obtain anion radii. Cation radii were assumed to be constant and equal to the values in Table II. This is probably a very good approximation except for highly polarizable cations such as Rb^+ and Cs^+ , where there can be expansion ($\sim 0.08 \text{ \AA}$ for F^-) of their electron shells in the presence of a small anion such as F^- . The combination of experimental data from the X-ray density diagrams and interionic distances in many crystals with the empirical relation (1) represents an attempt to obtain the best possible set of ionic radii in the absence of experimental values. The values obtained in this way are plotted in Figure 1 with the contraction of the Cl^- radius by a given ion relative to Na^+ as abscissa (see below for details). This is a convenient means of representation and also arranges the cations in order of decreasing effective positive field (polarizing power). When chlorides had layer lattices, data for fluorides were used to obtain a cation position for Figure 1. The values given are for anions in a spherical potential as represented by a coordination number (CN) of 6 in crystals. When data were taken from crystals with other coordination numbers for the anions, appropriate corrections¹ were made to obtain interionic distances for CN = 6 (decrease of 3% for CN = 8, increase of 4% for CN = 4), again assuming r_c to be constant. Data for layer lattices (e.g., CdCl_2 type) were omitted since the ions are not in a spherically symmetric environment.

A mean value for radius of an anion can be useful for discussions of anion properties. On Figure 1 mean values are taken for anion radii for sodium salts of various anions. These r_a values are given in Table III which also gives the crystal radii values calculated for anions by Tosi and Fumi²⁰ using the Born-Mayer model. There is quite good agreement as there was with cation radii. The contraction of anions in the field of cations is appreciable, e.g., r_{Cl^-} decreases from 1.87 in CsCl to 1.25 \AA in CuCl ($\Delta r = 0.57 \text{ \AA}$). The smallest decrease is observed for perchlorates where $r_{\text{ClO}_4^-}$ decreases from 2.33 in CsClO_4 to 2.22 \AA in AgClO_4 ($\Delta r = 0.11 \text{ \AA}$). Within the alkali and alkaline earth (excluding Be) compounds the contractions of anions are small ($\Delta r \approx 0.17 \text{ \AA}$). Thus, previous values of ionic radii gave approximate additivity when only cations with a rare gas configuration were considered. However, the experimental radii from X-ray determination show that the partition of radii for anion and cation was incorrect and in addition did not take into account the extensive contraction of anions especially by non rare gas cations.

The gradations of radii for anions show largest slopes for H^- , O^{2-} , S^{2-} , Se^{2-} , Te^{2-} , lower slopes for I^- , Br^- , and Cl^- , and a lowest slope for ClO_4^- which is about the order expected for the decreasing polarizability of anion. The data for r_1^- show the greatest deviations, and this is expected both because distortions from spherical symmetry will be expected for I^- and because anion repulsions (in Li com-

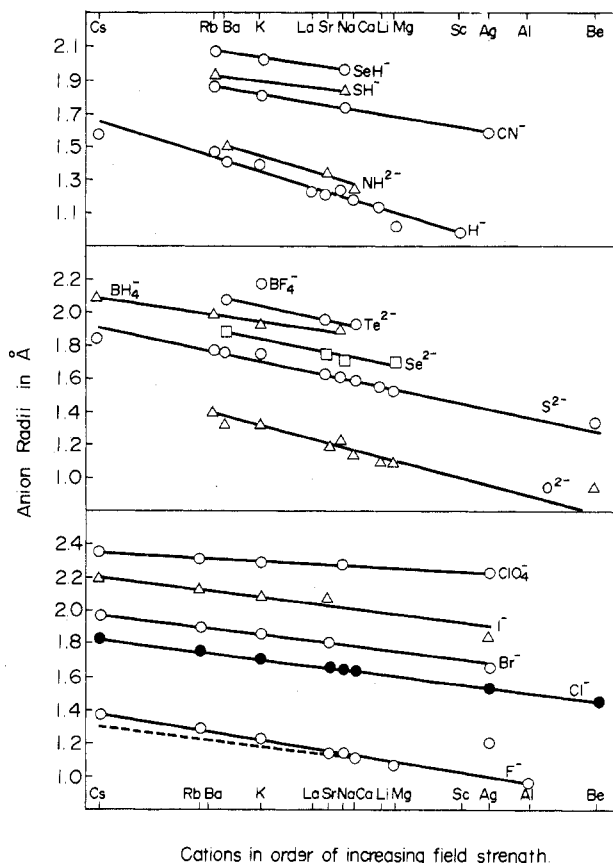


Figure 1. Variation of anion radii with effective positive field of cations.

Table III. Ionic Radii for Anions in Spherical Symmetric Surroundings

	$r_a, \text{\AA}$	
	Mean values ^a	Tosi and Fumi ^b
F^-	1.12	1.19
Cl^-	1.64	1.65
Br^-	1.79	1.80
I^-	2.02	2.01
O^{2-}	1.16	
S^{2-}	1.58	
Se^{2-}	1.74	
Te^{2-}	1.92	
ClO_4^-	2.26	
BF_4^-	2.1 ^c	
NO_3^-	2.0	
H^-	1.18	
CN^-	1.72	
NH_2^-	1.24	
SH^-	1.84	
SeH^-	1.96	
BH_4^-	1.88	

^a Taken from Figure 1 for the Na^+ salt. These are in close agreement with the anion values calculated by a least-squares method by P. A. Sysio, *Acta Crystallogr., Sect. B*, **25**, 2374 (1969).
^b Reference 20. ^c 2.18 \AA for K^+ salt.

pounds) can affect interionic distances. The larger slope for F^- compared to those of other halogens is evidence for the expansion of the more polarizable ions by F^- . The dotted line represents the corrected F^- radii and leads to an increase in r_{Cs^+} of 0.08 \AA (1.65 to 1.73 \AA in CsF). No correction appears necessary for other anions.

The variation in radius of anion with the strength of positive field of cation makes it possible to estimate ionic radii for anions when there is no contraction by cations, i.e.,

(21) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, **10**, 128 (1960); see also K. S. Chua, *Nature (London)*, **220**, 1317 (1968).

for "free" anions. This can be done by extrapolation of the straight lines in Figure 1 to zero field strength. However, it is necessary to find some means of representing a zero field strength. This would be the case at infinite interionic distance, and such an extrapolation of a plot of the variation of r_{Cl^-} with the reciprocal of interionic distance of halides gives a value of 2.3 Å for the radius of "free" Cl^- at zero value of (interionic distance) $^{-1}$. An extrapolation of the linear plot of r_{Cl^-} vs. work function of the corresponding metal to zero work function gives a value of 2.4 Å for the radius of "free" Cl^- . An average value of 2.35 Å will be taken as the radius of free Cl^- from these approximate determinations by extrapolation. The linear relations in Figure 1 make it possible to determine relative values of other free anions to a greater accuracy. These data are given in Table IV. It is assumed that expansion of the cations in the field of anions is very small and cation radii from Table II are taken as also representing "free" cation radii. Table IV gives the "free" ion radii and shows the ratios of radii of alkali ions to those of the corresponding rare gases (e.g., $\text{Na}^{11+}/\text{Ne}^{10+}$) are ~ 0.75 and those of alkaline earths (e.g., $\text{Mg}^{12+}/\text{Ne}^{10+}$) are ~ 0.65 . The ratios of corresponding anions are for halides (e.g., $\text{F}^{9+}/\text{Ne}^{10+}$) ~ 1.22 and for chalcogens (e.g., $\text{O}^{8+}/\text{Ne}^{10+}$) ~ 1.4 . The gradations provide a further check on the consistency of the ionic radii proposed in this paper.

Effective Positive Field Strength of Cations

The order of increasing positive field for cations in Figure 1 was based on their relative contraction of chloride ion. Since effective positive fields or polarizing power of cations is an important property, a more precise definition should be considered. The contraction in size of anions can be considered as resulting from an additional positive charge (ΔZ) added to the nuclear charge (Z) of the anion. This is a common practice in treating wave functions of orbitals and gives good results (see, e.g., ref 22). Thus, effective positive fields of cations in ionic crystals will be taken as represented by ΔZ , the additional charge on the neighboring anion which produces the contraction in size. ΔZ can be evaluated in terms of Δr as follows. The radius of free Cl^- is proportional to $1/Z$ and the radius in the presence of a cation is proportional to $1/Z + \Delta Z$. Thus

$$\frac{r(\text{free})}{r(\text{contracted})} \approx \frac{Z + \Delta Z}{Z} \quad (2)$$

This leads to the relation

$$\Delta Z \approx \Delta r/r(\text{contracted}) \quad (3)$$

where $\Delta r = r(\text{free}) - r(\text{contracted})$.

Effective positive fields (relative to Na^+) obtained from relation 3 are given in Table V. This provides experimental values for relative effective positive fields of cations which should be quantitatively applicable for spherically symmetrical environments of ions and qualitatively applicable to more general chemical comparisons. The absolute gradations agree very well with previous estimates²³ of effective positive field strength for Be^{2+} , Si^{4+} , Al^{3+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} based on molar refraction of oxide ion in the respective orthosilicates. The relative effective positive field strength (or polarizing power) can replace a parameter such as Z/r which only approximated the field strength of cations.

(22) D. P. Craig and E. A. Magnusson, *Discuss. Faraday Soc.*, **26**, 116 (1958).

(23) K. Fajans and N. J. Kreidl, *J. Amer. Ceram. Soc.*, **31**, 105 (1948).

Table IV. Comparison of Radii of Anions, Cations, and Rare Gases

	r_c , Å	r_c/RG^a	Rare gas radii, ^b Å	r_a/RG	r_a (for "free" anion) ^c
Li^+	0.92	0.60	He 1.53	1.70	H^- 2.6
Na^+	1.18	0.74	Ne 1.58	1.20	F^- 1.9 ^d
K^+	1.45	0.76	Ar 1.92	1.22	Cl^- 2.35
Rb^+	1.56	0.77	Kr 2.02	1.25	Br^- 2.53
Cs^+	1.68	0.75	Xe 2.24	1.23	I^- 2.76
Be^{2+}	0.69	0.45			
Mg^{2+}	1.02	0.64		1.55	O^{2-} 2.46
Ca^{2+}	1.26	0.66		1.40	S^{2-} 2.68
Sr^{2+}	1.38	0.68		1.33	Se^{2-} 2.80
Ba^{2+}	1.40	0.63		1.34	Te^{2-} 3.01

^a RG = rare gas radii. ^b Half the interatomic distance in crystals. ^c Obtained by extrapolation of data in Figure 1; see text. ^d Used r_a values corrected for cation expansion.

Table V. Relative Positive Field Strength of Cations^a

Cation	P	Cation	P
Be	1.44	Na	1.00
Al	1.33	Sr	0.98
Ti	1.33	La	0.96
Sc	1.20	K	0.87
Mg	1.20	Ba	0.81
Y	1.09	Rb	0.78
Li	1.06	Cs	0.67
Ca	1.04		

^a Based on data for chlorides; Δr for several cations obtained from graphs by interpolation. For comparison the P values for Ag^+ and Cu^+ are 1.27 and 1.74, respectively.

Discussion

An important feature of the ion core radii derived from experimental X-ray electron densities and relation 1 for intermetallic distances is that both r_c and k are subject to future experimental check and revision if necessary. It is possible that there may be minor variations of k within a group. However, experimental difficulties may prevent unambiguous determination of radii for all ions by X-ray diffraction measurements, so the present radii may represent the best values obtainable. Clearly the usual ionic radii represented arbitrary and incorrect division of interionic distances and should be replaced; a consistent set of empirical crystal radii¹⁰ is also of importance. The use of a different value for anion radii when in combination with cations with different positive fields is conceptually clear and has long been recognized as a necessity. The near constancy of the ratios of r_c to rare gas given in Table IV is a further indication of the consistency of the data.

The derivation of ionic radii in this paper was based on the assumption of spherical symmetry of anion and cation and of negligible interpenetration of their electronic systems. The small deviations from spherical symmetry have been already noted. Mutual interpenetration is indicated by appreciable electron density at the ion boundaries (electron density minima). However, in LiF and CaF_2 , where this occurs, the electron count around cation and anion still closely corresponds to the ideal value. Thus, for rare gas ions the degree of electron interpenetration does not interfere with a partition of ionic radii through use of the minimum in electron density between anion and cation. On the other hand, the large deformation and mutual interpenetration of electronic systems for a diatomic molecule makes ionic radii meaningless for these systems.

In metals the intermetallic distances represent distances between metal ion cores with large portions of the space for the electrons in binding regions between the cores; i.e., there is no physical significance to metallic radii other than

half the intermetallic distance. Similarly, the interatomic distance in covalent compounds represents distance between ion cores with relatively high electron density between them.²⁴ In this case half the interatomic distance represents a portion of the total electron density and clearly will depend on the nature of the second ion core. Thus, it is reasonable to speak of ion cores and electrons in covalent compounds, but partition into radii has no clear meaning when electrons are delocalized.

Ionic radii for rare earth, actinide, d¹⁰, and transition metal cations will be given in part II of this series.

Registry No. Li⁺, 17341-24-1; Na⁺, 17341-25-2; K⁺, 24203-36-9; Rb⁺, 22537-38-8; Cs⁺, 18459-37-5; Be²⁺,

(24) K. Fajans, *Chimia*, 13, 349 (1959).

22537-20-8; Mg²⁺, 22537-22-0; Ca²⁺, 14127-61-8; Sr²⁺, 22537-39-9; Ba²⁺, 22541-12-4; B³⁺, 22537-21-9; Al³⁺, 22537-23-1; Sc³⁺, 22537-29-7; Y³⁺, 22537-40-2; Lu³⁺, 22541-24-8; Si⁴⁺, 22537-24-2; Ti⁴⁺, 16043-45-1; Zr⁴⁺, 15543-40-5; Hf⁴⁺, 22541-25-9; V⁵⁺, 22537-31-1; Nb⁵⁺, 22537-41-3; Ta⁵⁺, 22541-26-0; Cr⁶⁺, 18540-29-9; Mo⁶⁺, 16065-87-5; W⁶⁺, 22541-27-1; F⁻, 16984-48-8; Cl⁻, 16887-00-6; Br⁻, 24959-67-9; I⁻, 20461-54-5; O²⁻, 16833-27-5; S²⁻, 18496-25-8; Se²⁻, 22541-48-6; Te²⁻, 22541-49-7; ClO₄⁻, 14797-73-0; BF₄⁻, 14874-70-5; NO₃⁻, 14797-55-8; H⁻, 12184-88-2; CN⁻, 57-12-5; NH₂⁻, 32323-01-6; SH⁻, 15035-72-0; SeH⁻, 16661-43-1; BH₄⁻, 16971-29-2.

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Electrochemistry and Boron-11 Nuclear Magnetic Resonance Spectra of Monocarbon Carboranes

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The electrochemistry and 80.5-MHz ¹¹B nmr spectra of the monocarbon carboranes B₁₁CH₁₂⁻, B₁₀CH₁₁⁻, B₁₀CH₁₃⁻, and B₉CH₁₀⁻ have been investigated. It has been found that B₉CH₁₀⁻ undergoes a one-electron oxidation to yield the coupled product B₁₈C₂H₁₈²⁻ in high yield. The 80.5-MHz ¹¹B nmr spectrum of B₁₀CH₁₁⁻ has been found to exhibit doublets in the ratio of 1:5:4 which is incompatible with the previously proposed structure. An alternative structure for B₁₀CH₁₁⁻, based on the ¹¹B nmr spectrum, is proposed and a possible mechanism for facile rearrangements in 11-particle polyhedra is discussed.

Introduction

The polyhedral borane ions B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ have been found to undergo a variety of reactions with oxidizing agents. The aqueous chemical oxidation of B₁₀H₁₀²⁻ was found to produce B₂₀H₁₈²⁻, the result of a two-electron oxidation per B₁₀ unit.¹⁻⁵ Under milder conditions, it was also possible to isolate B₂₀H₁₉³⁻ in good yield, the result of a one-electron oxidation of B₁₀H₁₀²⁻.^{1,4,5} The electrochemical oxidation of B₁₀H₁₀²⁻ has been characterized as an initial one-electron transfer, followed by a homogeneous chemical reaction to yield B₂₀H₁₉³⁻. The B₂₀H₁₉³⁻ ion can undergo a further two-electron oxidation to give B₂₀H₁₈²⁻.⁶ The B₁₂H₁₂²⁻ ion undergoes a one-electron electrochemical oxidation in acetonitrile to yield B₂₄H₂₃³⁻.⁷

In the recent past, carboranes which contain only one carbon atom in the polyhedral structure have been reported. They can be considered to be members of the B_nCH_{n+2} or

the B_nCH_{n+4} series, or anions derived therefrom by H⁺ removal. The former series includes B₅CH₇^{8,9} and its ion B₅CH₆⁻⁹ and the ions B₉CH₁₀⁻¹⁰, B₁₀CH₁₁⁻¹¹ and B₁₁CH₁₂⁻¹⁰. The latter series includes B₅CH₉¹² and the ions B₁₀CH₁₃⁻¹⁰ and B₁₀CH₁₁^{3-,13,14}.

We have undertaken a study of the nature of the electrochemical behavior of the monocarbon carboranes B₉CH₁₀⁻, B₁₀CH₁₁⁻, B₁₀CH₁₃⁻, and B₁₁CH₁₂⁻ to determine whether the redox chemistry of the polyhedral borane ions could be extended to the monocarbon carborane species.

Results and Discussion

B₁₁CH₁₂⁻. The 80-MHz ¹¹B nmr spectrum of CsB₁₁CH₁₂ in acetonitrile exhibited three doublets at +7.0, +13.1, and +16.0 ppm (vs. BF₃·Et₂O) in the ratio of 1:5:5, which clearly supports an icosahedral geometry as previously proposed.¹⁰ The cyclic voltammetry of CsB₁₁CH₁₂ in acetonitrile indicated no oxidation waves to the anodic limit of the solvent system (see Table I).

B₁₀CH₁₃⁻. The 80.5-MHz ¹¹B nmr spectrum of Cs[7-

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