

Ionicity-Effective Radius Diagram of Tl^I

N. JOUINI

*Laboratoire de Chimie des Solides, U.A. 279, 2, rue de la Houssinière, F. 44072 Nantes Cedex; and Laboratoire de Chimie du Solide, Ecole Nationale d'Ingénieurs de Gabès, Route de Medenine, Gabes, Tunisie**

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The evolution of the effective radii of alkali-metals and pseudo-alkali-metals (K, . . .) as a function of ionicity is discussed. In agreement with the hypothesis of Shannon and Prewitt, these radii are seen to be practically independent of ionicity for the alkali-metals. Thallium(I) distinguishes itself by an evolution of the effective radius as a function of ionicity for a given coordination number. The relatively abundant structural data for the halogen compounds ABX_3 , A_4BX_6 , A_2BX_4 . . . ($X = \text{Cl, Br, I}$; $A =$ bulky alkali-metal or pseudo-alkali-metal; $B = +2$ transition element) have enabled the determination of the Tl^I effective radius for a given coordination number and ionicity f_{A-X} , and the establishment of an ionicity-effective radius diagram for this cation. This diagram forms a coherent set which enables the calculation "a priori" of Tl-X interatomic distances in different compounds by the application of the rule of addition of effective radii stated by Shannon and Prewitt for oxides and fluorides. © 1986 Academic Press, Inc.

Introduction

The notion of effective ionic radii was introduced by Prewitt and Shannon (1, 2). These radii, which are determined empirically, form a coherent set and thus allow the calculation "a priori" of interatomic distances in solid fluorides and oxides.

In order to determine the effective ionic radii, which may vary according to coordination (from 0 to 0.3 Å) and state of spin (0.1 Å), Prewitt and Shannon assumed the following:

- (1) Ionic radii are additive: $d_{AC} = R_A + R_C$.
- (2) The effect of covalency is similar for all A-F or A-O bonds.
- (3) Radii are independent of structure.
- (4) Radii vary with coordination number.

- (5) The average cation-anion distance in similar polyhedrons is the same, even if, for a given polyhedron, these distances are not all equal.
- (6) For the same anion, the unit cell volume of a compound in a particular isostructural series is proportional to its cationic volume.

Several thousand average distances used by the authors cited above were obtained from over 700 structural determinations of oxygen or fluorine compounds with various cations.

The substantial number of structural determinations of ternary compounds ABX_3 , A_2BX_4 , A_4BX_6 ($X = \text{Cl, Br, I}$; $A =$ bulky alkali-metal or pseudo-alkali-metal; $B = +2$ transition metal ion) presently available enables effective ionic radii which allow for the effects of covalency to be determined.

* Permanent address.

Ionicity Effect

The ionicity (or percentage ionic character) of an $A-X$ bond is defined by Pauling (3) as

$$f(A-X) = 1 - \exp[-\frac{1}{4}(\chi_A - \chi_X)^2]$$

In this equation, χ_A and χ_X are, respectively, the electronegativity of A and X element. Some $A-X$ bond ionicities are listed in Table I. Shannon and Prewitt proposed that the effect of ionicity on the effective ionic radii is similar for all oxides and fluorides. However, there should be an apparent difference in ionic radius in cases where the $A-X$ bond ionicity is lower than that of the $Tl-O$ bond (0.51): that is to say, in $Tl-Cl$, $Tl-Br$, and $Tl-I$ bonds. The object of this work is to see whether the experimental results confirm such an effect. It should be noted that the effective ionic radii given by Prewitt and Shannon for Tl^I are for coordination numbers higher than 6 and thus correspond to compounds where this ion acts as a pseudo-alkali-metal. Many studies carried out on thallium-oxygen compounds have shown that lower coordination numbers correspond to a higher degree of polarization of this cation. The halogen compounds discussed here display high coordination numbers, namely, 8, 9, and 12.

Experimental Results

For each structure and for each anion, the compounds of known crystal structure

TABLE I
Z-X BOND IONICITIES

$f(A-X)$	F	O	Cl	Br	I
Cs	0.93	0.86	0.73	0.67	0.56
Rb	0.92	0.84	0.70	0.63	0.51
K	0.92	0.84	0.70	0.63	0.51
Tl	0.70	0.51	0.30	0.21	0.11

TABLE II
STRUCTURAL DATA FOR ABX_3 COMPOUNDS WITH
2L STRUCTURE^a

Compound	A	a (Å)	c (Å)	Z	V (Å ³)	Ref.
ANiCl ₃	Cs	7.170	5.941	2	264.5	(4)
	Rb	6.954	5.906	2	247.3	(4)
	NH ₄	6.921	5.915	2	245.4	(4)
	Tl	6.863	5.887	2	239.9	(4)
ACoCl ₃	K	6.90	11.27	4	464.6	(4)
	Cs	7.202	6.032	2	270.9	(4)
	Rb	6.999	5.996	2	254.4	(4)
	NH ₄	6.967	6.010	2	252.6	(4)
AFelCl ₃	Tl	6.907	5.981	2	247.1	(4)
	K	6.870	6.091	2	248.9	(4)
	Cs	7.237	6.045	2	274.2	(4)
	Rb	7.060	6.020	2	259.8	(4)
AVCl ₃	NH ₄	7.019	6.058	2	258.5	(4)
	Tl	6.976	6.008	2	253.2	(4)
	K	7.00	5.80	2	246.1	(5)
	Cs	7.23	6.03	2	273.0	(6)
AVBr ₃	Rb	7.04	6.00	2	257.5	(6)
	NH ₄	7.00	6.00	2	254.6	(7)
	Tl	6.96	5.97	2	250.4	(8)
	K	6.90	5.98	2	246.6	(4)
AFelBr ₃	Cs	7.56	6.32	2	312.8	(6)
	Rb	7.432	6.297	2	301.1	(9)
	Tl	7.283	6.247	2	287.1	(9)
AMnBr ₃	Cs	7.51	6.315	2	308.5	(10)
	Rb	7.38	6.28	2	296.2	(10)
	Tl	7.185	6.23	2	278.5	(11)
AMgBr ₃	Cs	7.618	6.519	2	327.6	(12)
	Rb	7.462	6.543	2	315.5	(12)
AMgBr ₃	Cs	7.60	6.50	2	325.1	(13)
	Rb	7.44	6.53	2	313.1	(13)

^a BX_6 octahedrons form infinite chains along the c axes of the hexagonal lattice by sharing faces. A^+ coordination number 12.

are given in Tables II–VI. The listings for a given structure type correspond to decreasing unit cell volume.

In order to give an overall view, the normalized volume as a function of the nature of the alkali cation is shown in Fig. 1. The abscissa is arbitrary. In each series, normalization is obtained by allocating a value of 1 to the largest unit cell volume. The point representing K_2CoBr_4 is anomalous: the data available for this compound is ob-

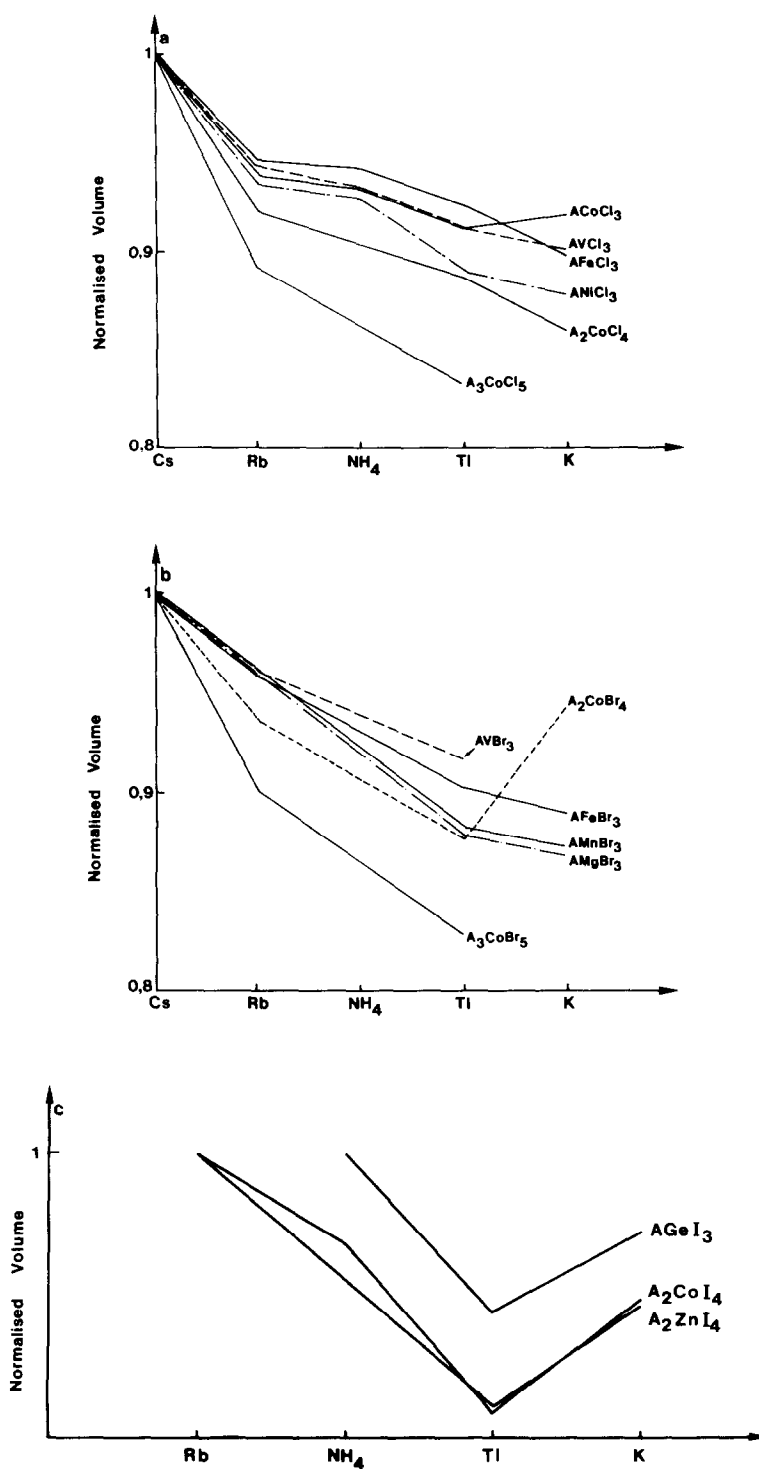


FIG. 1. Normalized volume as a function of the cation.

TABLE III
STRUCTURAL DATA FOR ABX_3 COMPOUNDS WITH
 NH_4CdCl_3 STRUCTURE^a

Compound	A	a (Å)	b (Å)	c (Å)	Z	V (Å ³)	Ref.
AMnBr ₃	Tl	9.383	4.039	15.27	4	578.7	(14)
	K	9.185	4.026	15.48	4	572.4	(12)
AMgBr ₃	Tl	9.38	3.98	15.30	4	571.2	(13)
	K	9.29	4.03	15.08	4	564.4	(13)
AGeI ₃	NH ₄	10.244	4.510	16.656	4	769.5	(15)
	K	10.129	4.499	16.443	4	749.3	(15)
AFeBr ₃	Tl	10.066	4.414	16.359	4	726.9	(16)
	K	9.22	4.00	14.9	4	549.5	(17)

^a BX_6 octahedrons form infinite double chains by sharing edges. A^+ has tricapped coordination in X (coordination number 9).

viously incorrect because it results in K_2CoBr_4 having a unit cell volume larger than that of Rb_2CoBr_4 .

Whatever the structure or the nature of the halide ion, when the A^+ cation is either an alkali-metal or ammonium the unit cell volume of the compound varies according to the sequence

$$V(K) < V(NH_4) < V(Rb) < V(Cs).$$

The position of thallium in this series depends on the halide ion. When $X = Cl$ (the only exception being $KCoCl_3$) or $X = Br$,

$$V(K) < V(Tl) < V(Rb)$$

or, when $V(NH_4)$ is known,

TABLE V
STRUCTURAL DATA FOR A_2BX_4 COMPOUNDS WITH
 $\beta-K_2SO_4$ STRUCTURE^a

Compound	A	a (Å)	b (Å)	c (Å)	Z	V (Å ³)	Ref.
A_2CoCl_4	Cs	9.737	7.392	12.972	4	933.7	(18)
	Rb	9.272	7.283	12.723	4	859.2	(18)
	Tl	9.131	7.182	12.632	4	828.4	(18)
A_2CoBr_4	K	8.933	7.240	12.421	4	803.3	(18)
	Cs	10.181	7.723	13.492	4	1060.8	(18)
	Rb	9.718	7.651	13.371	4	994.2	(18)
	Tl	9.424	7.52	13.14	4	931.2	(18)
K	9.61	7.77	13.43	4	1002.8	(18)	

^a Orthorhombic symmetry. BX_4 tetrahedrons isolated. A^+ coordination number 9.

$$V(K) < V(Tl) < V(NH_4).$$

The sequence for ternary iodides is always

$$V(Tl) < V(K).$$

This indicates that covalency has an important effect on the radius of the thallium ion. This study aims to quantify this relationship by expressing the effective radius of thallium in terms of the halide ion and coordination number. For a given halide ion X , the effects of covalency shall be assumed to be similar for all $A-X$ bonds when A is an alkali-metal. This hypothesis is substantiated by ionicity calculations.

TABLE IV
STRUCTURAL DATA FOR A_3BX_5 COMPOUNDS WITH
 Cs_3CoCl_5 STRUCTURE^a

Compound	A	a (Å)	c (Å)	Z	V (Å ³)	Ref.
A_3CoCl_5	Cs	9.219	14.554	4	1236.9	(18)
	Rb	8.799	14.239	4	1102.4	(18)
	Tl	8.431	14.497	4	1030.4	(18)
A_3CoBr_5	Cs	9.643	15.127	4	1406.6	(18)
	Rb	9.239	14.875	4	1269.7	(18)
	Tl	8.747	15.232	4	1165.4	(18)

^a Quadratic symmetry. BX_4 tetrahedrons isolated. A^+ coordination numbers 8 and 10.

TABLE VI
STRUCTURAL DATA FOR A_2BX_4 COMPOUNDS WITH
 Sr_2GeS_4 STRUCTURE^a

Compound	A	a (Å)	b (Å)	c (Å)	β (°)	Z	V (Å ³)	Ref.
A_2CoI_4	Rb	10.384	8.144	7.657	109.8	2	609.3	(18)
	NH ₄	10.166	8.101	7.603	109.5	2	590.2	(18)
	K	9.677	8.09	7.702	108.4	2	572.1	(18)
	Tl	9.762	7.972	7.519	108.9	2	553.6	(18)
A_2ZnI_4	Rb	7.642	8.176	10.371	109.84	2	609.5	(19)
	NH ₄	7.745	8.121	9.665	109.24	2	577.4	(19)
	K	7.548	7.997	9.730	109.00	2	555.3	(19)
	Tl	7.471	7.967	9.827	109.57	2	551.1	(19)

^a Monoclinic symmetry. BX_4 tetrahedrons isolated. A^+ coordination number 6 + 2.

Determination of the Tl^I Effective Ionic Radius

Method of Determination

Several different structures, in which thallium(I) adopts coordination numbers of 8, 9, and 12 have been evaluated. The procedure is as follows:

(1) For a given structure, the function $V^{1/3} = f(R_{A+})$ is given for each series of compounds, the series being classed by halide ion and transition metal ion. The R_{A+} value used is the Prewitt and Shannon effective ionic radius of the alkali-metal taking into account its coordination number. $V^{1/3} = f(R_{A+})$ is not linear, and for each series only a few experimental points (maximum of four) are available (see Tables II–VI). The curves given in Fig. 2 are accordingly drawn as curves of best fit.

(2) For each series, the effective radius of thallium can be determined from the unit cell volume of the thallium compound and the curves given in Fig. 2. For each coordination number, the average of all values obtained is then determined.

The radius of NH_4^+ , which is not given by Prewitt and Shannon, was determined by the above method using data relative to 2L type ABX_3 compounds where the ammonium compound is known. The value obtained (1.70 Å) was then used to determine the effective radius of Tl^I , the systematic variation of radius values with coordination number being taken into account. As in the case of the alkali-metals, the NH_4^+ radius was assumed to be independent of covalency.

In certain cases difficulties arose due to the lack of suitable data. This concerned the following:

(1) $AGeI_3$ and A_2ZnI_4 phases. Apart from thallium compounds, only the ammonium and potassium compounds of the former, and the rubidium and potassium compounds of the latter, are known. The general form of the curves given in Fig. 2 shows

that a good approximation of the effective radius of thallium can be obtained by a 1% increase in the value obtained by linear interpolation.

(2) The $AMnBr_3$ and $AMgBr_3$ series, involves a phase change: the cesium and rubidium compounds are hexagonal (coordination number 12) whereas the thallium and potassium compounds have the NH_4CdCl_3 structure (coordination number 9). This difficulty was resolved by observing that when a compound (e.g., $KFeCl_3$) exists as two allotropic forms, each one having a different structure, the ratio of the unit cell volumes of the two phases is 1/2. The volume of the hypothetical $ABBr_3$ phase ($A = Cs, Rb; B = Mn, Mg$) of the NH_4CdCl_3 structure is calculated on this basis.

Results and Discussion

The effective radii calculated for thallium(I) in chlorides, bromides, and iodides are given in Table VII and can be compared with those obtained by Prewitt and Shannon for thallium in oxides and fluorides. The values in brackets correspond to coordination numbers of thallium(I) with the corresponding ligand in phases which are as yet unknown. These values are calculated from the assumption of Prewitt and Shannon, and which has since been experimentally verified, that ionic radius varies regularly with coordination number. As well as showing the relationship between effective radius and coordination number,

TABLE VII
EFFECTIVE RADIUS OF Tl^I (Å)

Coordination number: Ion	8	9	12
O^{2-}, F^-	1.59	1.63	1.70
Cl^-	[1.55]	1.59	1.67
Br^-	[1.51]	1.55	1.65
I^-	1.46	1.50	[1.63]

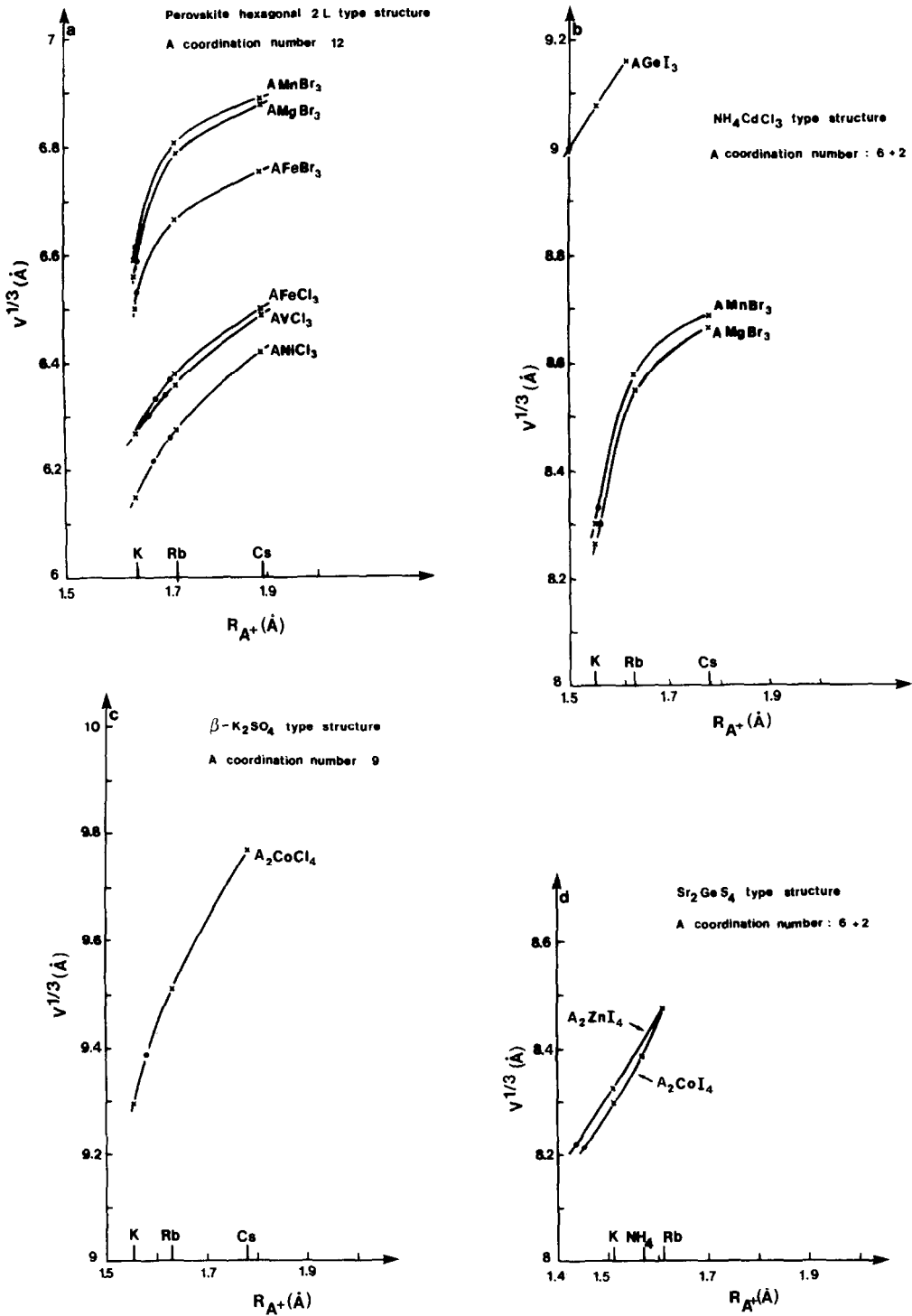


FIG. 2. Variation of the cube root of volume with the alkali ionic radius.

for a given ionicity, this classification allows the ionicity-effective radius diagram of Tl^I for a given coordination number to be established (Fig. 3). When the covalency of the $Tl-X$ bond increases (decreasing ionicity), the Tl^I effective radius decreases. This behavior constitutes an essential difference between thallium(I) and the alkali-metals and could be due to the high polarizability of Tl^I (5.11 \AA^3).

This difference can show itself in two ways.

—The thallium compound has the same structure as that of the alkali-metals: its relative unit cell volume is a function of the $Tl-X$ bond ionicity. When the latter increases so does the former.

—The thallium compound can adopt a structure which is different to that of the corresponding alkali-metal compounds. For example, in ABX_3 compounds: in the case of alkali-metal compounds the particular structure which they adopt depends essentially on the ratio R_{A^+}/R_{X^-} and is minimally affected by the $A-X$ bond ionicity. For thallium, the determination of the ef-

fective radius shows that the particular structure adopted is directly related to the $Tl-X$ bond ionicity.

Conclusions

The determination of the effective radius of Tl^I constitutes a means of quantification of covalency. The radii thus determined are consistent with the rule of additivity of radii, whatever the degree of covalency, in the calculation of interatomic distances. The anionic radii of Prewitt and Shannon used in these calculations are practically independent of the coordination number ($R_{Cl^-} = 1.81 \text{ \AA}$, $R_{Br^-} = 1.96 \text{ \AA}$, and $R_{I^-} = 2.2 \text{ \AA}$).

The $Tl-X$ distances (D) calculated by this method are in good agreement with those established by structural determination (d) (Table VIII). The average d/D is of the order of 1 (0.95) and the corresponding deviation is 7×10^{-3} .

In conclusion, the effective radii of Tl^I form a coherent set for the calculation of $Tl-X$ bond distances ($X = Cl, Br, I$) in high

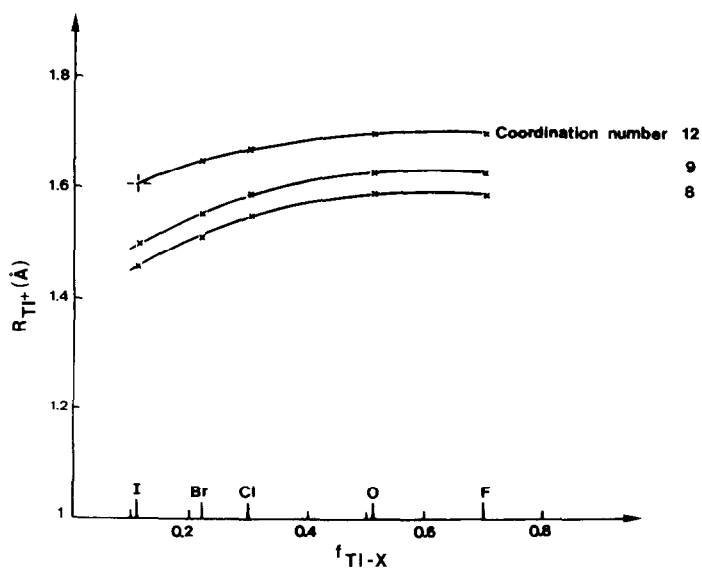


FIG. 3. Tl^I ionicity-effective radius diagram.

TABLE VIII
 Tl-X INTERATOMIC DISTANCES (Å)

Compounds	d_{Tl-X}	$D = R_{Tl^+} + R_{X^-}$	Coordination number	d/D
TlCl	3.32	3.36	8	0.988
TlBr	3.44	3.47	8	0.991
TlI α	3.64	3.66	8	0.995
TlPbI ₃	3.67	3.66	8	1.002
Tl ₄ PbI ₆	3.66	3.66	8	1.000
Tl ₄ HgI ₆	3.63	3.66	8	0.992
Tl ₄ HgBr ₆	3.46	3.51	8	0.986
Tl ₄ CrI ₆ α	3.62	3.66	8	0.989
TlMnI ₃	3.72	3.70	9	1.005
TlFeBr ₃ β	3.47	3.51	9	0.989
TlCdI ₃	3.72	3.70	9	1.005
TlGeI ₃	3.71	3.70	9	1.003
TlFeI ₃	3.69	3.70	9	0.996
TlFeCl ₃	3.49	3.48	12	1.003
TlCoCl ₃	3.45	3.48	12	0.991
TlNiCl ₃	3.43	3.48	12	0.986

coordination number Tl^I compounds while overcoming the problem of covalency.

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