Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

Heats of Formation and Crystal Structures of Some Group 3 Tetrahalides. N[MX_4](c) (N = Cs or Na, M = Al or Ga, and X = Cl or Br) and [$(C_6H_5)_4As$][MCl_4](c) (M = Ga or In). Donor–Acceptor Bond Energies for MX_3–X^- where M = Al, Ga, or In, and X = Cl or Br

RICHARD C. GEARHART, Jr., JAMES D. BECK, and ROBERT H. WOOD*

Received March 14, 1975 AIC50193T

The heats of formation, crystal structure, lattice energies, and donor–acceptor bond energies for some N[MX_4] salts (N = Na or Cs; M = Al or Ga; X = Cl or Br) have been determined. The salts $CsAlCl_4$, $CsGaCl_4$, $CsAlBr_4$, and $CsGaBr_4$ are all isomorphous with $BaSO_4$ (space group *Pnma*, four molecules per unit cell). Their heats of formation (ΔH_f, salt (c)) are as follows: $CsAlCl_4$ (−292.0 kcal/mol), $CsGaCl_4$ (−252.0 kcal/mol), $CsAlBr_4$ (−239.4 kcal/mol), and $CsGaBr_4$ (−203.4 kcal/mol). The lattice energies of these salts are: $CsAlCl_4$ (120 kcal/mol), $CsGaCl_4$ (119 kcal/mol), $CsAlBr_4$ (115 kcal/mol), and $CsGaBr_4$ (116 kcal/mol). The bond dissociation energies $D(MX_3–X^-)$ for the four anions are: $AlCl_3–Cl^-$ (87 ± 7 kcal/mol), $GaCl_3–Cl^-$ (87 ± 7 kcal/mol), $AlBr_3–Br^-$ (80 ± 7 kcal/mol), and $GaBr_3–Br^-$ (75 ± 7 kcal/mol). There is apparently little difference in the donor–acceptor properties between these group 3 metal trihalides and the respective halide ligands. A new method of estimating donor–acceptor energies for $MX_3–X^-$ has been developed using the fact that the tetraphenylarsonium salts are structurally isomorphous and have low lattice energies due to the large cation. The compounds [$(C_6H_5)_4As$]I and [$(C_6H_5)_4As$][$GaCl_4$] were used to calibrate the method and measurements on [$(C_6H_5)_4As$][$InCl_4$] were used to derive a value for the bond dissociation energy $D(InCl_3–Cl^-)$ = 98 ± 10 kcal/mol. The method appears promising.

Introduction

Most of the studies of donor–acceptor bond energies are limited to complexes with no net charge because of the difficulty of correcting for the lattice energy of ionic solids. With the help of digital computers these calculations can be made but they still are quite limited in application since crystal structures for all of the compounds must be known. The present paper reports some new results for chloride and bromide ion donor–acceptor energies with a series of group 3 halides. In addition a method for avoiding the tedious calculations is proposed. The method is based on the fact that the tetraphenylarsonium salts of the group 3 tetrahalides have isomorphous crystal structures with very little variation in the lattice constants. The method must be calibrated with known compounds and this is reported in the present paper.

The details of the experimental procedure have been described elsewhere[1,2] so only a brief description will be given here. Final purification of all compounds was by zone melting. In addition, fractional freezing using an apparatus similar to that described by Gunn[3] was used for purity determinations of the samples. Compounds were made by standard techniques. In all cases fractional freezing showed that the impurities were less than 0.2%. The quantitative analysis of all samples was satisfactory. Tetraphenylarsonium salts of the tetrachlorogallate and tetrachloroindate ions were made by adding solid tetraphenylarsonium chloride to $GaCl_3$ or $InCl_3$ in concentrated hydrochloric acid forming the insoluble product. Satisfactory analyses were obtained for these compounds.

A 250 ml dewar calorimeter[1,4] and an LKB batch microcalorimeter[5,6] were used in this study.

Heats of Formation

The results of the heat of solution measurements with the dewar calorimeter at 25° are given in Table I. The heats of solution of the alkali halides and group 3 halides are in reasonable agreement with literature values considering the differences in solvents used.[1] From the heats of solution given in Table I, together with heats of formation of the alkali halides and group 3 halides taken from standard sources,[7–10] the heats of formation of the crystalline alkali metal tetrahalides can be calculated. The results are also given in Table I.

The heats of solution of the tetraphenylarsonium salts listed in Table I have a higher standard deviation because of the slow rate of solution for these salts (complete solution took from 30 to 60 min). The heat of solution of tetraphenylarsonium tetrachlorogallate could not be measured directly since the rate of solution was even slower. Instead, the heat of solution of tetraphenylarsonium tetrachlorogallate in anhydrous acetonitrile was measured in the LKB batch microcalorimeter. The resulting solution was removed from the calorimeter and its heat of solution in 1.021 mol/l. HCl was measured in a dewar calorimeter. A third experiment measured the heat of solution of anhydrous acetonitrile into a solution of tetraphenylarsonium tetrachlorogallate in HCl to produce the same final solution as obtained in the previous two experiments. Combining these results in a simple thermochemical cycle gives the heat of solution of the solid tetraphenylarsonium tetrachlorogallate in 1.02 mol/l. HCl. The resulting heat of solution for three separate experiments was 19.8 ± 0.8 kcal/mol.

Table I shows that the heat of solution measurements for cesium tetrabromoaluminate fall into two strikingly different classes depending on the sample used. Samples I, IV, and V gave −66.7 ± 0.4 kcal/mol while samples II and III gave −40.9 ± 0.5 kcal/mol. It is believed that the result for samples I, IV, and V is correct and that samples II and III contained excess cesium bromide. This choice of value is based on the fact that the analysis for sample III was not as good (calcd.: Al, 5.6; Br, 66.6. Found: Al, 5.4; Br, 64.9) and sample II was not analyzed. The phase diagram[11,12] for the CsBr, $AlBr_3$ system shows a eutectic at 52.5% CsBr which could have formed if a slight excess of cesium bromide had been used in one of the samples. Further calculations of the bond energies using both results show that the values obtained from samples II and III do not fit in with the regular trend expected for the donor–acceptor bond energies.[1]

Lattice Energy Calculations and Crystal Structures of NMX_4

The lattice energies were calculated by modification of the equation of Ladd and Lee.[13] For salts of polyatomic anions this equation must be modified because the polyatomic anion is not a point charge but an array of point charges. This means the Madelung constant for separation of the anion from the cation is now a function of the cube root of the molecular volume (δ).[2] A second modification is necessary because we have expressed the Madelung constant as a function of δ rather than r_0, the nearest neighbor distance between the center of the anion and the center of the cation. The derivation of the

Table I. Heats of Solution of Various Substances at 25°

Substance	Amount,[a] mmol	Solvent[b]	N[c]	ΔH soln, kcal/mol	$\Delta H_f°$,[f] kcal/mol
CsCl(c)	4–7	0.103 mol/l. HCl	4	4.22 (0)[d]	
	4–5	1.02 mol/l. HCl	3	4.06 (1)	
CsBr(c)	7–9	0.092 mol/l. HBr	3	6.25 (0)	
	6–10	1.01 mol/l. HBr	3	5.89 (1)	
$AlCl_3$(c)	0.8–2.4	0.103 mol/l. HCl	6	−78.6 (1)	
$GaCl_3$(c)	0.7–0.9	1.02 mol/l. HCl	5	−44.2 (2)	
$AlBr_3$(c)	0.6–1.9	0.092 mol/l. HBr	10	−92.0 (2)	
$GaBr_3$(c)	0.9–1.3	1.01 mol/l. HBr	5	−42.3 (1)	
$NaAlCl_4$(c)	0.6–1.4	0.103 mol/l. HCl	11	−71.5 (2)	−272.5[g]
$CsAlCl_4$(c)	0.8–1.3	0.103 mol/l. HCl	8	−54.5 (1)	−292.0
$NaGaCl_4$(c)	0.9–1.3	1.02 mol/l. HCl	8	−33.3 (1)	−233.6
$CsGaCl_4$(c)	0.7–1.0	1.02 mol/l. HCl	8	−17.0 (1)	−252.0
$NaAlBr_4$(c)	0.3–0.6	0.092 mol/l. HBr	8	−83.4 (1)	−220.7
$CsAlBr_4$(c)	0.5–1.0	0.092 mol/l. HBr	8	−66.7 (4)[e]	−239.4
			3	−40.9 (5)[e]	
$NaGaBr_4$(c)	0.5–0.8	1.01 mol/l. HBr	8	−36.0 (0)	−184.8
$CsGaBr_4$(c)	0.3–0.6	1.01 mol/l. HBr	8	−19.7 (1)	−203.4
$[(C_6H_5)_4As]I$(c)	0.2–0.4	Water	3	6.9 (2)	
$[(C_6H_5)_4As]InCl_4$(c)	0.3–0.4	1.021 mol/l. HCl	6	−2.2 (2)	

[a] Range of sample sizes used. [b] In all cases 250 g of solvent were used. The 250 ml dewar calorimeter was used in all experiments. [c] Number of determinations. [d] The number in parentheses is the average deviation of the last digit for all experiments. [e] Samples I, IV, and V gave −66.7 kcal/mol. Samples II and III gave −40.9 kcal. [f] Heat of formation calculated from the heats of solution and data from Wagman et al.,[7] Rossini et al.,[8] and Coughlin[10] ($AlCl_3$). [g] Rossini et al.[8] find $\Delta H_f° = -270.6$ from the heats of solution measurements of E. Baud, *Ann. Chim. Phys.*, **1**, 8 (1904).

Table II. Lattice Parameters of the Cesium Group 3 Tetrahalides

Salt	a_0, Å	b_0, Å	c_0, Å
$Cs[GaCl_4]$	11.66	7.16	9.41
$Cs[AlCl_4]$	11.83	7.16	9.13[a]
$Cs[GaBr_4]$	12.15	7.48	9.88
$Cs[AlBr_4]$	12.18	7.50	9.89

[a] Value calculated from cone-axis photograph; all other lattice parameter values obtained from zero-level precession photographs ($\mu = 30°$, $\lambda = Mo_{K\alpha}$). The standard deviation of the lattice parameter measurements is estimated to be 0.2%.

Table III. Final Atomic Parameters for $Cs(GaBr_4)$ Fractional Coordinates

Atom	x[a]	y[b]	z
Cs	0.1810 (10)	$^1/_4$	0.173 (4)
Ga	0.0677 (30)	$^1/_4$	0.692 (11)
Br(1)	−0.0925 (20)	$^1/_4$	0.575 (6)
Br(2)	0.215 (20)	$^1/_4$	0.555 (7)
Br(3)	0.0825 (9)	0.0054 (13)	0.825 (3)

[a] The estimated standard deviation of the last digit is given in parentheses. [b] The y coordinates of Cs, Ga, Br(1), and Br(2) are fixed by symmetry.

Table IV. Final Atomic Parameters for $Cs(GaCl_4)$ Fractional Coordinates

Atom	x	y	z
Cs	0.1800 (4)	$^1/_4$	0.167 (1)
Ga	0.0712 (7)	$^1/_4$	0.692 (1)
Cl(1)	−0.0920 (25)	$^1/_4$	0.584 (3)
Cl(2)	0.2140 (25)	$^1/_4$	0.552 (2)
Cl(3)	0.0805 (11)	0.0060 (18)	0.828 (1)

new equation involves differentiating the total lattice energy[13] with respect to δ and setting this equal to zero at the equilibrium interatomic distances. The result[2] is that the repulsive energy at 0°K ($U(\delta^{0°K})_{rep}$), is given by:

$$U(\delta^{0°K})_{rep} = -(\rho/r_0)[U_{coul} + e^2 \frac{\partial M_\delta}{\partial \delta} + 6U_{vdw}] \qquad (1)$$

U_{coul} is the coulomb energy, U_{vdw} is the van der Waals energy, and ρ is usual repulsion exponent.[4,13]

The lattice energies and van der Waals sums were calculated by the method of Wood.[14,15] The derivative of the Madelung constant with respect to molar volume was calculated by varying the molar volume by a small amount and calculating the change in the Madelung constant. Calculations were performed for various charge distributions on the anions. The correct result was taken as the average of the results with chloride ion charges of 0, −0.2, and −1.0 electron. The van der Waals energies were calculated in the same way as before.[4] The van der Waals sum (S_{ij}) for the Ga^+–Cl^- interaction reported previously[4] was found to be in error by a factor of 10. (The correct sum is 241.3, not 24.13.)

The $Cs(MX_4)$ salts, with M = Ga or Al and X = Cl or Br, all crystallize in the space group *Pnma* and are isomorphous with $BaSO_4$. The lattice parameters are given in Table II. The intensity data for $Cs(GaBr_4)$ were obtained using an integrating Weissenberg camera with Mo radiation. For the $Cs(GaCl_4)$ an integrating precession camera was used with Mo radiation. The film intensities were read with a densitometer. Appropriate absorption corrections were applied. For $Cs(GaBr_4)$, there were 131 observed and 66 systematically extinct reflections out of a total of 345 possible observations. The final structure gave an R for the observed reflections of 21%. For $Cs(GaCl_4)$, there were 399 observed and 83 systematically extinct reflections out of 1001 possible observations. The final structure gave an R for observed reflections of 12.6%. The final fractional coordinates for the two structures are given in Tables III and IV. The details of the structure solution are reported elsewhere.[2] In the lattice energy calculations, it was assumed that the aluminum compounds had the same fractional coordinates as their gallium analogs. The final values of the coulombic, van der Waals, repulsion, and total lattice energies are reported in Table V for various charge distributions on the anion. The best value is taken as the average of the values for the three charge distributions. The heat of formation of the gaseous anion is calculated in the usual way[4] and the results are given in Table VI. From this, the donor–acceptor bond energy for the gaseous anion is calculated and the results are given in Table VII together with values from previous studies. The estimated accuracy of the donor–acceptor bond energies is ±7–9 kcal/mol.

Bond Energies from Heats of Formation of Tetraphenylarsonium Salts

Because of the tedious nature of the previous calculations, and the fact that crystal structures need to be determined for

Table V. Lattice Energies

Salt	ϵ^a	$U_{\text{coul}}{}^b$	U_{vdw}	U_{rep}	$U_z{}^c$	U_{total}
Na(AlCl$_4$)	−1	−147.32	−14.0	+18.86	+1.0	−141.5
	−0.2	−133.40		+18.33		−128.1
	0	−132.73		+17.54		−129.2
Ga(GaCl$_4$)	−1	−131.45	−18.5	+23.57		−125.3
	−0.2	−127.46		+19.84		−126.1
	0	−124.86		+19.67		−123.6
Cs(GaCl$_4$)	−1	−116.23	−20.2	+20.41		−115.0
	−0.2	−119.74		+17.81		−121.1
	0	−119.44		+17.42		−121.2
Cs(AlCl$_4$)	−1	−117.08	−20.4	+20.72		−115.7
	−0.2	−120.32		+17.73		−122.0
	0	−120.13		+17.47		−122.1
Cs(GaBr$_4$)	−1	−111.82	−20.6	+19.21		−112.2
	−0.2	−114.49		+16.79		−117.3
	0	−114.11		+16.43		−117.2
Cs(AlBr$_4$)	−1	−111.62	−20.0	+18.78		−111.8
	−0.2	−114.25		+16.37		−116.8
	0	−113.87		+16.12		−116.7

[a] ϵ is the charge on the halide ion. [b] All energies are expressed in kcal/mol and are calculated at 0°K. [c] Estimated zero point energy.[2]

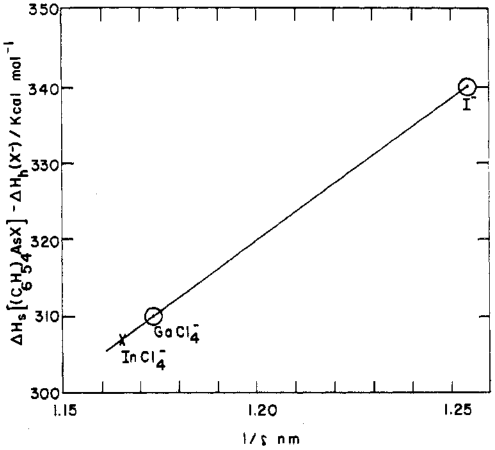

Figure 1. Enthalpies of solution of tetraphenylarsonium salts minus enthalpy of hydration of the anion $\Delta H_s[(C_6H_5)_4AsX(c)] - \Delta H_h(X^-)$ plotted vs. reciprocal of the cube root of the molecular volume ($1/\delta$). The points for $X^- = I^-$ and $GaCl_4^-$ are calibration points involving the known heats of solution and hydration. The point for $X^- = InCl_4^-$ is used to estimate the enthalpy of hydration of $InCl_4^-(g)$.

each new compound, an approximate method of obtaining donor–acceptor bond energies was developed.[2] The method uses a simple thermochemical cycle involving heats of solution and heats of hydration. The resulting equation is

$$[\Delta H_h(M^+) - U] = \Delta H_s(MX) - \Delta H_h(X^-) \qquad (2)$$

where U is the lattice energy of the salt MX, $\Delta H_h(M^+)$ and $\Delta H_h(X^-)$ are the heats of hydration of the M^+ and X^- ions, and $\Delta H_s(MX)$ is the heat of solution of MX(c) in water. For a series of salts with a common cation, the left side of eq 2 will vary as the lattice energy (approximately linearly as $1/\delta$). Thus, if the right side of eq 2 is plotted vs. $1/\delta$ for a series of known compounds the resulting graph will be a slightly curved line. To obtain the heat of hydration of a new cation all that is needed is to measure the heat of solution of the salt of that ion and its molecular volume. The calibration graph gives the left side of eq 1. The heat of solution is known so the heat of hydration of the anion is found. This leads by simple thermochemistry[2] to the heat of formation of the gas phase ion and to other quantities of interest. In order for this method to achieve any accuracy the compounds should be structurally isomorphous so that the lattice energy varies smoothly with $1/\delta$. In addition, it is helpful if the lattice energy is rather small and does not vary greatly as the size of the anion changes. The tetraphenylarsonium salts meet these criteria. The tetraphenylarsonium cation forms a number of structurally isomorphous MX_4^- salts (including the group 3 tetrahalides) and the large size of the cation lowers both the lattice energy of the salts and the change in the lattice constants with the size of the ions. Precession photographs of all of the tetraphenylarsonium salts showed that they belonged to space group $I\bar{4}$. Mooney[16] determined the crystal structure of tetraphenylarsonium iodide and Zaslow and Rundle[17] determined the crystal structure of tetraphenylarsonium tetrachloroferrate (space group $I\bar{4}$ with $A = 13.16$ Å and $C = 7.15$ Å). These two salts are isomorphous with a $FeCl_4^-$ ion replacing a I^- ion in the lattice. It seems safe to assume that all of the tetraphenylarsonium salts of space group $I\bar{4}$ are isomorphous. The lattice parameters for all of the salts are given in Table VIII. The present result for the c axis of tetraphenylarsonium iodide differs from the original report of Mooney[16] by a large amount. Repeated measurements on two crystals gave the same values so we conclude that there is an error in Mooney's result.

Figure 1 is a plot of $[\Delta H_s(Ph_4AsX) - \Delta H_h(X^-)]$ vs. $1/\delta$ where Ph = C_6H_5. The heats of solution for the salts were obtained in this work. The heat of hydration of the iodide ion is known[7] and the heat of hydration of the tetrachlorogallate ion is calculated from the previous results.[4] Drawing a straight line through these two values, and knowing the lattice constants for tetraphenylarsonium tetrachloroindate, we find $\Delta H_s(Ph_4AsInCl_4) - \Delta H_h[InCl_4-] = 307$ kcal/mol.

This value, combined with the heat of solution of $Ph_4AsInCl_4(s)$, the heat of sublimation of $InCl_3(c)$,[7] and the heat of solution of $InCl_3(c)$ into 1.0 mol/l. HCl,[18] gives the $InCl_3$–Cl^- bond dissociation energy, $\Delta H_{\text{diss}} = 98 \pm 10$ kcal/mol.

The present results indicate that this method of determining bond dissociation energies is promising although it needs further calibration. Figure 1 shows that the lattice energy does not vary greatly as the size of the anion changes (the difference is only 30 kcal/mol in going from I^- to $GaCl_4^-$). Also the lattice parameters are very similar for all of the MCl_4^- ions. Therefore, even if the straight line extrapolation of Figure 1 is not quite right, the error in the derived heat of hydration will not be large. This method should be particularly good at getting comparative donor–acceptor bond energies because the systematic errors in the procedure should be similar for a series of MX_4^- salts.

Discussion of Donor–Acceptor Bond Energies

The agreement of the donor–acceptor bond energies calculated from data on different salts (see Table VII) is very

Table VI. The Heat of Formation of the Gaseous Mx_4^- Ion and the Values Comprising It

Salt	$U(\delta\ 0\,°K)^a$	$\Delta H_{f,\text{salt(c)}}$	$\Delta H_{\text{sub(N)}}$	IP$_{\text{(N)}}$	$\Delta H_f[MX_4]^-(g)$
Na(AlCl$_4$)	133	−272.5	+26.0	+120.0	−286 ± 7
Ga(GaCl$_4$)	125	−168.2	+66.2	+139.8	−249 ± 7
Cs(GaCl$_4$)	119	−252.0	+18.8	+91.3	−243 ± 7
Cs(AlCl$_4$)	120	−292.0			−282 ± 7
Cs(GaBr$_4$)	116	−203.4			−198 ± 7
Cs(AlBr$_4$)	115	−239.4			−235 ± 7

[a] All energies are expressed in kcal/mol. Except for U, all values are at 25°.

Table VII. The Heat of Dissociation of the MX_3-X^- Bond and the Values Comprising It

MX_3	$\Delta H_f°$ $(MX_3(g))$	$\Delta H_f°$ $(X^-(g))$	$\Delta H_f°(MX^-_4(g))$	$D_{MX_3\text{-}X^-}$ [a]
$GaCl_3$	−107.0	−57.7	−249,[b] −243[c]	85,[b] 79[c]
$AlCl_3$	−139.4		−286,[d] −282[c]	89,[d] 85[c]
$GaBr_3$	−70	−53.0	−198[c]	75[c]
$AlBr_3$	−101.6		−235[c]	80[c]

[a] All heats are expressed in kcal/mol. [b] Value calculated from $Ga[GaCl_4]$. [c] Value calculated from respective Cs salt; [d] Value calculated from $Na(AlCl_4)$.

Table VIII. Lattice Parameters of $(Ph_4As)(M'X_4)$ Salts (M' = Ga and In)

Salt	a_0	c_0
$(Ph_4As)(GaCl_4)$[a]	13.156 (4)	7.163 (3)
$(Ph_4As)(InCl_4)$[a]	13.267 (4)	7.192 (3)
$(Ph_4As)I$[b]	12.15 (3)	6.88 (3)

[a] Parameters of D. E. Scaife, *Aust. J. Chem.*, **23**, 2205 (1970). Zero layer precession photographs gave similar but less accurate values. All values are in ångströms. [b] From several zero layer precession photographs of two different crystals. Mooney[16] found 12.194 and 7.085. There is evidently an error in the value for *c*.

encouraging. The estimated accuracy of any one value is about 7 kcal/mol and all of the different results are closer together than this error estimate.

One of the most common methods of estimating lattice energy is to use Kapustinskii's equation[19] as modified by Yatsimirskii.[20] This method can be checked using the present data. Table IX gives values of the thermochemical radius necessary to give the correct lattice energy in the Kapustinskii–Yatsimirskii equation together with the crystallographic radius and the thermochemical radius estimated in the usual manner: that is, from a knowledge of the heats of solution of salts with different cations. The results show that the equation gives useful results when not enough data are available for more sophisticated calculations.

A comparison of the donor–acceptor bond energies calculated in this work with donor–acceptor bond energies for a wide variety of neutral ligands[21–27] indicates that the halide ions form much stronger donor–acceptor bonds than a wide variety of ethers, thioethers, esters, and amines. Toward the halide ions aluminum chloride is a slightly stronger acid than gallium chloride. Substituting bromide ion for chloride ion slightly decreases the donor–acceptor bond energy. The present results for halide donors are consistent with these trends.

The way in which the values for indium trihalides fit into these trends is not clear. Greenwood, Perkins and Twentyman[28] found the order of decreasing acidity Al > Ga > In for the $(C_6H_5)_4M$ adducts with pyridine. In contrast to this the present results indicate that there is not a great difference in donor–acceptor bond energies of $AlCl_3$, $GaCl_3$, and $InCl_3$ toward the chloride ion (87 ± 7, 82 ± 7, and 98 ± 10 kcal/mol) but that $InCl_3$ is probably a slightly better acid toward Cl^- than either $AlCl_3$ or $GaCl_3$. Greenwood and Prince found evidence that the acidity of the indium trihalides is insensitive to the halogen atom involved[29] and this is what has been found for the aluminum and gallium compounds.

Table IX. Thermochemical Radii of MX_4^- Ions

				"Thermochemical radii"	
Salt	r_+, Å	$U(\delta\ 0° K)$	r_-, Å[a]	r_-, Å[b]	r_-, Å[c]
$Na[AlCl_4]$	0.95	132.7	3.94	3.17	3.14
$Ga[GaCl_4]$	1.13	126.5	4.00	3.23	3.00
$Cs[GaCl_4]$	1.69	118.9	3.96	2.98	3.00
$Cs[GaBr_4]$		115.4	4.21	3.15	3.02
$Cs[AlCl_4]$		119.7	3.95	2.95	3.14
$Cs[AlBr_4]$		115.0	4.21	3.16	3.03

[a] These radii are calculated assuming that the radius is the sum of the M–X bond length plus the radius of the X^- ion. [b] Thermochemical radius necessary to give the correct lattice energy. [c] Thermochemical radius estimated by Beck[1] from a knowledge of the heats of solution of the sodium and cesium salts.

Acknowledgment. The authors wish to acknowledge Robert Pribush for assistance in the preparation and analysis of the sodium tetrabromoaluminate.

Registry No. CsCl, 7647-17-8; CsBr, 7787-69-1; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; $AlBr_3$, 7727-15-3; $GaBr_3$, 13450-88-9; $NaAlCl_4$, 7784-16-9; $CsAlCl_4$, 17992-03-9; $NaGaCl_4$, 15007-28-0; $CsGaCl_4$, 21646-31-1; $NaAlBr_4$, 23630-67-3; $CsAlBr_4$, 18041-30-0; $NaGaBr_4$, 30487-88-8; $CsGaBr_4$, 52582-09-9; $[(C_6H_5)_4As]I$, 7422-32-4; $[(C_6H_5)_4As]InCl_4$, 30862-71-6; $Ga(GaCl_4)$, 24597-12-4; HCl, 7647-01-0; HBr, 10035-10-6; water, 7732-18-5.

References and Notes

(1) J. D. Beck "Donor Acceptor Interaction Energies in Group III Halide Complexes", Ph.D. Thesis, University of Delaware, Newark, Del., June 1969.
(2) R. C. Gearhart, Jr., "A Study of the Crystal Structures Lattice Energies, and Donor-Acceptor Properties of Some Group III Tetrahalides", Ph.D. Thesis, University of Delaware, Newark, Del., June 1972.
(3) S. R. Gunn, *Anal. Chem.*, **34**, 1292 (1962).
(4) J. D. Beck, R. H. Wood, and N. N. Greenwood, *Inorg. Chem.*, **9**, 86 (1970).
(5) LKB-Produkter AB. Model 10700-2
(6) I. Wadsö, *Acta Chem. Scand.*, 22, 927 (1968).
(7) D. D. Wagman, W. H. Evans, V. B. Parker, I. Hahn, S. M. Bailey, and R. H. Schum. *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3**, (1968).
(8) F. D. Rossini, D. D. Wagman, W. Evans, S. Levine, and I. Jaffe, *Natl. Bur. Stand.* (*U.S*), *Circ.*, **No. 500** (1952).
(9) V. B. Parker, *Natl. Stand. Ref. Data Ser.*, *Natl. Bur. Stand.*, **No. 2** (1965).
(10) J. P. Coughlin, *J. Phys. Chem.*, **62**, 419 (1958).
(11) V. I. Mikheeva, S. M. Arkhipov, and T. V. Revzina *Zh. Neorg. Khim.*, **13**, 1697 (1968).
(12) C. T. H. M. Cronenberg and J. W. van Spronsen, *Z. Anorg. Allg. Chem.*, **354**, 103 (1967).
(13) M. F. C. Ladd and W. H. Lee *J. Inorg. Nucl. Chem.*, **11**, 264 (1959).
(14) R. H. Wood, *J. Chem. Phys.*, **32**, 1690 (1960); **37**, 598 (1962).
(15) R. H. Wood and L. A. D'Orazio, *J. Phys. Chem.*, **69**, 2558 (1965).
(16) R. C. L. Mooney, *J. Am. Chem. Soc.*, **62**, 2955 (1940).
(17) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).
(18) Obtained by interpolating the data of N. N. Greenwood and D. J. Prince, *J. Chem. Soc. A*, 2876 (1969).
(19) A. F. Kapustinskii, *Q. Rev.*, *Chem. Soc.*, 283 (1956).
(20) K. B. Yatsimirskii, *Zh. Neorg. Khim.*, **6**, 518 (1961).
(21) N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.*, 1145 (1960).
(22) N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc.*, *A*, 267 (1966).
(23) R. L. Richards and A. Thompson, *J. Chem. Soc. A*, 1244 (1967).
(24) M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 5826 (1965).
(25) D. D. Eley and H. Watts, *J. Chem. Soc.*, 1319 (1954).
(26) V. W. Klemm, E. Clausen, and H. Jacobi, *Z. Anorg. Chem.*, **200**, 367 (1931).
(27) J. Wilson and I. J. Worrall, *J. Chem. Soc. A*, 382 (1967).
(28) N. N. Greenwood, P. G. Perkins, and M. E. Twentyman, *J. Chem. Soc. A*, 249 (1969).
(29) N. N. Greenwood and D. J. Prince, *J. Chem. Soc. A*, 2876 (1969).