Molecular Structures of Monomeric Gallium Trichloride, Indium Trichloride and Lead Tetrachloride by Gas Electron Diffraction†

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Gas electron diffraction data for monomeric $GaCl_3$, monomeric $InCl_3$ and $PbCl_4$ have been recorded with nozzle temperatures of about 380, 480 and 20 °C respectively. The data for $GaCl_3$ and $InCl_3$ are consistent with equilibrium structures of D_{3h} symmetry and bond distances r_e = 210.8(3) and 228.9(5) pm respectively. The data for $PbCl_4$ are consistent with an equilibrium structure of T_d symmetry and r_e = 237.3(3) pm. Bond energies and distances from the literature show that the M–Cl bonds in MCl(g) are stronger, but longer, than in MCl_3(g) for M = Al, Ga or In, and that M–Cl bonds in MCl_2(g) are stronger, but longer, than in MCl_4(g) for M = Ge, Sn or Pb. It is suggested that the relative weakness of the bonds in group-valent chlorides is due to the energy required to promote the Group 13 metal atoms from the $^2P(s^2p)$ ground states to $^4P(sp^2)$ valence states, or to promote the Group 14 metal atoms from $^3P(s^2p^2)$ ground states to $^5S(sp^3)$ valence states. Further that the decreasing stability of the group-valent relative to sub-valent chlorides as the Groups are descended is due both to increasing promotional energies and to decreasing M–Cl bond strengths.

Several years ago we reviewed the structures of chlorides of main-group elements (Groups 1 and 2 and 12–17) and discussed the variation of element-to-chlorine bond distances across the Periodic Table.[1] Since then we wished to determine the structures of the remaining homoleptic chlorides of main-group elements which are stable under the conditions of gas electron diffraction (GED), and have published the structures of $SeCl_2$,[2] $TeCl_2$,[3] $BiCl_3$[4] and (monomeric) $CdCl_2$.[5] The gas-phase structure of $ZnCl_2$ has been determined by the Hungarian GED group.[6] An up-to-date survey of the structures of gaseous metal halides has recently been published by Hargitta.[7]

In this article we report the gas-phase structures of monomeric $GaCl_3$, monomeric $InCl_3$ and $PbCl_4$ and discuss the structure and bonding in group-valent and sub-valent chlorides of the Group 13 and 14 elements based on bond energies, bond distances and bond-stretch force constants.

Experimental

Gallium trichloride of stated purity >99.99% was purchased from Schuchart, Munich. Indium trichloride was prepared from the metal and chlorine at 300–400 °C and purified by sublimation in a stream of Cl_2.[8]

Gas electron diffraction data were recorded on a Balzers Eldigraph KDG-2[9] instrument with nozzle-to-plate distances of about 50 and 25 cm. For $GaCl_3$ and $InCl_3$ we used a nozzle system of stainless steel which consisted of two ovens, one for heating the sample to a temperature corresponding to an adequate vapour pressure of about 1 Torr (*ca.* 133 Pa), the other for superheating the vapour to a temperature where the proportion of dimer present in the molecular beam is negligible. Mass spectra recorded with the same nozzle system under the same temperature conditions failed to indicate detectable quantities of iron chlorides which might have been formed in the inlet system.

Lead tetrachloride decomposes at room temperature according to equation (1) and may detonate in vacuum. The sample

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2 \qquad (1)$$

was synthesised by addition of concentrated sulfuric acid to diammonium hexachloroplumbate[10] [equation (2)]. The solid

$$[NH_4]_2[PbCl_6](s) + H_2SO_4(l) \longrightarrow PbCl_4(l) + [NH_4]_2[SO_4](sln) + 2HCl(g) \qquad (2)$$

plumbate was placed on a sintered disc and sulfuric acid added. Liquid $PbCl_4$ (m.p. −15 °C) is denser than the other phases and covered the disc. The underside of the disc was connected through a valve to the all-glass inlet system of the evacuated electron diffraction unit. When the valve was carefully opened $PbCl_4$ penetrated the disc and was condensed with solid CO_2. Gas electron diffraction diagrams were recorded by allowing small amounts of the sample to warm to room temperature. Further information about the experiments is given in Table 1.

Calculations

Structure Refinements.—Optical densities were recorded on the Snoopy densitometer and the data processed by standard procedures.[11] Atomic scattering factors $|f'(s)|\exp[i\eta(s)]$, where $s = \sin(\theta/2)/4\pi\lambda$ (θ = scattering angle, λ = electron wavelength), were taken from ref. 12. Backgrounds were drawn as polynomials to the difference between the total experimental and calculated molecular intensities. Experimental molecular intensity curves modified through multiplication with $s/[|f'_M(s)||f'_{Cl}(s)|]$ are shown in Fig. 1. Experimental radial distribution functions obtained by Fourier inversion of modified molecular intensity curves are shown in Fig. 2.

Molecular structures were refined by least-squares calculations on the modified molecular intensity curves with diagonal weight matrices.[11]

The radial distribution curves of $GaCl_3$ and $InCl_3$ consist of two peaks, one representing the M–Cl bond distance, the other the non-bonded Cl $\cdots$ Cl distance: no additional peaks indicate

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† *Non-SI unit employed:* D ≈ 3.33 × 10^{-30} C m.

Table 1 Reservoir and nozzle temperatures, number of exposed plates and s limits and increments for GED intensity curves of $GaCl_3$, $InCl_3$ and $PbCl_4$

	$GaCl_3$	$InCl_3$	$PbCl_4$
Reservoir temperature (°C)	80 ± 3	315 ± 3	0 ± 10
Nozzle temperature (°C)	383 ± 6	480 ± 6	20 ± 3
Number of plates			
50 cm	6	5	6
25 cm	5	5	6
Backgrounds, degree of polynomial			
50 cm	5	6	5
25 cm	8	8	8
s limits (nm^{-1})			
50 cm ($\Delta s = 1.25\ mm^{-1}$)	20.0–145.0	30.0–142.5	18.75–145.0
25 cm ($\Delta s = 2.50\ nm^{-1}$)	27.5–245.0	40.0–210.0	40.0–300.0
Least-squares weights			
50 cm	1.0	1.0	1.0
25 cm	0.5	0.4	0.4

Table 2 Interatomic distances (r_a), root-mean-square vibrational amplitudes (l), M–Cl anharmonicity constants (κ) and Cl ··· Cl shrinkages (δ), in $GaCl_3$, $InCl_3$ and $PbCl_4$ determined by GED. In addition the mole fractions of impurities, of the monochlorides GaCl and InCl in the case of $GaCl_3$ and $InCl_3$ and of Cl_2 in the case of $PbCl_4$, were refined as independent parameters. Estimated standard deviations in parentheses are in units of the last digit. Non-refined parameters in square brackets. Vibrational amplitudes and correction parameters for thermal vibration, $D = r_\alpha - r_a$, calculated from a molecular force field (FF)

	r_a(GED)/pm	l(GED)/pm	κ(GED)/pm^3	l(FF)/pm	D(FF)/pm
(*a*) $GaCl_3$					
Ga–Cl	210.8(3)	6.1(2)	1(6)	6.1	−1.00
Cl ··· Cl	364.3(5)	15.3(4)	[0]	14.4	+0.09
δ(GED) = 0.8(5) pm, δ(FF) = 1.8 pm, χ(GaCl) = 0.09(6); R 0.022 (50), 0.049 (25 cm), 0.030 (total)					
(*b*) $InCl_3$					
In–Cl	228.9(5)	7.0(6)	[0]	7.0	−1.68
Cl ··· Cl	394.5(15)	19.8(13)	[0]	19.7	+0.23
δ(GED) = 1.9(15) pm, δ(FF) = 3.1 pm, χ(InCl) = 0.59(5); R 0.048 (50), 0.082 (25 cm), 0.053 (total)					
(*c*) $PbCl_4$					
Pb–Cl	237.3(3)	5.8(2)	16(5)	4.9	−0.60
Cl ··· Cl	386.4(4)	14.5(4)	[0]	13.9	−0.02
δ(GED) = 1.1(4) pm, δ(FF) = 1.0 pm, χ(Cl_2) = 0.19(3); R 0.030 (50), 0.105 (25 cm), 0.047 (total)					

the presence of dimeric species M_2Cl_6 in the molecular beam. Exploratory refinements were nevertheless carried out where the mole fraction of the dimer with fixed structure[13,14] was refined as an independent parameter along with the structure parameters of the monomer MCl_3. The mole fractions thus obtained, $\chi(Ga_2Cl_6) = 0.002(8)$ and $\chi(In_2Cl_6) = 0.03(2)$, were not significantly different from zero, and in subsequent refinements they were disregarded.

The monochlorides MCl are known to be present in equilibrium with the trichlorides in the gas phase at higher temperatures. Any peaks in the radial distribution curves representing the M–Cl bond distances in the monochlorides would, however, be concealed beneath the peaks representing the bond distances in the trichlorides. The mole fractions of the monochlorides MCl were therefore introduced as independent parameters. The M–Cl vibrational amplitudes (l) in the monochlorides were calculated from the vibrational frequencies, $\bar{\omega}_e$, as described by Cyvin.[15] The equilibrium bond distances of the monochlorides were converted into r_a through the relation (3) where the Morse constant a is given by equation (4) where c is the speed of light, μ is the reduced mass and x_e is an anharmonicity parameter. Values for r_e, $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ were taken from ref. 16. The parameter values thus obtained were r_a(Ga–Cl) = 220.9 pm and l(Ga–Cl) = 7.2 pm and r_a(In–Cl) = 241.1 pm and l(In–Cl) = 8.2 pm.

$$r_a = r_e + l^2[(3a/2) - (1/r_e)] \qquad (3)$$

$$a^2 = 8\pi^2\mu c\bar{\omega}_e x_e/h \qquad (4)$$

For $GaCl_3$ we refined the M–Cl bond distance, root-mean-square vibrational amplitude and anharmonicity constant, and the length and vibrational amplitude of the non-bonded Cl ··· Cl distance and two scale factors as independent parameters. The Ga–Cl bond distance is strongly correlated to the vibrational amplitude, to the anharmonicity constant and the mole fraction of monochloride, the relevant correlation coefficients being 0.73, 0.81 and −0.93 respectively. Least-squares refinements nevertheless proceeded without difficulty to yield the best values listed in Table 2.

For $InCl_3$ the correlation coefficients between the M–Cl bond distance and the vibrational amplitude, the anharmonicity constant and the mole fraction of monochloride were even larger, 0.93, 0.92 and −0.98 respectively, and refinements failed to converge. As the anharmonicity constant of the M–Cl bond in $GaCl_3$ was found to be very small, $\kappa = 0.1(6)\ pm^3$, the anharmonicity constant in $InCl_3$ was fixed at zero. The refinements then proceeded without difficulty to yield the best values listed in Table 2.

The radial distribution curve of $PbCl_4$ also consists of two peaks which represent the Pb–Cl and Cl ··· Cl distances respectively. The Pb–Cl bond distance, vibrational amplitude and anharmonicity constant as well as the non-bonded

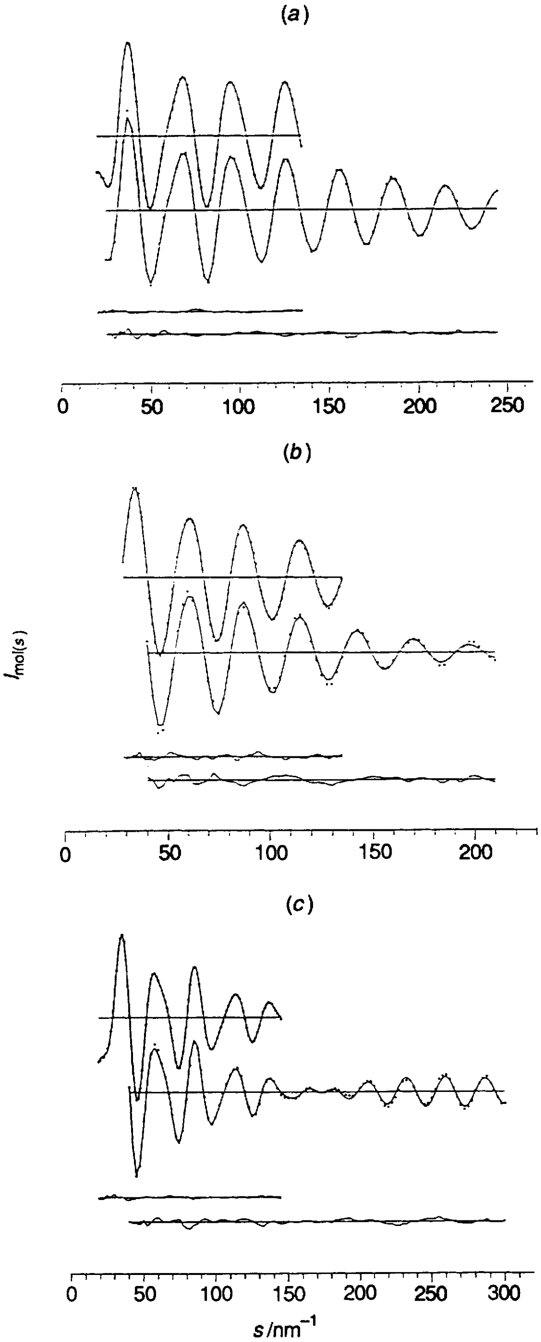

Fig. 1 Calculated (full lines) and experimental (●) modified molecular intensity curves of (*a*) $GaCl_3$, (*b*) $InCl_3$ and (*c*) $PbCl_4$ with difference curves shown below

Cl ··· Cl distance and amplitude, two scale factors and the mole fraction of Cl_2 with fixed bond distance and amplitude[16] were refined as independent parameters. In this molecule correlation between structure parameters was less severe, the largest correlation coefficient, linking the M–Cl bond distance and anharmonicity coefficient, being 0.60, and refinements converged without difficulty. Comparison of experimental and calculated intensity curves suggested, however, that the beatout of the Pb–Cl interference term in the molecular intensity corresponding to cos $[\eta_{Pb}(s) - \eta_{Cl}(s)] = 0$ occurred at lower s than indicated by the scattering functions. The discrepancy was at least partly remedied by multiplying the phase shift, $\eta(s)$, of Pb with a constant which was varied to give optimum agreement between experimental and calculated modified molecular intensity curves. The best fit was obtained with a multiplicative constant of 1.0325, and the molecular parameters obtained with this constant are listed in Table 2.

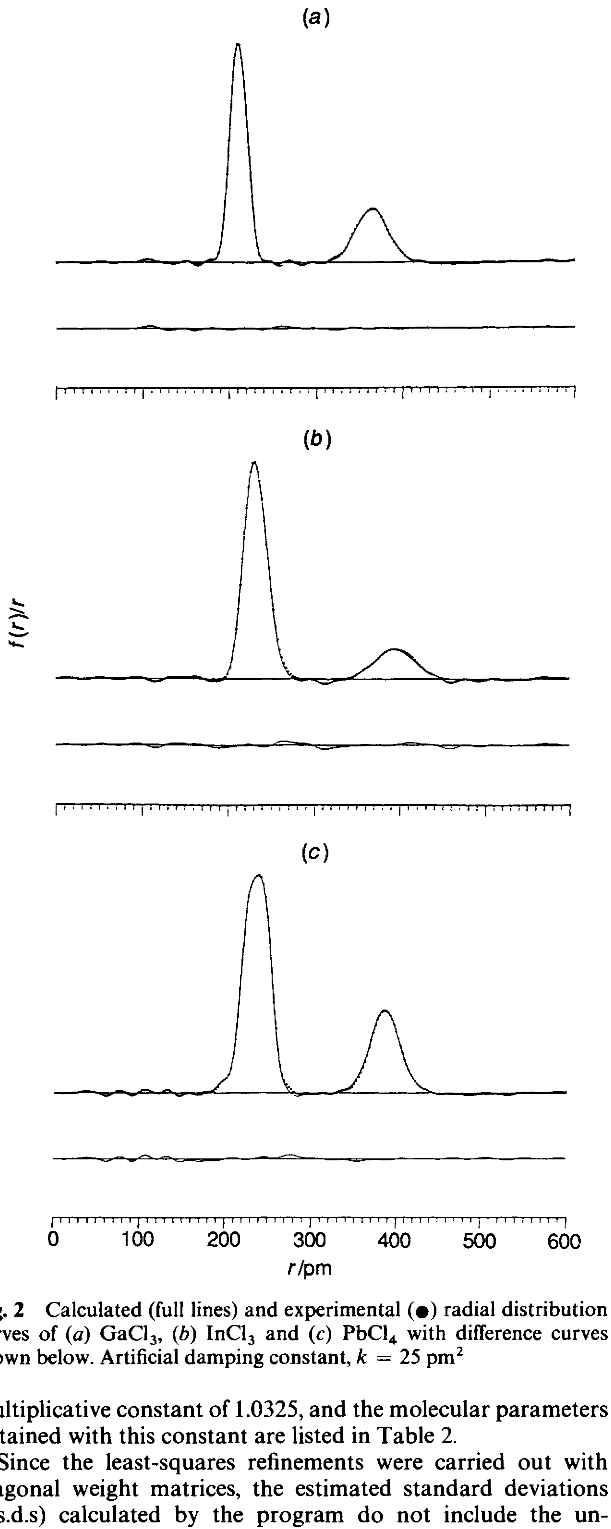

Fig. 2 Calculated (full lines) and experimental (●) radial distribution curves of (*a*) $GaCl_3$, (*b*) $InCl_3$ and (*c*) $PbCl_4$ with difference curves shown below. Artificial damping constant, $k = 25$ pm^2

Since the least-squares refinements were carried out with diagonal weight matrices, the estimated standard deviations (e.s.d.s) calculated by the program do not include the uncertainty due to data correlation.[17] The estimated standard deviations listed in Table 2 have therefore been multiplied by a factor of two, and have also been expanded to include an estimated scale uncertainty of 0.1%.

Force-field Calculations.—All force-field calculations were carried out with the program ASYM.[18] The complete symmetry force field of gaseous monomeric $GaCl_3$ has been determined by Sjøgren and co-workers[19] under the assumption that the equilibrium configuration has D_{3h} symmetry. This force field was used to calculate root mean square (r.m.s.) vibrational amplitudes (l) and vibrational correction parameters, D [equation (5)]. The values obtained are listed in Table 2.

Table 3 Normal vibrational modes and diagonal symmetry force constants for $InCl_3$[a]

Mode number	Symmetry	$\tilde{\nu}$/cm^{-1}	Force constant, F_{ii}/N m^{-1}
1	a'_1	350[b]	256
2	a''_2	110[c]	31
3	e'	400[d]	239
4	e'	94[b]	27

[a] The interaction force constant F_{34} was fixed at −28 N m^{-1}. See text. [b] Gas phase, Raman.[20] [c] Gas phase, IR.[21] [d] Argon matrix, Raman.[22]

$$D = r_\alpha - r_a \qquad (5)$$

The complete symmetry force field of monomeric $InCl_3$ does not appear to have been determined. In Table 3 we list the four normal modes of $InCl_3$.[20–22] These are, however, not sufficient to determine the five symmetry force constants. The interaction constant F_{34} was therefore fixed at −28 N m^{-1} as compared to −30 N m^{-1} in $GaCl_3$.[19] The four diagonal symmetry force constants listed in Table 3 and the l and D values listed in Table 2 were calculated under the assumption that the molecular symmetry is D_{3h}.

The bond-stretch force constant, f_r, obtained from the relationship (6) is listed in Table 4.

$$f_r = \tfrac{1}{3}(F_{11} + 2F_{33}) \qquad (6)$$

A diagonal force field of $PbCl_4$ based on the four normal modes assigned for a solution in pentane[23] yielded the l and D values listed in Table 2.

Discussion

The gas electron diffraction diagram obtained for $GaCl_3$ with a nozzle temperature of 383 ± 6 °C indicates that neither the dimer Ga_2Cl_6 nor the monochloride, GaCl, is present in the molecular beam in significant amounts. The diagram obtained for $InCl_3$ with a nozzle temperature of 480 ± 6 indicates, however, that the molecular beam contained about 60% monochloride, InCl. The difference between the two data sets reflects both the increased nozzle temperature and the lower stability of $InCl_3$ relative to the sub-chloride. Since $InCl_3$ contains three In–Cl bonds and the monochloride only one, the contribution to the molecular intensity is about twice as large for MCl_3.

While the present work was in progress, Girichev and co-workers[14,24] in Ivanov published GED studies of both $GaCl_3$ and $InCl_3$ with nozzle temperatures considerably lower than in this study. The diffraction pattern of $GaCl_3$ recorded with a nozzle temperature of 49 ± 3 °C indicated that the mole fraction of the dimer was about 0.79 and that of the monomer about 0.21, while the monochloride was absent. They assumed that the (r_α) Ga–Cl bond distance in the monomer was equal to the (r_α) terminal bond distance in the dimer and obtained a bond distance of r_a = 211.8(5) pm in $GaCl_3$ which is in good agreement with our result.[24]

The GED data for $InCl_3$ recorded with a nozzle temperature of 338 ± 5 °C indicated that the mole fraction of dimer was about 0.17 and that of the monomer 0.83, while the monochloride was absent.[14] Since In_2Cl_6 contains eight In–Cl bond distances, the contribution of the MCl_3 bond distance to the observed molecular intensity is, however, somewhat smaller than in our data. The assumption that the (r_a) In-Cl bond distance in the monomer was equal to the (r_a) terminal bond distance in the dimer yielded a common value of r_a = 228.1(5) pm.[14] Again the agreement between the results obtained in the two laboratories is satisfactory.

Inspection of the radial distribution curve of $PbCl_4$ reveals a very small, partly resolved peak centred at about 200 pm, corresponding to the bond distance in Cl_2 and refinement of the mole fraction of Cl_2 as an impurity yielded $\chi(Cl_2)$ = 0.16(2). Chlorine may have been formed by decomposition to $PbCl_2$, but since the latter is non-volatile at room temperature it would be left on the walls of the inlet system, and so we did not find it necessary to consider it as an impurity in the molecular beam.

Molecular Shapes.—If $GaCl_3$ and $InCl_3$ were rigid molecules of D_{3h} symmetry the non-bonded Cl ··· Cl distance should be exactly $\sqrt{3}$ times the M–Cl bond distance. The thermal average (r_a) Cl ··· Cl distances are, however, found to be smaller than $\sqrt{3}$ times the thermal average M–Cl distances [equation (7)];

$$\delta(\mathrm{GED}) = 3^{\frac{1}{2}}r_a(\mathrm{M{-}Cl}) - r_a(\mathrm{Cl\cdots Cl}) \qquad (7)$$

δ(GED) is equal to 0.8(5) pm when M = Ga and 1.9(15) pm when M = In. Neither discrepancy is significantly different from zero. If real, such discrepancies might indicate that the molecules are in fact slightly pyramidal, or that the thermal average Cl ··· Cl distances have been shortened by out-of-plane vibrations, The latter effect (often referred to as shrinkage) may be assessed from the vibrational correction parameters calculated from the molecular force field [equation (8)]. As seen in

$$\delta(\mathrm{FF}) = D(\mathrm{Cl\cdots Cl}) - 3^{\frac{1}{2}}D(\mathrm{M{-}Cl}) \qquad (8)$$

Table 2, the observed discrepancies δ(GED) are slightly smaller than the calculated shrinkages. The GED data are therefore in good agreement with equilibrium structures of D_{3h} symmetry.

If $PbCl_4$ were a rigid molecule of T_d symmetry the Cl ··· Cl distances should be equal to $(8/3)^{\frac{1}{2}}$ times the Pb–Cl bond distance. The thermal average Cl ··· Cl distance is however found to be slightly shorter [equation (9)]. The discrepancy

$$\delta(\mathrm{GED}) = (8/3)^{\frac{1}{2}}r_a(\mathrm{M{-}Cl}) - r_a(\mathrm{Cl\cdots Cl}) = 1.1(4)\,\mathrm{pm} \qquad (9)$$

hovers at the edge of statistical significance. It is, however, very close to the shrinkage calculated from the vibrational correction

Table 4 Bond distances (r_e or r_a), bond-stretch force constants (f_r) and mean bond dissociation energies (D^0) in sub-valent MCl(g) and group-valent MCl_3(g) chlorides of the Group 13 elements

	MCl			MCl_3		
M	r_e[a,b]/pm	f_r[a,b]/N m^{-1}	D^0[b,c]/kJ mol^{-1}	r_a[a]/pm	f_r[c]/N m^{-1}	D^0[c]/kJ mol^{-1}
B	171.6	348	—	174[d]	329[e]	456[f]
Al	213.0	208	494	207[g]	276[h]	430[i]
Ga	220.2	183	475	211[j]	279[k]	355[l]
In	240.1	159	428	229[j]	245[j]	327[l]
Tl	248.5	142	369	—	—	—

[a] Error limits ±1 in the last digit or less. [b] Ref. 16. [c] Error limits ±10 in the last digit or less. [d] Ref. 29. [e] Ref. 31. [f] Ref. 33. [g] Ref. 30. [h] Ref. 32. [i] Ref. 34. [j] This work. [k] Ref. 19. [l] See text.

Table 5 Bond distances (r_a), bond-stretch force constants (f_r) and mean bond dissociation energies (D^0) in sub-valent MCl(g) and group-valent MCl_4(g) chlorides of the Group 14 elements

	MCl_2			MCl_4		
M	$r_a{}^a$/pm	f_r/N m^{-1}	$D^{0\,b}$/kJ mol^{-1}	$r_a{}^a$/pm	f^b/N m^{-1}	$D^{0\,b}$/kJ mol^{-1}
C	—	$299^{b,c}$	—	177^d	280^e	327^f
Si	209^g	$229^{b,c}$		202^h	320^e	381^f
Ge	219^g	206^c	394^i	211^g	289^e	349^j
Sn	235^g	190^k	386^j	228^g	272^e	323^j
Pb	245^g	170^k	304^j	237^i	214^l	249^m

[a] Error limits ±1 in last digit or less. [b] Error limits ±10 in last digit or less. [c] Ref. 35. [d] Ref. 38. [e] Ref. 40. [f] Ref. 33. [g] Ref. 7. [h] Ref. 39. [i] See text. [j] Ref. 37. [k] Error limits ±20 in last digit. [l] Ref. 23. [m] Ref. 34.

Table 6 The $^2P \longrightarrow {}^4P$ excitation energies for Group 13 atoms, ΔE^*,[a] mean bond energies in MCl_3(g) when formed from atoms in the ^4P state, $D^*(MCl_3)$, and estimated enthalpies of reaction (14), ΔH_r

M	ΔE^*/kJ mol^{-1}	D^*/kJ mol^{-1}	$-\Delta H_r$/kJ mol^{-1}
B	345	571	
Al	347	546	−404
Ga	454	505	−259
In	418	467	−201
Tl	540	—	+39

[a] Error limits ±1 in last digit or less.[41]

parameters [equation (10)]. The GED data are thus in good

$$\delta(FF) = D(Cl \cdots Cl) - (8/3)^{\frac{1}{2}}D(M\text{–}Cl) = 1.0 \text{ pm} \qquad (10)$$

agreement with a molecular model of T_d symmetry.

Comparison of Bond Distances and Strengths in Group-valent and Sub-valent Chlorides.—The standard enthalpies of formation of $GaCl_3$(g), $InCl_3$(g) and $GeCl_2$(g) are $\Delta H^\circ_f = -428.4 \pm 8.4$, -375.7 ± 5.0 and -171.2 ± 3.6 kJ mol^{-1} respectively.[25–27] Combination with the enthalpies of formation of the gaseous atoms Cl, Ga, In and Ge[28] yields the mean M–Cl bond energies in $GaCl_3$, $InCl_3$ and $GeCl_2$ listed in Tables 4 and 5.

A nearly complete set of bond distances, mean bond energies and bond-stretch force constants is now available for the sub-valent and group-valent chlorides of the Groups 13 and 14 elements (see Tables 4 and 5). A number of general trends are immediately apparent.

(*i*) In each of the series MCl, MCl_3, MCl_2 and MCl_4 bond distances increase as the Groups are descended.

(*ii*) With the exception of $SiCl_4$ *versus* CCl_4, mean bond energies decrease as the Groups are descended.

(*iii*) With the exception of $SiCl_4$ *versus* CCl_4 and the possible exception of $GaCl_3$ *versus* $AlCl_3$, force constants decrease as the Groups are descended.

We suggest that steric repulsion between Cl atoms is responsible for the relatively low bond energy and small force constant in CCl_4. Otherwise these trends cannot be regarded as unexpected.

(*iv*) Hargittai and co-workers[35] have pointed out that bond distances in sub-valent chlorides of Si and the heavier Group 14 elements are longer than those in the group-valent chlorides. Inspection of Table 4 shows that the same is true for Al and the heavier Group 13 elements.

(*v*) Andrews and Frederick[36] have pointed out that the bond-stretch force constants of sub-valent chlorides of Si and the heavier Group 14 elements are smaller than the force constant in the group-valent analogues. Inspection of Table 4 shows that the same is true for Al and the heavier Group 13 elements.

The greater bond distances and smaller force constants of the subvalent chlorides might be taken as an indication that these bonds are weaker than in group-valent chlorides.

(*vi*) Inspection of the tables shows that in the cases where mean bond energies are available, that is for the metals Al, Ga, In, Ge, Sn and Pb, the M–Cl bonds in the sub-valent chlorides are stronger than in the group-valent analogues.

It is thus clear that the general expectation that the longer of two bonds between a given atom pair is the weaker is not fulfilled when one of the atoms is a Group 13 or 14 metal in different valence states.

The difference between the bond distances in sub-valent and group-valent compounds shows that the bonding radius is larger for the sub-valent atom. Such a difference may in turn be rationalized by assuming that the non-bonding electron pair on the sub-valent atom occupies an atomic orbital of predominant s character, or at least is sufficiently close to the metal atom to repel the bonding electrons strongly. In fact the Cl–M–Cl angles in the dichlorides of the Group 14 elements are smaller than tetrahedral and decrease from 103° in $SiCl_2$ to about 98° in $PbCl_2$.[7]

Such a rationalization, however, suggests that the bonds in the sub-valent chlorides should be weaker than in the group-valent analogues. Since polar bonds generally are stronger than non-polar, the unexpected strength of the bonds in the sub-valent species might be due to greater polarity, but the dipole moments of gaseous GaCl and InCl, 3.79 and 4.51 D respectively,[16] do not indicate that the ionic contribution is very large; division by the observed bond distances yields atomic charges of ±0.33 and ±0.38 respectively. Rather than assuming the bonds in the sub-valent chlorides to be unexpectedly strong, we believe that the bonds in the group-valent chlorides are unexpectedly weak.

The ground state of the atoms in Group 13 is $s^2p(^2P)$.[41] The atom thus has one unpaired electron available for formation of the bond in the sub-valent monochloride. In order to form two more bonds the atom must be excited to the sp^2 configuration. The lowest atomic state arising from the sp^2 configuration is ^4P where the three valence electrons have parallel spins.[41]

The mean bond energies of the trichlorides listed in Table 4 are equal to 1/3 of the energy of reaction (11) where M is in the

$$MCl_3(g) \longrightarrow M(g) + 3Cl(g) \qquad (11)$$

ground electronic state ^2P. The strength of the three M–Cl bonds when formed from the ^4P state, D^*, is 1/3 of the energy of reaction (12) where M* is in the excited ^4P state. Equation (13)

$$MCl_3(g) \longrightarrow M^*(g) + 3Cl(g) \qquad (12)$$

$$D^*(MCl_3) = D(MCl_3) + (\Delta E^*/3) \qquad (13)$$

follows where ΔE^* is the energy required to promote M to the valence state. In Table 6 we list the ΔE^* for the Group 13 elements[41] and $D^*(MCl_3)$ for M = B, Al, Ga or In. It is seen that $D^*(MCl_3)$ is larger than the bond energy of the monochloride MCl. We suggest, therefore, that the reason for the weakness of the bonds in the trichlorides relative to the monochlorides is the large energies required to promote the Group 13 atoms to an sp^2 configuration.

The group-state electron configuration of a Group 14 element is $s^2p^2(^3P)$ and the atom contains two unpaired electrons for formation of the two bonds in a sub-valent chloride.[41] In order to form two more bonds the atom must be excited to an sp^3 valence state. The lowest atomic state arising from this configuration is ^5S where the four electrons in the valence shell have parallel spins. Information about the atomic energy levels of the Group 14 metals is more sparse than for the Group 13 metals; the ^5S state has only been assigned for the Sn atom. The promotional energy[41] is $\Delta E^* = 474$ kJ mol^{-1} which suggests that the mean bond energy in $SnCl_4$ when formed from the ^5S state is 442 kJ mol^{-1}, as compared to 386 kJ mol^{-1} in the dichloride.

Why are the sub-valent compounds of the Group 13 and 14 metals increasingly stable relative to the group-valent analogues as the Groups are descended? The answer may be sought in an increasing energy required for promotion of s electrons and in a decreasing strength of the bonds formed after promotion. Ionization energies are often used to assess the energies required for promotion of s electrons, and since these do not show an increase as the groups are descended it is often concluded that the 'inert pair' effect is due solely to the weakening of bonds with increasing atomic number.[42] We would suggest that the energies required to excite the atoms from s^2p to sp^2 or from s^2p^2 to sp^3 configurations are more relevant than ionization energies.

Let us consider reaction (14). If it is assumed to proceed

$$MCl(g) + Cl_2(g) \longrightarrow MCl_3(g) \qquad (14)$$

through breaking of the bonds in the reactants followed by excitation of the metal atom to the ^4P state and the formation of three bonds from this state, the enthalpy of the reaction is given approximately by equation (15). An independent estimate

$$\Delta H_r = D(\text{M–Cl}) + D(\text{Cl–Cl}) + \Delta E - 3D^*(MCl_3) - RT \qquad (15)$$

of the reaction enthalpy may be obtained by assuming that the bond energies D(M–Cl) and $D^*(MCl_3)$ are equal [equation (16)]. The estimates obtained in this manner are listed in the last column of Table 6. The reaction enthalpies are seen to decrease in magnitude monotonically from $\Delta H_r = -404$ kJ mol^{-1} for M = Al to -201 kJ mol^{-1} for M = In and to become positive for $TlCl_3$ which does not appear to exist in the gas phase. The increase in the estimated reaction enthalpy when going from In to Tl is due in equal measure to the increase in the promotion energy and a decrease in the bond strength.

$$\Delta H_r = D(\text{Cl–Cl}) + \Delta E - 2D(\text{MCl}) - RT \qquad (16)$$

We suggest, therefore, that these factors are equally responsible for the decreasing stability of the group-valent relative to the sub-valent chlorides of the Group 13 metals.

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