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Thermochemical Bond Energies and Chlorine-35 Nuclear Quadrupole Resonance Spectra of $GeCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$ Ions

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Thermochemical bond strength measurements and the ^{35}Cl nqr spectra were compared for isostructural salts of $GeCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$. The energy for the reaction $MCl_6^{2-}(g) \rightarrow M^{4+}(g) + 6Cl^-(g)$ best reflects the trend in bond strength and was found to be 2364 ± 20 kcal/mol for M = Ge, 2144 ± 20 kcal/mol for Sn, and 2151 ± 22 kcal/mol for Pb. The ^{35}Cl nqr frequencies for $[(CH_3)_4N]_2MCl_6$ salts (19.6 MHz for M = Ge, 16.7 MHz for M = Sn, and 18.3 MHz for M = Pb) do not mimic this trend but are consistent with it recognizing that the response of the halogen coupling constant to σ-bond changes is opposite that of π-bond changes, whereas the bond energy reflects the net bond order. $PbCl_6^{2-}$ appears to show the effect of the "lanthanide contraction" in its nqr spectrum. Neither the bond strength nor the nqr measurements are consistent with the fact that the electronegativity of lead is higher than that of germanium or tin on most scales.

Introduction

Chemical trends within the group IVb elements Si, Ge, Sn, and Pb have produced considerable debate[1,2] during the 20 years since Sanderson[3] first called attention to the irregularities. For example the trend in electronegativity is nonuniform on commonly used scales such as those of Allred and Rochow,[4] Pauling,[5] Sanderson,[6] and Mulliken-Jaffe.[7] The optical electronegativities for Ge, Sn, and Pb in MCl_6^{2-} ions are respectively 1.45, 1.50, and 1.90.[8] Because of the extent of contradiction between predicted and observed properties of these elements,[9] we decided to examine closely a series of hexachlorometalate salts of Ge, Sn, and Pb by determining the metal-chlorine bond energy from calorimetric measurements for comparison with the ^{35}Cl nuclear quadrupole resonance spectra. To minimize the number of anisotropic variables, the compounds chosen were isostructural in all cases. $[(CH_3)_4N]_2MCl_6$ salts were used for the nqr spectra because the large cations isolate the anions and reduce the repulsive potential between them. Such repulsions between ions appear to be very important in determining crystal lattice effects in nqr spectroscopy.[10] Thus, to a very large extent the nqr spectra of these salts reflect the intramolecular bonding trend without a complicating "crystal lattice effect." For solubility reasons, salts having different cations were employed in the thermochemical measurements. This presented no interpretational problem because variations in the cation parameters were subtracted out before any comparison was made.

Experimental Section

Syntheses. The salts K_2SnCl_6, $[(CH_3)_4N]_2SnCl_6$, Rb_2PbCl_6, and $[(CH_3)_4N]_2PbCl_6$ were prepared as described before.[11] Cs_2GeCl_6 was prepared by the method of Laubengayer, *et al.*,[12] recrystallized from methanol-12 *M* HCl (1:2 by volume), and then washed with ethanol and ether. Rb_2GeCl_6 and $[(CH_3)_4N]_2GeCl_6$ have been prepared previously[13] by Laubengayer's method. For this work, Rb_2GeCl_6 was prepared in that manner, but $[(CH_3)_4N]_2GeCl_6$ was prepared by a new route. Here 5 ml (0.043 mol) of $GeCl_4$ was added to a solution of 13 g (0.12 mol) of $(CH_3)_4NCl$ in 25 ml of anhydrous methanol. The resulting white precipitate was recrystallized from absolute methanol and yielded hygroscopic colorless crystals. All of the above salts were dried in a vacuum desiccator. The syntheses of other R_2GeCl_6 salts (notably NH_4^+ and K^+) were unsuccessful because of the incompatible solubility of $GeCl_4$ and most cation chlorides in sufficiently unreactive solvents. One other salt, $[(CH_3CH_2)_4N]_2GeCl_6$, is known and has been prepared in thionyl chloride.[14]

Nqr Spectra. ^{35}Cl nqr spectra were recorded on a system described before.[15] Errors in the measurements are estimated to be about 0.005 MHz and the temperature in each case was 298°K. The results are reported in Table I.

X-Ray Powder Patterns. Powder patterns were obtained by the use of a Debye-Scherrer camera and Cu Kα radiation. Visual comparisons were made of the films to determine whether or not the compounds studied were isostructural. No indexing was done.

Calorimetry. Cs_2GeCl_6, K_2SnCl_6, and Rb_2PbCl_6 from the above syntheses were dried carefully in a vacuum oven. Cesium chloride (Apache, 99.999%), rubidium chloride (ROC-RIC, 99%), potassium chloride (MCB), and lead dioxide (Fisher, 97.5%) were dried at 110° before use. Germanium tetrachloride (ROC-RIC, 99.999%) and stannic chloride (Fisher) were used without further purification. All samples were placed in thin glass bulbs and sealed inside a glove bag filled with nitrogen.

The constant-temperature environment Dewar calorimeter used has been described in detail previously.[16] The heat of solution of tris(hydroxymethyl)aminomethane (NBS Standard Reference Material No. 724) in 0.1 *M* hydrochloric acid was used to check the calorimeter performance. An average value of 7107 cal/mol at 25° was obtained for five runs with the standard deviation for a single measurement being 9 cal/mol (0.13%). This value compares well with previous results of 7112 ± 5 cal/mol.[17]

Sample ampoules were broken in 247 ml of calorimetric solution after the temperature had been adjusted to 25.00 ± 0.01°. One calibration was performed on each run after the bulb breaking. The calorimeter solutions used in each case were 0.298 *M* HCl for the K_2SnCl_6 cycle, 6.04 *M* HCl for the Rb_2PbCl_6 cycle, and 2:1.5:1 by

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Table I. ^{35}Cl Nuclear Quadrupole Resonance Frequencies[a] at 298°K for R_2MCl_6 Salts and Ionization Potentials for M = Ge, Sn, and Pb

			IP,[b] eV			
R_2MCl_6	$\nu_{^{35}Cl}$, MHz	M	1st	2nd	3rd	4th
Rb_2GeCl_6	18.87 (6)	Ge	7.90	15.93	34.22	45.71
$[(CH_3)_4N]_2GeCl_6$	19.61 (8)					
Rb_2SnCl_6	15.60[c]	Sn	7.34	14.63	30.50	40.73
$[(CH_3)_4N]_2SnCl_6$	16.67[c]					
$[(CH_3)_4N]_2PbCl_6$	18.54[c]	Pb	7.42	15.03	31.94	42.32

[a] Parenthetical numbers are signal-to-noise ratios. [b] C. E. Moore, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 34 (1970). [c] Reference 11.

volume 1-propanol–H_2O–12 *M* HCl for the Cs_2GeCl_6 cycle. The method of calculation of temperature changes has been discussed elsewhere.[16]

Results

Structural Information. In order validly to compare solid-state spectral data, it is desirable that the salts under study have the same crystal structures. All of the salts discussed here have the cubic antifluorite structure of space group F_{m3m}. The structures of K_2SnCl_6 and Rb_2PbCl_6 were reported by Engel.[18] Laubengayer, *et al.*,[12] determined the structure of Cs_2GeCl_6 to be F_{m3m}. Wyckoff and Corey[19] reported the same structure for $[(CH_3)_4N]_2SnCl_6$. The structural parameters for the K^+, Cs^+, and $[(CH_3)_4N]^+$ salts of $SnCl_6^{2-}$ have been greatly improved recently.[10]

X-Ray powder patterns indicate that the $[(CH_3)_4N]^+$ salts of $GeCl_6^{2-}$ and $PbCl_6^{2-}$ are isostructural with that of $SnCl_6^{2-}$ and, hence, cubic antifluorite. The powder patterns of Cs_2GeCl_6 which is cubic antifluorite[12] and of Rb_2GeCl_6 are also essentially identical.

Nqr Spectra. ^{35}Cl nqr frequencies for these $SnCl_6^{2-}$ salts and $PbCl_6^{2-}$ salts have been reported before,[10,11,20,21] but to our knowledge none have been reported previously for $GeCl_6^{2-}$. The observation of the ^{35}Cl signals for $GeCl_6^{2-}$ completes the first triad of MCl_6^{2-} salts in the same group of the periodic table for which ^{35}Cl nqr frequencies have been recorded.

It is interesting to note that the observed ^{35}Cl nqr frequencies in $GeCl_6^{2-}$ further support the conclusions about crystal field effects in MCl_6^{2-} salts reached in previous work from this laboratory.[10] A plot of $\nu_{^{35}Cl}$ for $GeCl_6^{2-}$ *vs.* $\nu_{^{35}Cl}$ in $SnCl_6^{2-}$ for the Rb^+ and $[(CH_3)_4N]^+$ salts yields a line of slope $m = 0.69$, which is the same as the slope for the $PtCl_6^{2-}$ salts. This is expected because $d_{Pt-Cl} = d_{Ge-Cl} = 2.35$ Å, and, thus, the anions are equal in size. The size of the anion, MCl_6^{2-}, in the cubic lattice is found to be important in determining the crystal field effect on the ^{35}Cl nqr frequency.[10]

An attempt was made to record and compare the temperature dependence of the ^{35}Cl nqr frequencies of the tetramethylammonium salts of $GeCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$. Unfortunately, reduced signal-to-noise ratios at lower temperatures hampered this experiment and no further work was attempted along this line.

Lattice Energies. The lattice energies of Cs_2GeCl_6, K_2SnCl_6, and Rb_2PbCl_6 were calculated using a method described previously.[22-25] The characteristic energies and polarizabilities in Table II were used to calculate the interaction constants in the interaction force constant, C_{ij}, and the van der Waals sums, S_{ij} (Table III), using procedures described previously.[24] The calculations were performed assuming the following self-consistent charge distributions and Cl atom positions: for Cs_2GeCl_6, Cs = 1+, Ge = 0.802+, Cl = 0.467–, $x = 0.2302$; for K_2SnCl_6, K = 1+, Sn = 1.0+, Cl = 0.50–, $x = 0.2415$; for Rb_2PbCl_6, Rb = 1+, Pb = 0.898+, Cl = 0.483–, $x = 0.2452$. Table IV summarizes the results. Webster and Collins[26] have shown that variation in the charge distribution produces significant changes in the calculated lattice energy. The charge distributions used in this calculation were estimated from the ^{35}Cl nqr coupling constants,[11] $(e^2Qq/h)_{mol}$, using the equation $(e^2Qq/h)_{mol}/(e^2Qq/h)_{at} - 1 = e_{Cl}$, where $(e^2Qq/h)_{at} = 109.7$ MHz. The charges are internally consistent as well as chemically reasonable. Structural details were taken from the crystallographic data described above. Errors in the calculated energies, *U*, are estimated to be *ca.* 5%.

Table II. Polarizabilities and Characteristic Energies for Ions

Ions	Polarizability[a] × 10^{-24}, cm^{-3}	Characteristic energies[a] × 10^{-12}, ergs/molecule
Cs^+	2.45	36.2
K^+	1.33	45.6
Rb^+	1.42	39.8
Ge^{4+}	0.21	135
Sn^{4+}	0.50[b]	104
Pb^{4+}	0.83	99.2
Cl^-	3.45	15.6

[a] Calculated as in ref 22. [b] M. Webster and P. H. Collins, *J. Chem. Soc., Dalton Trans.*, 588 (1973).

Table III. Interaction Force Constants (C_{ij}) and van der Waals Sums (S_{ij}) Used in the Lattice Calculation

Salt	Ion pair	C_{ij}[a] × 10^{-60}, ergs cm^3/molecule	S_{ij},[a] Å^{-6}
Cs_2GeCl_6	Cs-Cs	163	33.6[b]
	Cs-Ge	22.0	82.5
	Ge-Ge	4.46	7.21[b]
	Cs-Cl	138	851
	Ge-Cl	15.2	65.5
	Cl-Cl	139	416
K_2SnCl_6	K-K	60.5	33.6[b]
	K-Sn	31.6	82.5
	Sn-Sn	19.5	7.21[b]
	K-Cl	80.0	856
	Sn-Cl	35.1	67.9
	Cl-Cl	139	490
Rb_2PbCl_6	Rb-Rb	60.1	33.6[b]
	Rb-Pb	50.2	82.5
	Pb-Pb	51.2	7.21[b]
	Rb-Cl	82.3	857
	Pb-Cl	57.9	68.7
	Cl-Cl	139	528

[a] Calculated as in ref 22. [b] These are slightly larger than the values obtained by M. Webster and P. H. Collins, *J. Chem. Soc., Dalton Trans.*, 588 (1973). The effect on the lattice energy is negligible, however.

Heat of Formation of Cs_2GeCl_6(s). The heats of solution of the following reactions were measured at 25° and results are shown in Table V. No assumptions need to be made

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Table IV. Lattice Energies[a]

	Cs_2GeCl_6	K_2SnCl_6	Rb_2PbCl_6
Coulombic energy	+337.94	+333.18	+325.08
Madelung constant[b]	6.5363	6.3040	6.2822
van der Waals energy	+39.73	+35.60	+33.68
Repulsion energy	−41.12	−40.34	−38.57
Zero point energy	−1.0	−1.0	−1.0
Lattice energy[c]	+335.55	+327.44	+319.19

[a] All energies in kilocalories per mole at 0°K. [b] These Madelung constants lie on a smooth curve drawn through the results in ref 26 when plotted *vs.* charge on metal and chlorine parameter x. [c] Error ±5%.

Table V. Heats of Solution for the Germanium Cycle[a]

Compd	ΔH, kcal/mol
CsCl[b]	+3.80 ± 0.1
$GeCl_4$[c,d]	−17.47 ± 0.5
Cs_2GeCl_6[b]	+3.01 ± 0.6

[a] The calorimeter solution was 247 ml of 2:1.5:1 (by volume) 1-propanol-H_2O-concentrated HCl. [b] Based on three separate measurements. [c] Based on two separate measurements. [d] The calorimeter solution also contained a stoichiometric amount of CsCl.

about the species present in solution other than that the same germanium-containing species were formed in reactions 1 and 2. The solution in each case is 2:1.5:1 by volume 1-propanol-H_2O-12 M HCl. Adding (2) and (3) and subtracting (1) give

$$Cs_2GeCl_6(c) + 2{:}1.5{:}1\ \text{soln} \rightarrow Cs_2GeCl_6\ (\text{in } 2{:}1.5{:}1\ \text{soln}) \quad (1)$$

$$GeCl_4(l) + 2CsCl\ (\text{in } 2{:}1.5{:}1\ \text{soln}) \rightarrow Cs_2GeCl_6\ (\text{in } 2{:}1.5{:}1\ \text{soln}) \quad (2)$$

$$2CsCl(c) + 2{:}1.5{:}1\ \text{soln} \rightarrow 2CsCl\ (\text{in } 2{:}1.5{:}1\ \text{soln}) \quad (3)$$

$$2CsCl(c) + GeCl_4(l) \rightarrow Cs_2GeCl_6(c) \quad (4)$$

Using the data in Table V, ΔH for reaction 4 is calculated to be −12.9 kcal/mol. Using $\Delta H_f^\circ[CsCl(c)] = -103.5$ kcal/mol[27] and $\Delta H_f^\circ[GeCl_4(l)] = -127.1$ kcal/mol,[28] the standard heat of formation of $Cs_2GeCl_6(c)$ is determined to be −347.0 kcal/mol at 25°.

Heat of Formation of $GeCl_6^{2-}(g)$. The standard heat of formation of $GeCl_6^{2-}(g)$ at 298°K can be expressed as[25]

$$\Delta H_f^\circ[GeCl_6^{2-}(g)] = U + \Delta H_f^\circ[Cs_2GeCl_6(c)] - 2\Delta H_{subl}(Cs) - 2IP(Cs) + \int_0^{298}[C_p(Cs_2GeCl_6(c)) + 2C_p(e^-(g)) - 2C_p(Cs(g)) - C_p(GeCl_6^{2-}(g))]\,dT \quad (5)$$

U is the calculated lattice energy at 0°K and is equal to 335.6 kcal/mol, $\Delta H_f^\circ[Cs_2GeCl_6(c)] = -347.0$ kcal/mol, $\Delta H_{subl}(Cs) = 18.7$ kcal/mol,[29] and the ionization potential of cesium is 89.8 kcal/mol.[30] The integral term may be shown to be negligible in the following manner. The heat capacity terms involving $Cs_2GeCl_6(c)$ and $GeCl_6^{2-}(g)$ were neglected since they are estimated to be about 7 kcal/mol and should cancel one another (±1 kcal/mol).[25,26,28] The cesium heat capacity term (1.5 kcal/mol)[27] and the electron heat capacity term (1.5 kcal/mol)[25] also effectively cancel. (The same assumptions are made regarding the integral terms in $\Delta H_f^\circ[SnCl_6^{2-}(g)]$ and $\Delta H_f^\circ[PbCl_6^{2-}(g)]$ and will not be mentioned further. From ref 27, $\int_0^{298}C_p[K(g)]\,dT = \int_0^{298}C_p[Rb(g)]\,dT = \int_0^{298}C_p[Cs(g)]\,dT = 1.5$ kcal/mol.) Thus, $\Delta H_f^\circ[GeCl_6^{2-}(g)] = -228.4 \pm 20$ kcal/mol.

Table VI. Heats of Solution for the Tin Cycle[a]

Compd	ΔH, kcal/mol
KCl[b]	+4.19
$SnCl_4$[c,d]	−30.99 ± 0.2
K_2SnCl_6[e]	+0.24 ± 0.05

[a] The calorimeter solution was 247 ml of 0.2978 M HCl. [b] Calculated; see text. [c] Based on two separate measurements. [d] The calorimeter solution also contained a stoichiometric amount of KCl. [e] Based on three separate measurements.

Heat of Formation of $K_2SnCl_6(s)$. The heats of solution of the following reactions were determined at 25° and results are shown in Table VI. Again no assumptions need to be made about the species present in solution other than that the same tin-containing species were formed in reactions 6 and 7. The heats of reactions 6 and 7 were measured and reported in Table VI. The values for the heat of solution of $SnCl_4(l)$ compare well with those of Webster and Collins, who reported −31.4 kcal/mol in 0.93 M HCl.[26] The heat of solution of KCl(c) in 0.298 M HCl is calculated in the following manner using data from Parker.[31] Numbers preceding formulas indicate the number of moles.

$$K_2SnCl_6(c) + 0.298\,M\,HCl \rightarrow K_2SnCl_6\ (\text{in } 0.298\,M\,HCl) \quad (6)$$

$$SnCl_4(l) + 2KCl\ (\text{in } 0.298\,M\,HCl) \rightarrow K_2SnCl_6\ (\text{in } 0.298\,M\,HCl) \quad (7)$$

$$2KCl(c) + 0.298\,M\,HCl \rightarrow 2KCl\ (\text{in } 0.298\,M\,HCl) \quad (8)$$

$$0.0737HCl\ (\text{in } 13.39H_2O) + 0.00133KCl\ (\text{in } 0.2417H_2O) \rightarrow 0.00133KCl\ [\text{in } 0.0737HCl\ (\text{in } 13.63H_2O)] \quad (9)$$

$$0.0737HCl\ (\text{in } 13.63H_2O) \rightarrow 0.0737HCl\ (\text{in } 13.39H_2O) + 0.24H_2O \quad (10)$$

$$0.00133KCl(c) + 0.2417H_2O \rightarrow 0.00133KCl\ (\text{in } 0.2417H_2O) \quad (11)$$

Adding reactions 9, 10, and 11 gives

$$0.00133KCl(c) + 0.0737HCl\ (\text{in } 13.63H_2O) \rightarrow 0.00133KCl\ [\text{in } 0.0737\ HCl\ (\text{in } 13.63H_2O)] \quad (12)$$

This corresponds to the 6.672 × 10^{-4} mol sample of K_2SnCl_6 in Table VI. The change in enthalpy for reaction 12 is calculated to be 4.193 kcal/mol of KCl. The enthalpy change for reaction 9 is negligible.[32]

The sum of reactions 7 and 8 minus reaction 6 yields

$$2KCl(c) + SnCl_4(l) \rightarrow K_2SnCl_6(c) \quad (13)$$

with a ΔH of −22.85 kcal/mol. Using $\Delta H_f^\circ[KCl(c)] = -104.175$ kcal/mol[27] and $\Delta H_f^\circ[SnCl_4(l)] = -122.4$ kcal/mol,[28] the heat of formation of $K_2SnCl_6(c)$ is calculated to be −353.4 kcal/mol. $\Delta H_f^\circ[K_2SnCl_6(c)]$ agrees reasonably well with the value of ref 27[33] when it is corrected for the differences in $\Delta H_f^\circ[SnCl_4(l)]$ in the two computations; *i.e.*, the value of ref 27 becomes $\Delta H_f^\circ[K_2SnCl_6(c)] = -354.9$ kcal/mol.

Heat of Formation of $SnCl_6^{2-}(g)$. The standard heat of formation of $SnCl_6^{2-}(g)$ at 25° can be calculated using the calculated lattice energy, $U = 327.44$ kcal/mol, $\Delta H_f^\circ[K_2SnCl_6(c)] = -353.4$ kcal/mol, $\Delta H_{subl}(K) = 21.3$ kcal/mol,[29] and the ionization potential of potassium, 100.1 kcal/mol.[30] Thus, $\Delta H_f^\circ[SnCl_6^{2-}(g)] = -268.8 \pm 20$ kcal/mol at 25°. This value is within experimental error of the value

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Table VII. Heats of Solution for the Lead Cycle[a]

Compd	ΔH, kcal/mol
RbCl[b]	+3.61 ± 0.4
PbO_2[b,c]	−18.45 ± 0.5
Rb_2PbCl_6[b]	+15.89 ± 1.5

[a] The calorimeter solution was 250 ml of 6.04 *M* HCl. [b] Based on three separate measurements. [c] The calorimeter solution also contained a stoichiometric amount of RbCl.

of −248 ± 17 kcal/mol obtained by Webster and Collins when corrected for $\Delta H_f^\circ\,[SnCl_4(l)]$ considering that they determined their value from data on Rb_2SnCl_6.[26]

Heat of Formation of $Rb_2PbCl_6(s)$. The heats of solution of the following reactions were determined at 25° and results are shown in Table VII.

$$Rb_2PbCl_6(c) + (n-4)HCl\cdot(m+2)H_2O \rightarrow Rb_2PbCl_6\ [\text{in } (n-4)HCl\cdot(m+2)H_2O] \tag{14}$$

$$PbO_2(c) + 2RbCl\ [\text{in } nHCl\cdot mH_2O] \rightarrow Rb_2PbCl_6\ [\text{in } (n-4)HCl\cdot(m+2)H_2O] \tag{15}$$

$$2RbCl(c) + nHCl\cdot mH_2O \rightarrow 2RbCl\ [\text{in } nHCl\cdot mH_2O] \tag{16}$$

$$nHCl\cdot mH_2O \rightarrow 4HCl(aq) + (n-4)HCl\cdot mH_2O \tag{17}$$

$$nHCl\cdot mH_2O + 2H_2O \rightarrow nHCl\cdot(m+2)H_2O \tag{18}$$

n and m represent moles of HCl and H_2O, respectively. The heats of reactions 14 and 15 were measured in the same solution as reaction 16. The difference between the measured heats of (14) and (15) in this solution (6.04 *M* HCl) and the thermochemically exact solutions represented in reactions 14 and 15 was assumed to be negligible because the change in HCl concentration was very small.

The heat of solution of $PbO_2(c)$ in concentrated hydrochloric acid has been reported by Szychlinski and Lenarcik to be −37.5 kcal/mol.[34] The measured heat of reaction 15 is −18.45 kcal/mol in 6.04 *M* HCl. This indicates that less $PbCl_6^{2-}$ is formed at equilibrium in 6.04 *M* HCl than in 12 *M* HCl. The heat of solution of RbCl(c) ($\Delta H = 3.6$ kcal/mol from reaction 16) compares well with the ΔH reported by Webster and Collins of 4.7 kcal/mol at 298°K in 0.93 *M* HCl.[26]

The heat of reaction 18 can be calculated and is negligible.[31] The heat of reaction 17 was calculated per mole of lead for each of the three amounts of PbO_2 used. Adding reactions 15 and 16 and then subtracting reactions 14, 17, and 18 give

$$PbO_2(c) + 2RbCl(c) + 4HCl(aq) \rightarrow Rb_2PbCl_6(c) + 2H_2O \tag{19}$$

where HCl(aq) is HCl at infinite dilution. ΔH for reaction 19 is calculated to be −13.71 kcal/mol. Using this value and $\Delta H_f^\circ\,[PbO_2(c)] = -66.3$ kcal/mol,[28] $\Delta H_f^\circ\,[RbCl(c)] = -102.91$ kcal/mol,[27] $\Delta H_f^\circ\,[HCl(aq)] = -39.952$ kcal/mol,[28] and $\Delta H_f^\circ\,[H_2O(l)] = -68.315$ kcal/mol, [23] we obtain $\Delta H_f^\circ\,[Rb_2PbCl_6(c)] = -309.0$ kcal/mol.

Heat of Formation of $PbCl_6^{2-}(g)$. The standard heat of formation of $PbCl_6^{2-}(g)$ at 25° is calculated using the calculated lattice energy $U = 319.19$ kcal/mol, $\Delta H_f^\circ\,[Rb_2PbCl_6(c)] = -309.0$ kcal/mol, $\Delta H_{subl}(Rb) = 19.5$ kcal/mol,[29] and the ionization potential of rubidium, 96.33 kcal/mol.[30] Thus, $\Delta H_f^\circ\,[PbCl_6^{2-}(g)]$ equals −221.5 ± 22 kcal/mol.

MCl_6^{2-} Donor-Acceptor Bond Energy. The bond dissociation energy corresponding to the enthalpy change for reaction 20 was calculated for M = Ge, Sn, and Pb. Data

$$MCl_6^{2-}(g) \rightarrow MCl_4(g) + 2Cl^-(g) \tag{20}$$

and results are shown in Table VIII. The $\Delta H_f^\circ\,[PbCl_4(g)]$ was estimated from $\Delta H_f^\circ\,[PbCl_4(l)]$ and the gaseous heats of formation of germanium and tin tetrachloride.

Table VIII. MCl_6^{2-} Donor–Acceptor Bond Energies at 25°[a]

M	$\Delta H_f^\circ\,[MCl_6^{2-}(g)]$	$\Delta H_f^\circ\,[MCl_4(g)]$[b]	$\Delta H_f^\circ\,[Cl^-(g)]$	Bond dissocn energy
Ge	−228.4	−118.5	−58.8	−7.7 ± 20
Sn	−268.8	−112.7	−58.8	+38.5 ± 20
Pb	−221.5	−68 ± 2[c]	−58.8	+35.9 ± 24

[a] All energies in kilocalories per mole for the reaction $MCl_6^{2-}(g) \rightarrow MCl_4(g) + 2Cl^-(g)$. [b] Reference 28. [c] Estimated.

Table IX. MCl_6^{2-} Coordinate Bond Energies at 25°[a]

M	$\Delta H_f^\circ\,[MCl_6^{2-}(g)]$	$\Delta H_f^\circ\,[M^{4+}(g)]$[b]	$\Delta H_f^\circ\,[Cl^-(g)]$[b]	Coordinate bond energy
Ge	−228.4	+2488.6	−58.8	2364.2 ± 20
Sn	−268.8	+2228.3	−58.8	2144.3 ± 20
Pb	−221.5	+2282.7	−58.8	2151.4 ± 22

[a] All energies in kilocalories per mole for the reaction $MCl_6^{2-}(g) \rightarrow M^{4+}(g) + 6Cl^-(g)$. [b] Reference 28.

It is evident from the results in Table VIII that it is considerably more difficult to form the last two coordinate bonds in $GeCl_6^{2-}$ than in $SnCl_6^{2-}$ and $PbCl_6^{2-}$. The less favorable enthalpy is reflected in the relative difficulty of forming $GeCl_6^{2-}$ [6] and conceivably is caused by the crowded nature of $GeCl_6^{2-}$ relative to $SnCl_6^{2-}$ and $PbCl_6^{2-}$ ($d_{Ge-Cl} = 2.35$ Å,[12] $d_{Sn-Cl} = 2.41$ Å,[10] $d_{Pb-Cl} = 2.50$ Å[18]).

MCl_6^{2-} Coordinate Bond Energy. The coordinate bond energy corresponds to the enthalpy change for the reaction[35]

$$MCl_6^{2-}(g) \rightarrow M^{4+}(g) + 6Cl^-(g) \tag{21}$$

Results are shown in Table IX for M = Ge, Sn, and Pb.

The coordinate bond energy represents the removal of all six Cl^- ions from the metal ion. Of course, it becomes more difficult to remove successive chlorides, and it is important to realize that the coordinate bond energy does not equal the energy of the six bonds in MCl_6^{2-}. However, it is necessary to consider the coordinate bond energies to obtain a realistic bond energy trend for $GeCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$ from the thermochemical data we collected. The gaseous heats of formation do not reflect the bond energy trend accurately because they include heats of atomization and are also dependent upon the spectroscopic state of the central atom. This is especially true for our results as different cations were used for each anion in the calorimetry. The trend of decreasing gaseous heats of formation is Sn > Ge > Pb while coordinate bond energies decrease in the order Ge > Pb ≃ Sn.

Discussion

A discussion of bonding trends in the series $GeCl_6^{2-}$, $SnCl_6^{2-}$, and $PbCl_6^{2-}$ necessitates consideration of the large amount of information available on the M-Cl bond for group IVb elements.[9] The information is often inconclusive, however, due to a lack of appropriate data, such as bond energies, for comparison. A particularly ambiguous facet of this subject is the extent of σ and π character in M-Cl bonds, and consideration of σ and π effects is important when attempting to examine and correlate relative trends in bond polarity and bond energy.

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Relative amounts of π character in M-Cl bonds have mainly been discussed for tetrahedral compounds of the group IVb elements.[9,36-41] The trend Si > Ge > Sn for π contribution to M-Cl bonding in various substituted halides of Si, Ge, and Sn has evolved form nqr[39] and ^{13}C nmr.[40] Such a trend is reasonable in terms of orbital matching, although it is difficult to ascertain the relative magnitude of σ and π bonding because no technique can truly separate the two contributions.

The nqr data presented in Table I can be interpreted in terms of the Townes-Dailey approximation[42] which yields the following equation for chlorine

$$(e^2Qq/h)_{\mathrm{mol}} = (e^2Qq/h)_{\mathrm{at}}\left[N_{\mathrm{p}_z} - \frac{N_{\mathrm{p}x} + N_{\mathrm{p}y}}{2}\right] \qquad (22)$$

N_{p_i} is the population of the p_x, p_y, or p_z orbital, and the z axis has been taken to be the bonding axis of an M-Cl bond. Care in devising the systems to study can improve the applicability of the Townes-Dailey model. For example, the use of salts with the same cation decreases variations in the electric field gradient (efg) due to crystal field effects, and the use of large cations, such as $(CH_3)_4N^+$, separates the anions and appears to reduce the crystal lattice contribution. All of the chlorine atoms in the anions lie on fourfold axes, and, hence, the efg asymmetry at each chlorine atom is zero. The nuclear quadrupole coupling constant, e^2Qq/h, is exactly twice the chlorine resonance frequency. According to eq 22 increasing σ bonding in the M-Cl bond should increase $\nu_{^{35}Cl}$ while increasing π bonding decreases $\nu_{^{35}Cl}$ in this situation.

Among the heavier main-group element compounds, σ-bonding differences are overall the dominant factor in variations in the M-Cl bonds. An intimation of the σ-bonding trend lies in the ionization potentials of Ge, Sn, and Pb (Table I), and the nqr frequencies follow this trend. The higher potential and nqr frequency for $PbCl_6^{2-}$ compared to $SnCl_6^{2-}$ is explicable in terms of the poor shielding of the "f" electrons of Pb. A similar effect probably also exists for $GeCl_6^{2-}$ where the first d shell has just been filled. Superimposed on this σ-polarity trend will be the smaller effects of π bonding.

Comparison of ^{35}Cl nqr frequencies in $GeCl_6^{2-}$ (19.61 MHz in $[(CH_3)_4N]_2GeCl_6$) and $SnCl_6^{2-}$ (16.67 MHz in $[(CH_3)_4N]_2SnCl_6$) with those in $SeCl_6^{2-}$ (20.43 MHz in K_2SeCl_6,[43] but from conclusions presented before,[10] $\nu_{^{35}Cl}$ in $[(CH_3)_4N]_2SeCl_6$ would be expected to be near 22 MHz) and $TeCl_6^{2-}$ (16.29 MHz in $[(CH_3)_4N]_2TeCl_6$)[11] indicates that there may be nonnegligible π character in the Ge-Cl bond in $GeCl_6^{2-}$ for the following reason. The $\nu_{^{35}Cl}$ in $SnCl_6^{2-}$ is about the same as that found in $TeCl_6^{2-}$. The similar result is expected for $\nu_{^{35}Cl}$ in $GeCl_6^{2-}$ and $SeCl_6^{2-}$. However, $\nu_{^{35}Cl}$ in $GeCl_6^{2-}$ is substantially *lower* than in $SeCl_6^{2-}$ which could result from greater π bonding in the Ge-Cl bond compared to the Sn-Cl bond. Considerably less π bonding would be expected in the Pb-Cl bond[9] so the resonance frequency in $PbCl_6^{2-}$ should reflect the σ bond almost exclusively.

The thermochemical results (Table IX) produce the trend in M-Cl coordinate bond energy of Ge > Sn ≃ Pb. Although correlations between bond polarity and bond energy are not expected to be straightforward, the relative bond energies are compatible with the nqr trend of covalency. Some π character along with greatest σ-bond character in the Ge-Cl bond will account for the higher bond energy observed in $GeCl_6^{2-}$ and this is also consistent with the nqr data. A lesser, but nonetheless observable, amount of π bonding along with the least σ-bond character in $SnCl_6^{2-}$ accounts for the lower ^{35}Cl nqr frequency in $SnCl_6^{2-}$ compared to $PbCl_6^{2-}$, but because $PbCl_6^{2-}$ appears to contain more σ character than $SnCl_6^{2-}$, the two would be expected to have similar bond energies as is observed.

The only electronegativity scale to which these experimental measurements are directly comparable is the optical scale[8] and it places $\chi_{\mathrm{Pb}} > \chi_{\mathrm{Sn}} \geqslant \chi_{\mathrm{Ge}}$. χ_{Pb} is also greater than χ_{Sn} or χ_{Ge} on most other scales. It is worthwhile to note that the results found here do not support such a trend and suggest that the concept of electronegativity may not be generally useful in the heavier group IVb elements.

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Registry No. Rb_2GeCl_6, 51548-85-7; $[(CH_3)_4N]_2GeCl_6$, 51548-86-8; Cs_2GeCl_6, 21780-84-7; K_2SnCl_6, 16923-42-5; Rb_2PbCl_6, 17362-47-9; $GeCl_6^{2-}$, 16920-88-0; $SnCl_6^{2-}$, 16871-48-0; $PbCl_6^{2-}$, 16871-56-0; ^{35}Cl, 13981-72-1; Cs^+, 18459-37-5; K^+, 24203-36-9; Rb^+, 22537-38-8; Ge^{4+}, 16065-84-2; Sn^{4+}, 22537-50-4; Pb^{4+}, 15158-12-0; Cl^-, 16887-00-6.

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