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Heat of Formation of Gallium(I) Tetrachlorogallate(III) and the Chloride–Gallium Trichloride Bond Energy

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The heat of formation of gallium(I) tetrachlorogallate(III) has been determined at 25° by measuring the heat of solution of $Ga(GaCl_4)$ and $GaCl_3$ in 0.548 M HCl. The result was $\Delta H_f(Ga(GaCl_4)) = -168.2$ kcal/mol. The Madelung constant and the lattice energy of $Ga(GaCl_4)$ were calculated and used to derive values for the heat of formation of $GaCl_4^-$ from $GaCl_3$ and Cl^- in the gas phase, $\Delta H_f(g) = -80$ kcal/mol. The chloride ion is a stronger donor by a factor of 2 than any neutral ligand that has been measured. A comparison of the results with other donor–acceptor bond energies shows that, on the average, aluminum chloride has slightly stronger complexes than gallium chloride with the difference between the two ranging from about 10 kcal/mol for hard bases to about zero for soft bases.

Most of the work on donor–acceptor bond energies has been limited to study of complexes with no net charge because of the difficulty of calculating the lattice energy of ionic solids. In recent years the calculation of lattice energies with a digital computer has been achieved[1–3] and the calculation has been used to study donor–acceptor bonds in transition metals[3] and in aluminum complexes.[4] The present paper reports the results of a study of the chloride ion–gallium trichloride bond.

Experimental Section

The details of the experimental procedure have been described elsewhere[5] so only a brief description will be given here. The gallium trichloride was prepared using the procedure recommended for gallium tribromide by Greenwood and Worrall.[6] Final purification was accomplished by repeated passes through a zone-melting apparatus. Gallium was determined by direct titration with EDTA using gallocyanine as an indicator.[7] Chloride ion was determined by titration with standard silver nitrate using dichlorofluorescein as an indicator. *Anal.* Calcd for $GaCl_3$: Ga, 39.6; Cl, 60.4. Found: Ga, 39.0; Cl, 61.4.

The gallium(I) tetrachlorogallate(III) was prepared by the method reported by Greenwood and Worrall[8] for gallium(I) tetrabromogallate(III) except that the reagents were weighed out in a drybox using a 1% excess of gallium chloride. The resulting product was purified by zone melting. Gallium was determined by the Wanninen–Ringbom method[9] as outlined by Nydahl.[10] A check with a standard gallium solution showed that this method is accurate for gallium as well as for aluminum. The chloride analysis was the same as that used for gallium chloride. *Anal.* Calcd for $Ga(GaCl_4)$: Ga, 49.6; Cl, 50.4. Found: Ga, 49.6; Cl, 50.6.

As a further check on the purity of both compounds, a melting point curve was taken with an apparatus similar to the one described by Gunn.[11] The apparatus was checked with a 0.32 mol % solution of sucrose in water; the melting curve indicated a concentration of 0.34 mol %. The gallium chloride samples used in this work were not tested, but tests on gallium chloride samples prepared in the same way as this one indicated total impurities of less than 0.1 mol %. Tests on the gallium(I) tetrachlorogallate(III) showed that the total impurities were also less than 0.1% and the melting point was 172°. Greenwood and Worrall[12] reported 172.4°. In calculating the mole per cent impurity, an estimated heat of fusion of 5.4 kcal/mol was used. Since this is a relatively high heat of fusion for compounds of this type, the impurity levels reported should be an upper limit.

The calorimeter has been described previously.[13] Several modifications have recently been made. The stainless steel tube used to grip the glass ampoules has been replaced by a polyethylene holder in order to eliminate the possibility of attack by acid solutions. The Beckman breaker–amplifier has been replaced by a Keithley Model 150B microvolt ammeter and the Wheatstone bridge has been rebuilt using precision resistors.

Several more runs on the heat of solution of Tris [tris(hydroxymethyl)aminomethane] have been performed. The average of a total of ten runs on Tris samples was 7108 cal/mol with a standard deviation of a single run of 0.29%. This compares with the values of 7107 cal/mol recommended by Gunn[14] and 7111 cal/mol recommended by Sunner and Wadso.[15]

In each run an ampoule containing the sample was broken in 250 g of calorimetric liquid. In most cases heat capacity determinations were made after the sample bulb was broken. For these cases, the initial temperature of the experiment was adjusted to 25.00 ± 0.02°. In some runs calibration was performed before the experiment and the final temperature of the experiment was then adjusted to 25.00 ± 0.02°. In all cases at least two independent heat capacity determinations were made with results agreeing to within 0.2%.

The resistance of the thermistor was related to the temperature by an equation of the form[16]

$$\Delta T' = \left(\frac{R_i - R_f}{R_i + R_f}\right)(T_i + T_f)^2 \qquad (1)$$

where $\Delta T'$ is a quantity proportional to temperature change, R_i is the resistance of the thermistor at the beginning of the reaction, R_f is the resistance of the thermistor at the completion of the reaction, T_i is the absolute temperature at the beginning of the reaction, and T_f is the absolute temperature at the completion of the reaction.

Results

Heat of Formation of $Ga(GaCl_4)$.—The heat of formation of $Ga(GaCl_4)$ was obtained from the cycle

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$$\begin{tikzcd}
Ga(GaCl_4)(c) + 2HCl(0.548\ M) \arrow[r, "\Delta H_1"] \arrow[dr, "\Delta H_{soln}(Ga(GaCl_4))"'] & 2GaCl_3(c) \arrow[d, "2\Delta H_{soln}(GaCl_3)"] & + & H_2(g) \arrow[d] \\
 & 2GaCl_3(\text{in } 0.548\ M\ HCl) & + & H_2(g)
\end{tikzcd}$$

using

$$\Delta H_4 = \Delta H_{soln}(Ga(GaCl_4)) - 2\Delta H_{soln}(GaCl_3)$$

and

$$\Delta H_1 = 2\Delta H_f°(GaCl_3(c)) + \Delta H_f°(H_2(g)) - \Delta H_f°(Ga(GaCl_4)) - 2\Delta H_f°(HCl(0.548\ M))$$

gives

$$\Delta H_f°(Ga(GaCl_4)(c)) = 2\Delta H_f°(GaCl_3(c)) + \Delta H_f°(H_2(g)) - 2\Delta H_f°(HCl(0.548\ M)) + 2\Delta H_{soln}(GaCl_3) - \Delta H_{soln}(Ga(GaCl_4))$$

Table I lists the results of the runs on the heat of solution of $GaCl_3$ in 250 g 0.548 M HCl at 25°. The average of five runs si $\Delta H_{soln} = -45.1 \pm 0.2$ kcal/mol. This is in excellent agreement with the value of Wagman, *et al.*,[17] for the heat of solution of $GaCl_3$ in water, $\Delta H_{soln} = -45.0$ kcal/mol.

TABLE I

HEAT OF SOLUTION OF $GaCl_3$ IN 250 G OF 0.548 M HCl

Run no.	Wt of $GaCl_3$, g	Amt of $GaCl_3$, mmol	10^3C_p	$10^{-3}\Delta T'^a$	q, cal		ΔH, kcal/mol
1	0.1699	0.9649	3.718	11.615	43.18		−44.8
2	0.1527	0.8672	3.702	10.536	39.00		−45.0
3	0.1754	0.9961	3.761	11.974	45.03		−45.2
4	0.1528	0.8678	3.720	10.512	39.10		−45.1
5	0.1314	0.7463	3.688	9.143	33.72		−45.2
						Av	−45.1 ± 0.2[b]

[a] ΔT is given by eq 1. [b] This is the estimated 95% confidence limit of the measurement.

TABLE II

HEAT OF SOLUTION OF $Ga(GaCl_4)$, SAMPLE II IN 250 G OF 0.548 M HCl

Run no.	Wt of $Ga(GaCl_4)$, g	Amt of $Ga(GaCl_4)$, mmol	Ga residue, mg	10^3C_p	$10^{-3}\Delta T'^a$	q, cal	q_{cor}, cal		ΔH, kcal/mol
1	0.2080	0.7395	8.3	3.697	16.96	62.70	69.01		−93.3
2	0.1438	0.5113	4.9	3.694	11.90	43.96	47.70		−93.3
3	0.1615	0.5742	4.7	3.695	13.57	50.14	53.76		−93.6
4	0.1512	0.5376	4.0	3.700	12.86	47.32	50.42		−93.8
5	0.1186	0.4217	2.9	3.693	10.00	36.93	39.17		−92.9
								Av	−93.4 ± 0.5[b]

[a] ΔT is given by eq 1. [b] This is the estimated 95% confidence limit of the measurement.

In the reaction of $Ga(GaCl_4)$ with HCl, some disproportionation occurred giving gallium metal and hydrogen gas as products. The gallium residue was filtered from the vessel liquid and dissolved in nitric acid. The filtration was completed within 10 min after completion of the reaction and tests showed that the amount of gallium dissolving in the HCl in this amount of time was negligible. The amount of gallium residue was determined by EDTA titration. The solution in the vessel was saturated with hydrogen gas before the reaction was initiated in order to avoid heat effects from the solution of the hydrogen evolved in the reaction.

Six runs on the heat of solution of a preliminary sample of $Ga(GaCl_4)$ in 0.548 M HCl gave an average value of 92.1 kcal/mol with a standard deviation of a single run of 1.6%. Table II summarizes the results of the runs on the heat of solution of a second sample of $Ga(GaCl_4)$ in 250 g of 0.548 M HCl at 25°. "Ga residue" is the amount of gallium metal remaining after completion of the reaction. The experimental "q" was heat corrected for vaporization of water by the hydrogen evolved and for the heat of dissolution of the gallium metal produced and the result is "$q_{cor.}$" The correction for gallium dissolution is obtained from the heat of the reaction

$$2Ga + 6HCl(0.548\ M) \longrightarrow 2GaCl_3(\text{in } 0.548\ M\ HCl) + 3H_2(g)$$

$\Delta H = -51.4$ kcal/mol of Ga. This value was calculated using the heat of solution of $GaCl_3(c)$ in 0.548 M HCl and the values reported by Wagman, *et al.*,[17] for the standard heats of formation of $GaCl_3(c)$ and 0.548 M HCl.

The corrected value of ΔH in Table II, therefore, refers to the enthalpy change for the reaction

$$Ga(GaCl_4)(c) + 2HCl(0.548\ M) \longrightarrow 2GaCl_3(\text{in } 0.548\ M\ HCl) + H_2(g)$$

Using Wagman's[17] value of −39.7 kcal/mol for the standard heat of formation of 0.55 M HCl and −125.4 kcal/mol for the standard heat of formation of $GaCl_3(c)$, the standard heat of formation of $Ga(GaCl_4)$ is calculated to be −168.2 kcal/mol.

Calculation of the Madelung Constant.—Garton and Powell[18] reported the crystal structure of $Ga(GaCl_4)$ as Pnna with $a = 7.24$, $b = 9.72$, and $c = 9.50$ Å and with four $Ga(GaCl_4)$ units in each orthorhombic unit cell. The coordinates of the atoms as given by Garton and Powell were used to calculate the Madelung constant using the method of Wood.[1] The Madelung constant

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(17) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(18) G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

TABLE III

MADELUNG CONSTANT FOR $Ga(GaCl_4)$

Case	Charge distribution	$M\delta$ $(Ga(GaCl_4))$	5th shell contribution, %
I	$Ga^+(Ga^{3+}Cl^-{}_4)^-$	2.1734	0.01
II	$Ga^+(Ga^{0.2-}Cl^{0.2-}{}_4)^-$	2.1070	0.1
III	$Ga^+(Ga^-Cl^0{}_4)^-$	2.0644	0.05

was calculated for the process

$$Ga(GaCl_4)(c) \longrightarrow Ga^+(g) + GaCl_4^-(g)$$

Table III lists the Madelung constants calculated for three different charge distributions on the tetrachlorogallate ion: a +3.0 charge on the gallium atom and a −1.0 charge on each chlorine atom (case I), a −0.2 charge on the gallium and on each chlorine atom (case II), a −1.0 charge on the gallium atom and zero charge on the chlorine atoms (case III). In cases I and II, the unit cell had a net dipole moment so that corrections of 0.4 and 6.6%, respectively, were necessary.[19] Five shells of unit cells were calculated with the contribution of the fifth shell serving as an estimate of the accuracy of the calculation. The Madelung constants are based on the cube root of the molecular volume as the characteristic distance.

Calculation of the van der Waals Energies.—The van der Waals energies were calculated from the formula proposed by London[20]

$$U_v = \frac{3}{2R^6}\left(\frac{\epsilon_i\epsilon_j}{\epsilon_i + \epsilon_j}\right)\alpha_i\alpha_j = \frac{C_{ij}}{R_6} \qquad (2)$$

TABLE IV

CHARACTERISTIC ENERGIES AND POLARIZABILITIES OF IONS

Ion	$10^{12}\epsilon$, ergs/molecule	$10^{24}\alpha$, cm^3
Ga^+	29.6	0.698
Ga^{3+}	92.5	0.198
Cl^-	15.6	3.45

Table IV lists the polarizabilities (α) and characteristic energies (ϵ) used to calculate the interaction constants (C_{ij}). The characteristic energies of the Ga^+ and Ga^{3+} ions were taken as 90% of the ionization potentials of the gaseous ions (ionization potentials were obtained from ref 21). This is the procedure used by Mayer[22] for Ag^+ and Tl^+ and by Mayer and Levy[23] for Cu^+. The characteristic energy and the polarizability of the Cl^- ion were taken from Mayer's calculation for AgCl and TlCl.[22] The Ga^+ ion was calculated from the Pauling[24] value for Cu^+ by assuming that the polarizability varies as the cube of the ionic radius (ionic radii were obtained from ref 25). This is the empirical relationship used by Wasastjerna[26] in determining the ionic radii which were used by Goldschmidt[27] as a starting point for his radii values.

TABLE V

INTERACTION CONSTANTS (C_{ij}) AND VAN DER WAALS SUMS (S_{ij})

Interaction	$10^{60}C_{ij}$, ergs cm^6/molecule	S_{ij}
Ga^+–Ga^+	10.8	4.381
Cl^-–Cl^-	139	171.526
Ga^+–Cl^-	36.9	24.134
Ga^{3+}–Ga^{3+}	2.72	4.956
Ga^{3+}–Ga^+	4.64	25.572
Ga^{3+}–Cl^-	13.7	55.754

The interaction constants calculated from eq 2 and the van der Waals sums calculated by the previously described method[28] are listed in Table V.

Calculation of the Lattice Energy.—The lattice energy of $Ga(GaCl_4)$ was calculated by the method of Ladd and Lee (see eq 13 of ref 28 and ref 29) for the hypothetical lattice at 0°K assuming a 1% decrease in the cube root of the molecular volume (*i.e.*, $\delta_{298°K} = 5.5084 \rightarrow \delta_{0°K} = 5.453$). The value of the repulsion constant, $\rho = 0.33$ Å, was taken from data on the alkali halides. The results of the lattice energy calculation are given in Table VI.

TABLE VI

LATTICE ENERGY FOR $Ga(GaCl_4)$

	Case I	Case II	Czse III
Coulomb energy, kcal/mol	132.4	128.4	125.8
van der Waals energy, kcal/mol	14.1	14.1	14.1
Repulsion energy, kcal/nol	−13.3	−13.0	−12.8
Lattice energy, kcal/mol	133.2	129.5	127.1

The average lattice energy (129.9 ± 3 kcal/mol) corresponds to a −0.2 charge on the gallium and chlorine atoms. The uncertainty due to the lack of knowledge of the charge distribution is larger than any uncertainty due to errors in the crystal structure parameters, the repulsion energy, or the van der Waals energy.

Heat of Formation of $GaCl_4^-$(g).—The heat of formation of the gaseous tetrachlorogallate ion at 298°K (−243 ± 3 kcal/mol) was calculated from the cycle

$$\Delta H_f°(GaCl_4^-(g)) = U + \Delta H_f°(Ga(GaCl_4)(c)) - \Delta H_{subl}(Ga) - IP(Ga) + \int_{298}^{0} [C_p(Ga(GaCl_4)(c) + C_p(e^-(g)) - C_p(Ga(g)) - C_p(GaCl_4^-(g))]\, dT$$

The values for the terms in this cycle are: U, 129.9 kcal/mol; $\Delta H_f°(Ga(GaCl_4)(c))$, −168.2 kcal/mol; $\Delta H_{subl}(Ga)$, 66.2 kcal/mol; IP(Ga), 138.4 kcal/mol; $\int_{298}^{0} C_p(e^-(g)) = \int_{298}^{0} C_p(Ga(g)) = 1.5$ kcal/mol. The heat of sublimation of gallium metal was taken from Wagman[17] and the ionization potential was taken from Finkelnburg and Humbach.[21] The heat capacity terms involving $Ga(GaCl_4)$ and $GaCl_4^-$ were neglected since they are estimated to be about 5 kcal/mol and should cancel each other (±1 kcal/mol).

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TABLE VII

HEATS OF FORMATION OF GALLIUM AND ALUMINUM CHLORIDE COMPLEXES (KCAL/MOL)

Donor	$-\Delta H_f$(cg)		$-\Delta H_f$(g)		Ref
	$AlCl_3$	$GaCl_3$	$AlCl_3$	$GaCl_3$	
$(C_2H_5)_2O$	53.0[c]	39.6[e]	37.8	26.7	*a, b*
C_4H_8O	57.1[c]	47.5[c]			*b*
$CH_3CO_2C_2H_5$	54.8	45.1			*c*
$(CH_3)_2S$	44.3	46.2	30.3	30.5	*d*
$(C_2H_5)_2S$	44.0	45.1	29.9	32.0	*a, d*
C_4H_8S	46.7	49.5	30.2	32.8	*d*
C_5H_5N	69.5	58.9[c]	45.7	35.2	*e–g*
$(C_2H_5)_3N$	64.4	52.0[c]	44.4	34.4	*g, h*
NH_3	60	52	40	28.7	*g–i*
Cl^-			83	80	

[a] N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc.*, *A*, 270 (1966). [b] R. L. Richards and A. Thompson, *ibid.*, *A*, 1244 (1967). [c] M. F. Lappert and J. K. Smith, *ibid.*, 5826 (1965). [d] R. L. Richards and A. Thompson, *ibid.*, *A*, 1248 (1967). [e] N. N. Greenwood and P. G. Perkins, *ibid.*, 1145 (1960). [f] J. W. Wilson and I. J. Worrall, *ibid.*, *A*, 316 (1968). [g] N. N. Greenwood and T. S. Srivastava, *ibid.*, *A*, 267 (1966). [h] D. D. Eley and H. Watts, *ibid.*, 1319 (1954); NH_3–$AlCl_3$ calculation based on data of W. Klemm, E. Clausen, and H. Jacobi, *Z. Anorg. Allgem. Chem.*, **200**, 363 (1931). [i] H. L. Friedman and H. Taube, *J. Am. Chem. Soc.*, **72**, 2236 (1950), NH_3–$AlCl_3$ calculation based on data of W. Klemm, W. Tilk, and H. Jacobi, *Z. Anorg. Allgem. Chem.*, **207**, 194 (1932).

Heat of Formation of the $Cl^- \rightarrow GaCl_3$ Bond.—The heat of formation of the $Cl^- \rightarrow GaCl_3$ bond ($\Delta H_f(g) = -80 \pm 3$ kcal/mol) was calculated from $\Delta H_f(g) = \Delta H_f{}^\circ(GaCl_4{}^-(g)) - \Delta H_f{}^\circ(Cl^-(g)) - \Delta H_f{}^\circ(GaCl_3(g))$ where all values are for 298°K. The heat of formation of $GaCl_3(g)$ (-107.0 kcal/mol) was taken from Wagman.[17] The heat of formation of the gaseous chloride ion (-55.8 kcal/mol) is from Nelson and Sharpe.[30] Note that this value for the $Cl^- \rightarrow GaCl_3$ bond energy includes the energy of reorganizing the gallium trichloride from a planar to a tetrahedral configuration.

Discussion

Table VII compares the interaction energies of a number of complexes of $AlCl_3$ and $GaCl_3$. $\Delta H_f(g)$ refers to the enthalpy change for the process

$$MX_3(g) + L(g) \longrightarrow LMX(g)$$

where L is a neutral or charged ligand. In most cases, $\Delta H_f(g)$ cannot be determined directly but is calculated from data on the formation of the liquid or solid complex. For neutral ligands, the quantity that is usually measured is $\Delta H_f(c)$ which refers to the enthalpy change for the process

$$MX_3(c) + L(l) \longrightarrow LMX_3(c)$$

In some cases the complex is a liquid so that $\Delta H(l)$, referring to the process

$$MX_3(c) + L(l) \longrightarrow LMX_3(l)$$

is determined. In either case, it is necessary to know the heat of sublimation of MX_3, the heat of vaporization of the ligand, and either the heat of vaporization or the heat of sublimation of the complex. The first two quantities are generally known but the last quantity often cannot be measured due to decomposition of the complexes. Consequently, values for heats of vaporization and sublimation of the complexes are usually estimated from known data for similar compounds.

Because of this uncertainty in the gas-phase heats of formation of the complexes, the quantity $\Delta H_f(cg)$ is included in Table VII. This is the heat of formation of the crystalline complex from gaseous halide and gaseous ligand

$$MX_3(g) + L(g) \longrightarrow LMX_3(c) \quad \Delta H_f(cg)$$

For a liquid complex $\Delta H_f(cg)$ refers to the heat of formation of the liquid adduct from gaseous components. The difference between $\Delta H_f(cg)$ for a liquid and a solid is the heat of fusion which is about 3 kcal/mol for these adducts.[31] The value for $\Delta H_f(g)$ for the $Cl^- \rightarrow AlCl_3$ bond in Table VII was calculated from the lattice energy of Wood and D'Orazio[4] together with the new value of the heat of formation of $NaAlCl_4(c)$, $\Delta H_f = -272.5$ kcal/mol, determined by Beck.[5] The heats of formation of the $Cl \rightarrow AlCl_3$ and $Cl^- \rightarrow GaCl_3$ bonds are very similar, -83 ± 7 and -80 ± 3 kcal/mol, respectively. Both of these bond energies are approximately twice as large as that of the strongest bond to a neutral donor listed in Table VII. Thus, for both $AlCl_3$ and $GaCl_3$, Cl^- is a strong donor. The results also emphasize that bond energies depend strongly on the state of the chlorine ligand. For example, the gas-phase energies of dissociation of dimeric Al_2Cl_6 and Ga_2Cl_6, when corrected for the reorganization from planar to tetrahedral geometry, lead[32] to approximate bond dissociation energies of $D(Cl \rightarrow AlCl_3) \simeq 50$ kcal/mol and $D(Cl \rightarrow GaCl_3) \simeq 43$ kcal/mol. Correcting the present results for the reorganization energy yields the values $D(Cl^- \rightarrow AlCl_3) \simeq 115$ kcal/mol and $D(Cl^- \rightarrow GaCl_3) \simeq 113$ kcal/mol; these are more than twice the magnitude of the energies obtained from the chloride bridge bonds. The fact that the bridge bonds are much weaker is confirmed by the measured force constants[33,34] and bond lengths.[18,35–37]

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An examination of Table VII shows that, on the average, aluminum chloride forms slightly stronger complexes than gallium chloride. For donors using N or O (hard bases)[38,39] alumium chloride forms bonds about 10 kcal/mol stronger than the gallium chloride bonds. Equilibrium measurements of gallium chloride and aluminum chloride with substituted anilines in ether also show that aluminum chloride is a slightly better acid toward these bases.[40] For donors using S or Cl^- as the bridging group (softer bases), the two acids form bonds of about the same strength (±3 kcal/mol). These regularities hold even though the actual values of the bond energies vary from 26 to 83 kcal/mol. This regularity can be used to predict bond energies where steric effects are small. For instance, Greenwood and Perkins[31] gave $\Delta H_f(g) = -34$ kcal/mol for the gallium chloride–piperidine complex. One would, therefore, predict that $-\Delta H_f(g)$ for the aluminum chloride complex was -44 ± 5 kcal/mol.

The slight preference of $GaCl_3$ for softer bases compared to $AlCl_3$ indicates that $GaCl_3$ is a softer acid than $AlCl_3$, as expected. The small difference between the two means that they have about the same acid strength. It is the similarity in acid strengths, together with the small difference in their preferences for hard bases, which allows predictions to be made.

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Perfluorocarboxylato Disulfides and Methylsilanes

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The reaction of disulfur dichloride, S_2Cl_2, with silver perfluorocarboxylates gives substituted disulfides, $(R_fCO_2S)_2$, where $R_f = CF_3, C_2F_5, C_3F_7$. They are thermally unstable and decompose to $(R_fCO)_2O$, SO_2, and S. Compounds of the general formula $(R_fCO_2)_nSi(CH_3)_{4-n}$, where $n = 1, 2, 3$ and $R_f = CF_3, C_2F_5, C_3F_7$, have been prepared similarly by reaction with the corresponding chloromethylsilanes. Infrared, nmr, and mass spectra as well as elemental analyses are reported for these new compounds.

Many perfluorocarboxylates or, at least, trifluoroacetates are known. However, none has been reported for group VI elements with the exception of chromium.[1,2] It was of interest to attempt the preparation of compounds containing sulfur to compare their stabilities with those of their carboxylate analogs. The tetrakis(trifluoroacetates), $(CF_3COO)_4M$, of several group IV elements have been prepared.[3] Silicon tetrakis(trifluoroacetate) was obtained from the reaction of silicon tetrachloride with trifluoroacetic acid in benzene solution.

In this work, bis(perfluorocarboxylato) disulfides, $(R_fCO_2S)_2$, where $R_f = CF_3, C_2F_5, C_3F_7$, and perfluorocarboxylatomethylsilanes of the general formula $(R_fCO_2)_nSi(CH_3)_{4-n}$ where $n = 1, 2, 3$, and $R_f = CF_3, C_2F_5, C_3F_7$, have been prepared by the reactions of silver perfluorocarboxylates with disulfur dichloride and the corresponding chloromethylsilanes.

Experimental Section

Apparatus.—A standard Pyrex high-vacuum system was used for handling volatile materials and for separating volatile products by trap-to-trap distillation. Reactions were carried out in 125-ml Pyrex bulbs fitted with 4-mm Teflon stopcocks (Fischer and Porter Co.). Kel-F No. 90 stopcock grease (3M Co.) was used on all ground joints.

Infrared spectra (Table I) were recorded with a Beckman IR5A spectrophotometer or a Perkin-Elmer Model 621 grating infrared spectrophotometer. Spectra of gases were obtained by introducing the vapors into a Pyrex cell with a path length of 100 mm and KBr windows. Spectra of liquids were taken after the liquids were placed between KBr windows in a dry box. High-resolution ^{19}F nmr spectra (Table II) were recorded with a Varian Model HA-100 spectrometer operating at 94.1 Mc and ^1H nmr spectra were recorded with an A-60 nmr spectrometer. The compounds were sealed in Pyrex tubes with CCl_3F and tetramethylsilane as internal references. Mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV. Elemental analyses (Table III) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Molecular weights were determined by Regnault's method with a calibrated bulb equipped with a Teflon stopcock.

Reagents.—Silver salts of the perfluorocarboxylic acids were obtained from Fisher Scientific Co. and Peninsular ChemResearch, Inc. They were ground to fine powders and dried overnight under dynamic vacuum. S_2Cl_2 (Eastman Kodak Co.) was purified by distillation. The fraction with a boiling point range of 133–134° was used. $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3 (Wilshire Chemical Co.) were dried over molecular sieves.

General Preparation.—All of the compounds were prepared by the same method. In a typical reaction, $(CH_3)_3SiCl$ (5.60

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