Previous Raman work[9] indicated the presence of equilibria such as

$$2Al_2Cl_7^- = Al_3Cl_{10}^- + AlCl_4^- \qquad (11)$$

and reaction 10 in acidic melts. The existence of Al_2Cl_6 and at least one uncharacterized species in compositions of high $AlCl_3$ content (possibly $Al_3Cl_{10}^-$) was also demonstrated by the Raman measurements.

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A Spectral and Conductance Study of Gallium Trihalides and Their Complexes in Acetonitrile

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Infrared and conductance measurements of gallium trihalides and their complexes in acetonitrile are reported. Gallium trihalides are found to dissociate in acetonitrile to give solvated dihalogallium ion $GaX_2S_2^+$ (where X = Cl, Br, or I and S = acetonitrile) and tetrahalogallate ion GaX_4^-. The cation solvation number of 2 was determined from pmr spectral measurements of concentrated solutions of gallium tribromide in acetonitrile at low temperatures. The stability of the tetrahalogallate ion in acetonitrile solutions was established from conductance and infrared measurements of $(C_2H_5)_4NGaX_4$ salts. Single-ion limiting conductance values of 98.0, 103.1, and 106.2 $ohm^{-1}\ cm^2\ mol^{-1}$ were obtained for $GaCl_4^-$, $GaBr_4^-$, and GaI_4^-, respectively. The preference of gallium for four-coordination in acetonitrile, in both the anion and the cation, is discussed in terms of the base strength and solvating power of the solvent. The 1:1 adducts of gallium trihalide with the strong basic bidentate ligand 1,10-phenanthroline are ionic salts containing the GaX_4^- as the anion. The cation is six-coordinate $Ga(phen)_2X_2^+$. Based upon this formulation, the salts behave as typical 1:1 electrolytes in acetonitrile with low single-ion conductance values of 63.1, 47.8, and 37.5 $ohm^{-1}\ cm^2\ mol^{-1}$ for the dichloro-, dibromo-, and diiodobis(1,10-phenanthroline)gallium(III) cations, respectively. Addition of $AgBF_4$ to their acetonitrile solutions results in the formation of salts formulated as $Ga(phen)_2(BF_4)_2GaX_4$. The tendency of gallium to assume a higher coordination number than 4 with strong basic ligands is also shown in the case of the 2:3 gallium trichloride- and gallium tribromide-pyridine complexes in which the cation probably is five-coordinated and the anion is GaX_4^-.

Introduction

This work is part of a continuing effort to define the nature of solute species in acetonitrile. Previously, boron trihalides and their complexes,[2,3] aluminum chloride, phosphorus pentachloride, antimony pentachloride,[4] and ionic salts[5] had been investigated. The growing use of acetonitrile as a solvent for polarographic studies,[6,7] for ionic reactions,[8] and for electrosynthesis[7] encourages continued activity in solute characterization.

Results

Tetraethylammonium Tetrahalogallates.—The measured molar conductances and corresponding concentrations for the teraethylammonium tetrahalogallate salts in acetonitrile at 25° are shown in Table I. The data indicate that the tetrahalogallate salts are typical 1:1 electrolytes in acetonitrile. Computer analysis of the data by the Fuoss–Onsager conductance equation[9,10] on a 7040 IBM computer showed that the salts are completely dissociated and have Λ_0 values of 183.0 ± 0.9 ($(C_2H_5)_4NGaCl_4$), 188.1 ± 0.7 ($(C_2H_5)_4NGaBr_4$), and 191.2 ± 0.8 $ohm^{-1}\ cm^2\ mol^{-1}$ ($(C_2H_5)_4NGaI_4$). Values of 98.0, 103.1, and 106.2 $ohm^{-1}\ cm^2\ mol^{-1}$ were obtained for the single-ion limiting conductance of $GaCl_4^-$, $GaBr_4^-$, and GaI_4^-, respectively. A value of 85.05[11] $ohm^{-1}\ cm^2\ mol^{-1}$ was used for λ_0 of the tetraethylammonium ion. The relative order of single-ion limiting conductances is that which is expected for the case where the smaller, more polarizing ion interacts more strongly with the polar solvent to produce a large solvodynamic radius and a reduced ion mobility.

The infrared spectrum of crystalline tetraethylammonium tetrabromogallate shows a strong band at 270 cm^{-1} which is assigned to the ν_3 frequency of the tetrahedral $GaBr_4^-$ ion.[12,13] This band appears at the same position in the infrared spectrum of its acetonitrile solution. The infrared spectrum of crystalline tetraethylammonium tetrachlorogallate shows a very strong band at 372 cm^{-1} (with a shoulder at 357 cm^{-1}), which is characteristic of the ν_3 vibration of $GaCl_4^-$ (T_d).[12,14,15] In the solution spectrum of the salt, this band cannot be observed because it is buried under the strong acetonitrile absorption band at 375 cm^{-1}. The ν_3 frequency of GaI_4^- (T_d) at 225 cm^{-1} [13,15] lies below the experimental limit of our instrument.

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TABLE I

CONDUCTANCE OF TETRAETHYLAMMONIUM TETRAHALOGALLATES IN ACETONITRILE AT 25°

$(C_2H_5)_4NGaCl_4$		$(C_2H_5)_4NGaBr_4$		$(C_2H_5)_4NGaI_4$	
10^3C	Λ	10^3C	Λ	10^3C	Λ
0.4475	177.6	0.6159	175.9	0.2780	182.0
0.5137	176.4	0.7070	173.8	0.3162	181.0
0.5906	175.2	0.8214	173.4	0.3692	180.1
0.6570	172.1	0.9352	172.3	0.4119	179.3
0.7322	170.9	1.076	168.9	0.4749	178.9
0.8812	168.6	1.272	167.7	0.5255	177.3
0.9785	165.9	1.362	166.8	0.5507	177.2
1.085	164.2	1.526	164.9	0.5986	175.9
1.240	161.9	1.584	161.9	0.6863	174.7
1.456	159.2	1.747	162.9	0.7293	174.6
1.724	153.5	1.831	159.7	0.7641	173.9
1.761	153.6	2.048	160.0	0.8627	172.5
1.961	150.4	2.096	156.8	0.9101	171.6
2.293	146.2	2.334	154.7	0.9955	170.1
2.534	143.8	2.437	156.9	1.164	168.2
2.849	140.2	2.600	151.9	1.390	165.7
3.374	135.4	2.938	148.8	1.718	163.7
3.747	131.8	3.388	145.4	2.323	158.8
4.089	128.5	4.029	139.6	2.759	154.8
4.214	128.2	4.650	136.9		
4.693	122.6				
4.808	122.0				
5.461	115.5				
5.618	116.6				
6.121	112.0				
6.641	105.3				

Gallium Trihalide–Acetonitrile Complexes.—Conductance measurements of gallium trihalides are summarized in Table II. Molecular weights corresponding to the dimer were used in computing molar conductances because interpretation of the *combined* infrared, nmr, and conductance data is consistent only with an ionic dimeric formulation, $GaX_2(CH_3CN)_2^+,GaX_4^-$. Plots of Λ *vs.* $\sqrt{C}$ are linear like that expected for strong electrolytes, but the limiting molar conductances are only approximately half of those typical of 1:1 electrolytes if a monomeric formula weight is assumed. Infrared data of the crystalline 1:1 gallium trichloride (tribromide)–acetonitrile complexes indicate a $GaX_2(CH_3CN)_2^+,GaX_4^-$ structure. In acetonitrile solutions of gallium tribromide the tetrabromogallate ion has been identified by infrared spectroscopy and proton nmr data support the existence of $GaBr_2(CH_3CN)_2^+$ (*vide infra*). Computer analysis of the data gave values of 120.8 ± 0.4, 119 ± 1, and 148 ± 1 $ohm^{-1}\ cm^2\ mol^{-1}$ for the limiting molar conductances of gallium trichloride, tribromide, and triiodide, respectively. These values are lower than the expected values of completely dissociated 1:1 electrolytes and indicate ion pairing. The large uncertainty in the calculated association constants from the Fuoss–Onsager conductance equation[9,10] for associated electrolytes makes these constants unreliable.

TABLE II

CONDUCTANCE OF GALLIUM TRIHALIDES IN ACETONITRILE AT 25°

Ga_2Cl_6		Ga_2Br_6		Ga_2I_6	
10^4C	Λ	10^4C	Λ	10^4C	Λ
1.526	117.0	0.8108	115.8	0.9319	139.2
4.421	113.4	1.642	106.3	1.572	136.7
7.099	110.2	2.064	110.1	2.386	131.6
10.30	107.4	2.668	110.8	3.334	129.4
13.47	103.3	3.196	109.3	4.706	125.7
13.49	105.0	4.046	109.7	7.003	119.9
18.18	102.2	4.624	109.5	8.738	116.1
21.88	100.5	5.310	109.5	10.18	114.1
24.37	99.15	6.211	109.5	11.48	112.4
26.73	97.51	8.111	108.5	12.86	109.9
27.13	98.44	9.307	106.8	15.58	106.2
29.79	97.34	9.736	107.7	19.34	102.0
32.42	94.85	11.54	104.6	25.04	95.3
42.04	89.85	13.77	102.6		
53.97	85.32	16.24	100.4		
65.24	81.56	19.73	97.91		
		24.05	94.86		
		30.97	90.99		
		36.59	88.51		
		41.58	87.34		

The infrared spectrum of crystalline $GaCl_3 \cdot CH_3CN$ shows a very strong band at 369 cm^{-1} due to the ν_3 vibration of $GaCl_4^-$ (T_d). The CN stretching frequency of acetonitrile which normally appears as a doublet at 2250 and 2290 cm^{-1} in free acetonitrile is shifted to 2294 and 2316 cm^{-1}. The increase is typical of coordinated acetonitrile in its various complexes. The infrared spectrum of crystalline $GaBr_3$–CH_3CN contains a strong band at 269 cm^{-1}, which may be assigned to the ν_3 vibration of $GaBr_4^-$ (T_d), and a strong doublet CN stretching band at 2299 and 2315 cm^{-1}. Crystalline $GaI_3 \cdot CH_3CN$ shows the strong doublet CN stretching band at 2287 and 2308 cm^{-1}.

Another band of strong to medium intensity appears at 414, 408, and 432 cm^{-1} in the infrared spectra of the crystalline acetonitrile complexes of $GaCl_3$, $GaBr_3$, and GaI_3, respectively. A band in this region also appears in the spectra of the gallium trihalide complexes with pyridine and 1,10-phenanthroline as well as in the spectrum of cystalline bis(1,10-phenathroline)gallium(III) perchlorate. Since Greenwood[16] and Carty[17] have identified the Ga–N vibration in gallium trihalide complexes at 250–270 cm^{-1}, the bands in the 400-cm^{-1} region are not due to a Ga–N stretching vibration. In the acetonitrile complexes the band in the 408–432-cm^{-1} region may be assigned to the acetonitrile frequency associated with the C–C–N bending mode[18] at 378 cm^{-1} (369 cm^{-1} in the gas phase), shifted to higher frequencies upon coordination. The band appearing in the same region in the infrared spectra of the pyridine and 1,10-phenanthroline complexes can be likewise assigned to shifted ligand frequencies (*vide infra*).

Only in the case of gallium tribromide was it possible to observe a characteristic band due to GaX_4^- (T_d) in acetonitrile solution (strong absorption at 270 cm^{-1}). For gallium trichloride this band is obscured by the strong absorption of the solvent, and for gallium triiodide the ν_3 absorption appears below 250 cm^{-1}.

The solvent coordination number of gallium tribromide in acetonitrile was measured directly by proton nmr spectroscopy.[19] A concentrated solution of gallium tribromide in acetonitrile gives a signal due to the methyl protons of acetonitrile bound to gallium which is 37 Hz downfield from the bulk acetonitrile signal as shown in Figure 1. By measuring the relative areas of the bound and bulk acetonitrile it is possible to show that 1 mol of acetonitrile is bound for every mole of gallium tribromide present. While an apparent solvation number of 1 can be accounted for in terms of a

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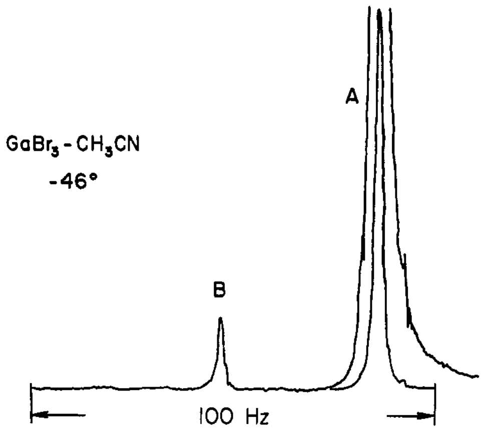

Figure 1.

molecular structure $GaBr_3 \cdot CH_3CN$ or an ionic structure $GaBr_2(CH_3CN)_2^+, GaBr_4^-$, the existence of the former, except in relatively minor concentrations, is eliminated by the combined conductance and infrared spectral data. The ionic structure is consistent with all of the data, however. The experimental results of the coordination number determination are summarized in Table III.

TABLE III

SOLVATION NUMBER, *n*, OF GALLIUM TRIBROMIDE IN ACETONITRILE

mmol of $GaBr_3$	mmol of CH_3CN	δ,[a] Hz	Temp, °C	n[b]
1.471	85.33	−38	−46	0.96
1.428	109.4	−36	−31	1.04

[a] Chemical shift of methyl proton for bound acetonitrile relative to the bulk acetonitrile. [b] Moles of bound acetonitrile per mole of gallium trihalide.

Line broadening of the signal due to bound acetonitrile was observed to occur as the temperature was increased. The results of kinetic studies of solvent exchange will be reported in a separate publication.

Gallium Trihalide–Phenanthroline Complexes.—Gallium trihalides react with 1,10-phenanthroline to give stable crystalline complexes with the empirical formula $GaX_3 \cdot$phen. The occurrence of these complexes as ionic dimers in the solid state was deduced from infrared spectroscopy. The crystalline $GaCl_3 \cdot$phen complex shows a strong band at 370 cm^{-1}, and $GaBr_3 \cdot$phen, a strong band at 270 cm^{-1} due to the ν_3 vibration of GaX_4^- (T_d). Both complexes contained a band of medium intensity at 425 and 426 cm^{-1}, respectively. This band may be assigned to the 408-cm^{-1} band of 1,10-phenanthroline shifted by complexation.[20,21] The $GaI_3 \cdot$phen complex which showed a weak band at 427 cm^{-1} was presumed also to have an ionic dimer structure. A more proper designation for the 1:1 adducts, which reflects their ionic character, is $[GaX_2(phen)_2^+][GaX_4^-]$. The appearance of a strong absorption band at 270 cm^{-1} due to the $GaBr_4^-$ ion in acetonitrile solutions of the gallium tribromide–phenanthroline complex indicates this solid-state ionic formulation is preserved in solution.

TABLE IV

CONDUCTANCE OF GALLIUM TRIHALIDE–PHENANTHROLINE COMPLEXES IN ACETONITRILE AT 25°

$(GaCl_3 \cdot phen)_2$		$(GaBr_3 \cdot phen)_2$		$(GaI_3 \cdot phen)_2$	
10^4C	Λ	10^4C	Λ	10^4C	Λ
0.2728	160.6	0.1164	149.2	0.1353	142.3
0.3920	159.0	0.1710	147.9	0.2225	141.8
0.5627	159.4	0.2225	148.1	0.3073	140.8
0.6477	157.4	0.3645	147.6	0.4153	140.6
0.7711	160.8	0.5150	146.6	0.8814	139.0
0.8958	156.6	0.5343	146.7	1.350	138.4
1.282	155.6	0.5768	146.5	1.842	136.6
1.332	159.4	0.7656	146.2	2.523	135.6
1.564	155.4	0.8815	145.9	3.048	135.8
1.805	157.8	1.350	144.6	3.753	134.4
2.264	158.2	1.832	144.1	4.295	133.7
2.629	156.2	2.522	142.8	5.231	132.6
3.181	157.8	3.048	142.6		
3.673	156.8	4.295	141.7		
4.544	156.0	5.231	140.2		

The ionic character is supported by the conductance measurements summarized in Table IV. If the compounds are formulated as ionic dimers, the molar conductances lie close to those typical of 1:1 electrolytes. Computer analysis of the data gave Λ_0 values of 161.1 ± 0.7, 150.9 ± 0.6, and 143.7 ± 0.4 ohm^{-1} cm^2 mol^{-1} for the chloride, bromide, and iodide complexes, respectively. Single-ion limiting conductances of the cations, calculated by subtracting the known values of the single-ion limiting conductances of the corresponding tetrahalogallate, were found to be 63.1, 47.8, and 37.5 ohm^{-1} cm^2 mol^{-1} for the dichloro-, dibromo-, and diiodobis(1,10-phenanthroline)gallium(III) cations, respectively.

When silver tetrafluoroborate was added to 1 mol equiv of the $GaBr_3 \cdot$phen or $GaCl_3 \cdot$phen in acetonitrile and the silver halide was removed, the resulting compounds have the empirical formula $Ga(phen)X_2BF_4$. The infrared spectra of these salts clearly show the characteristic bands of BF_4^- ion as a very broad absorption around 1020 cm^{-1} and a weak to medium doublet at 516 and 520 cm^{-1}. These bands appear around 1030 and 515, 520 cm^{-1} in the spectrum of silver tetrafluoroborate. In addition, however, the spectra of the crystalline chloro and bromo complexes show strong bands at 369 and at 271 cm^{-1}, respectively, due to the ν_3 vibration of GaX_4^-. Both spectra contain medium bands at 429–430 cm^{-1} due to the phenanthroline in the cationic species $Ga(phen)_2^{3+}$. These data favor an ionic structure $[Ga(phen)_2][GaX_4][BF_4]_2$ over $[GaX_2(phen)_2][BF_4]$. Conductance measurements are indiscriminating in this case.

Gallium Trihalide–Pyridine Complexes.—Several stoichiometric complexes of gallium trihalides with pyridine have been reported.[22–26] Both gallium trichloride and tribromide give 1:1 and 1:2 gallium trihalide–pyridine complexes by condensing the ligand onto the halide, whereas gallium triiodide gives only the 1:1 adduct.[23,26] Gallium trichloride forms the 1:1 adduct with pyridine from alcohol solution but forms the 1:2 complex from ether.[22] Both gallium tribromide and triiodide form 1:3 complexes with pyridine from ether solution.[22] In this study methylene chloride was

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used as the solvent and the complexes $2GaCl_3 \cdot 3py$, $2GaBr_3 \cdot 3py$, and $GaBr_3 \cdot 2py$ were isolated.

The infrared spectrum of crystalline $2GaCl_3 \cdot 3py$ contains a strong absorption at 372 cm^{-1}, indicative of the $GaCl_4^-$ ion. In the infrared spectrum of the corresponding bromide complex the strong absorption of $GaBr_4^-$ is observed at 270 cm^{-1}. In addition to these bands both spectra contain medium bands at 435 cm^{-1} assigned to the ν_{16b} vibration of pyridine shifted to higher frequencies by complexation.[27]

Conductance measurements of the 2:3 halide–pyridine complexes give very high molar conductance values in the range of 200–300 ohm^{-1} cm^2 mol^{-1}, which suggest the presence of three ions in solution. The appearance of a 270-cm^{-1} band in solutions of $2GaBr_3 \cdot 3py$ gives clear evidence for the tetrabromogallate ion. Further ionization of the cation $GaX_2(py)_3^+$, whose existence is suggested by studies on the solid state, to a four-coordinate gallium species would increase the conductance of these salts.

Discussion

The combined conductance and infrared and nmr spectral data for acetonitrile solutions of gallium tribromide indicate that it behaves as a slightly associated 1:1 electrolyte of the type $[GaBr_2(CH_3CN)_2^+][GaBr_4^-]$ While only in the case of gallium tribromide is spectral evidence obtained for the tetrahalogallate ion in solution, the similarity in conductance data for the three trihalides, the presence of the ν_3 vibration of $GaCl_4^-$ in crystalline $GaCl_3 \cdot CH_3CN$, and the same 1:1 stoichiometry of the adducts suggest equivalent ionization mechanisms and solute species for the three halides. Conductance measurements of the tetraethylammonium tetrahalogallates showed that these salts are typical 1:1 electrolytes and established the stability of the tetrahalogallate ions. The stability of the tetraiodogallate ion is notably different from that of the tetraiodoborate ion, which upon dissolution in acetonitrile dissociates completely to the solvated BI_2^+ cation and the iodide ion.[3]

The preference of gallium trihalides to form *four-coordinate, ionic* species in acetonitrile is best understood in terms of the coordination model,[28] which takes as its basic assumption that the intrinsic base strength and the solvating power of the solvent are the two most important factors which govern equilibria, composition, and geometry of solute species. The choice of equilibria in eq 1–6 reflects this assumption and permits a qualitative analysis of the effects of these factors. The term solvating power refers to solute–solvent Lewis acid–base interaction and electrostatic interactions beyond the first coordination sphere.

Acetonitrile, a solvent with a moderate dielectric constant (ϵ 36), favors reactions which result in charge separation (eq 2, 3, 5, 6). The limiting conductance values for the gallium trihalides, which are slightly lower than the values observed for typical 1:1 electrolytes, indicate that ion pairing occurs and must be considered. The existence of $BX_2S_2^+,BX_4^-$ ion pairs in acetonitrile solutions of boron trichloride and boron tribromide[3] and of $CoCl_5S^+,CoCl_3S^-$ in acetonitrile solutions of anhydrous cobalt(II) chloride[29] were reported previously.

$$Ga_2X_6 + 2S \rightleftharpoons 2GaX_3 \cdot S \quad (1)$$

$$GaX_3 \cdot S + nS \rightleftharpoons [GaX_2S_{n+1}{}^+ \cdot X^-] \quad (2)$$

$$[GaX_2S_{n+1}{}^+ \cdot X^-] \rightleftharpoons [GaX_2S_{n+1}{}^+] + X^- \quad (3)$$

$$GaX_3 \cdot S + X^- \rightleftharpoons GaX_4^- + S \quad (4)$$

$$GaX_3 \cdot S + [GaX_2S_{n+1}{}^+ \cdot X^-] \rightleftharpoons [GaX_2S_{n+1}{}^+ \cdot GaX_4^-] + S \quad (5)$$

$$[GaX_2S_{n+1}{}^+ \cdot GaX_4^-] \rightleftharpoons [GaX_2S_{n+1}{}^+] + GaX_4^- \quad (6)$$

On the basis of electrostatic repulsion alone, tetrahedral four-coordination would be the preferred geometry. The thermodynamic studies of Katzin[30,31] indicate that the relative bond energies of the metal–solvent and the metal–halide ion in four- and six-coordination govern the preference for a specific structure. Four-coordination is preferred in acetonitrile because the average bond energy of two additional gallium–solvent bonds is insufficient to overcome the loss in bond energy in passing from the tetrahedral, four-coordinate ions to the six-coordinate ions. Limited thermochemical data also indicate that the greater donor strength of the halide ions, relative to acetonitrile, favors formation of GaX_4^- in eq 4. The standard enthalpy of bond formation for $Cl^-(g) + GaCl_3(g) = GaCl_4^-(g)$ is -80 kcal mol^{-1},[32] which far exceeds that of -59.2 kcal mol^{-1} for $GaCl_3 \cdot C_5H_5N(g)$. While there are no thermochemical data for the gaseous $GaCl_3 \cdot CH_3CN$ adduct, the enthalpies of reaction[33] in carbon tetrachloride for $C_6H_5OH \cdot C_5H_5N$ (-8.3 kcal mol^{-1}) and $C_6H_5OH \cdot CH_3CN$ (-3.3 kcal mol^{-1}) indicate that the intrinsic donor strength of acetonitrile is much lower than those of pyridine and the chloride ion.

That strong neutral donor ligands favor the formation of complexed metal ions with high coordination numbers[31] (five- or six-coordination in the case of gallium) is supported by our studies with the donors pyridine and 1,10-phenanthroline. Pyridine and gallium trichloride or gallium tribromide combined to form the stable ionic salts $[GaX_2(C_5H_5N)_3^+][GaX_4^-]$ and $[GaBr_2(C_5H_5N)_4^+][GaBr_4^-]$. The crystalline $[GaX_2(phen)_2^+][GaX_4^-]$ salts were obtained for gallium trichloride, tribromide, and triiodide. Conductance measurements indicate that all three of the *o*-phenanthroline adducts behave as strong 1:1 electrolytes. The low and diminishing order of 63.1, 47.8, and 37.8 ohm^{-1} cm^2 mol^{-1} for the single-ion limiting conductances of the dichloro-, dibromo-, and diiodobis(1,10-phenanthroline)gallium(III) cations can be accounted for if the radius of the cation diminishes from the iodo to the chloro derivative, a trend that would occur if the ions are essentially unsolvated. Because the charge of the cation would be distributed over a large surface area in these cations, a weakly solvated cation would be expected. The low mobility of bulky ions is not without precedence. The $(C_6H_5)_2B(bipy)^+$ ion has a limiting ionic conductance in water of 23.7 ohm^{-1} cm^2 mol^{-1},[34] which is much lower than 38.7 ohm^{-1} cm^2 mol^{-1}, for the highly solvated lithium ion. The

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TABLE V
ANALYTICAL DATA

Compd	% C		%H		% N		% X	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$GaCl_3 \cdot CH_3CN$	10.96	11.06	1.66	1.38	6.26	6.45	46.61	48.97
$GaBr_3 \cdot CH_3CN$	6.62	6.85	0.85	0.86	3.77	3.99	63.19	68.41
$GaI_3 \cdot CH_3CN$	5.82	4.88	0.67	0.61	2.99	2.85	74.49	77.47
$(C_2H_5)_4NGaCl_4$	28.09	28.00	5.85	5.98	4.09	4.27	41.10	41.19
$(C_2H_5)_4NGaBr_4$	18.45	18.49	3.91	3.85	2.61	2.69	61.24	61.54
$(C_2H_5)_4NGaI_4$	13.74	13.58	2.91	2.85	2.01	1.98	71.55	71.74
$GaCl_3 \cdot$phen	41.49	40.45	2.30	2.25	8.08	7.86	29.14	29.84
$GaBr_3 \cdot$phen	29.24	29.43	1.64	1.63	5.71	5.72	48.71	48.95
$GaI_3 \cdot$phen	23.03	22.85	1.32	1.27	4.56	4.44	60.66	60.37
$GaCl_2$(phen)BF_4	34.86	35.36	2.29	1.96	6.85	6.87	17.24[a]	17.39
$GaBr_2$(phen)BF_4	27.46	29.00	1.89	1.61	5.32	5.64	33.82[a]	32.18
$2GaCl_3 \cdot 3$py	29.96	30.53	2.75	2.54	6.89	7.12	35.33	36.08
$2GaBr_3 \cdot 3$py	20.94	20.78	1.99	1.73	4.88	4.85	56.46	55.35
$GaBr_3 \cdot 2$py	24.28	25.68	2.09	2.14	5.64	5.98	50.32	51.26

[a] Chloride or bromide.

$(C_6H_5)_2B(C_5H_5N)_2^+$ ion has a λ_0 of 28 ohm^{-1} cm^2 mol^{-1} in acetonitrile.[2] Coetzee and Cunningham showed a significant decrease in limiting ionic conductance of tetraalkylammonium ions as the ion size increased from tetramethylammonium (94.55 ohm^{-1} cm^2 mol^{-1}) to tetraisoamylammonium (57.24 ohm^{-1} cm^2 mol^{-1}) in acetonitrile.[11]

The friction offered by the solvent to movement of the bulky cations may be augmented by elongation of the metal–halogen bonds. The moderate dielectric constant of acetonitrile would favor charge separation to the extent that the halide ion would move further from the metal ion than it lies in the crystalline state. Simultaneously the charge on the cationic portion would increase to a value greater than 1, thereby increasing the coulombic interaction between the halide ion and metal complex cation. Viewed in terms of this dynamic model, the halide ion would pulsate on the surface of the large cation, effectively enlarging the ionic radius and reducing ionic mobility. The conversion of the $[GaX_2(phen)_2][GaX_4]$ to $[Ga(phen)_2][GaX_4][BF_4]_2$ by the addition of an equivalent amount of silver tetrafluoroborate is consistent with the structural model for a $GaX_2(phen)_2^+$ ion in which the Ga–X bond is elongated and the halide ion is easily removed. The presence of the tetrahalogallate ion in the crystalline tetrafluoroborate salts eliminates the four-coordinate $GaX_2(phen)^+$ ion as the stable species in the solid state.

Experimental Section

Purification of Reagents.—Fisher reagent grade acetonitrile was purified by the method described previously.[5] Methylene chloride (Fisher reagent grade) was purified by fractional distillation from phosphorus pentoxide. The constant-boiling center fraction was retained. Tetraethylammonium halides (Eastman Kodak White Label) were dried in the oven at 120° before use. Gallium(III) chloride, bromide, and iodide, purchased from Alfa Inorganics, Inc., were sublimed under vacuum prior to use.

Preparation of Tetraethylammonium Tetrahalogallates.—A 1.381-g (7.85-mmol) sample of gallium trichloride was dissolved in methylene chloride. The solution turned yellow and then brown. A 1 mol equiv amount of dried tetraethylammonium chloride dissolved in 20 ml of methylene chloride was added to the gallium chloride solution dropwise. Upon evaporation of part of the solvent and cooling, fine white crystals formed. The solid was filtered, recrystallized from methylene chloride, and dried *in vacuo*. The final product was fine needlelike crystals, mp 267–269°.

Tetraethylammonium tetrabromogallate was prepared in like manner. The resulting white solid melts at 305–306°.

A 1.024-g (2.27-mmol) sample of gallium triiodide was suspended in 30 ml of methylene chloride and a 21-ml solution of 0.380 g (1.48 mmol) of dried tetraethylammonium iodide in the same solvent was added to it. The mixture was refluxed for 1 hr and the unreacted gallium iodide was removed by filtration. A white precipitate was filtered from the cooled filtrate, washed with chilled methylene chloride, recrystallized from methylene chloride, and dried at 65° *in vacuo*. The final product melts at 292–293° dec.

Synthesis of 1:1 Gallium Trihalide–Acetonitrile Complexes.—Gallium trihalides react exothermally and in some cases vigorously with acetonitrile. When excess acetonitrile was added to a solution of gallium trichloride in methylene chloride, a vigorous reaction occurred. After concentration of the mixture to half its original volume and cooling, white crystals formed. The solid was filtered, recrystallized from methylene chloride, and dried at room temperature *in vacuo*. The solid melts at 162–164° dec.

When treated in the same manner, the gallium tribromide gave a white crystalline $GaBr_3 \cdot CH_3CN$ adduct, which melts with decomposition between 142 and 152°. The gallium triiodide–acetonitrile complex is a white, crystalline solid, mp 183–186° dec, which slowly develops a brown color due to photodecomposition.

Synthesis of Gallium Trihalide–1,10-Phenanthroline Complexes.—A 0.100 *M* solution of sublimed 1,10-phenanthroline in methylene chloride was made for the preparation of these complexes. Dropwise addition of 20 ml of the standard phenanthroline solution to a 20-ml solution containing 0.352 g (2.0 mmol) of gallium trichloride in methylene chloride resulted in the formation of a white crystalline solid, mp 327–329°.

Treatment of a solution containing 0.286 g (0.92 mmol) of gallium tribromide in methylene chloride with 9.3 ml of the phenanthroline solution resulted in the separation of a white crystalline solid. A dried sample of this compound decomposes when heated in a sealed ampoule over 340°.

When a 0.451-g (1.00-mmol) sample of gallium triiodide was suspended in 25 ml of methylene chloride and 10 ml of the standard phenanthroline solution was added dropwise to it, a pale yellow precipitate formed. Upon heating in a sealed ampoule, the yellow color of the solid diminishes when heated over 100°, but the compound does not melt up to 300°.

Even when 2 or 3 mol of phenanthroline were used for every mole of gallium chloride or bromide, the same 1:1 complex was obtained. In the case of the iodide, a bright yellow precipitate separated under these conditions and elemental analysis was approximately that of a 1:3 complex.

Interaction of a 1:1 Gallium Trihalide–Phenanthroline Complex with Silver Tetrafluoroborate.—Addition of 9.6 ml of 0.10 *M* solution of $AgBF_4$ in acetonitrile to 0.344 g (0.96 mmol) of $GaCl_3 \cdot$phen in 25 ml of acetonitrile resulted in the immediate precipitation of AgCl. After removal of AgCl by filtration, the filtrate was evaporated to dryness. The resulting white solid was recrystallized from methylene chloride and dried *in vacuo*. On heating, the solid collapsed at 145° and began to decompose over 175°. Elemental analysis corresponds to the empirical formula $GaCl_2(phen)BF_4$.

By a similar procedure, a white solid was obtained from the reaction of mole equivalent amounts of $AgBF_4$ with $GaBr_3 \cdot$

phen. On heating, the solid began to decompose over 200° in a sealed ampoule. Elemental analysis was that for $GaBr_2(phen)BF_4$.

Interaction of Gallium Trihalides with Pyridine.—When a solution of 0.150 g (1.90 mmol) of pyridine in 10 ml of methylene chloride was added dropwise to a solution of 0.224 g (1.27 mmol) of gallium trichloride in 20 ml of methylene chloride, a highly vigorous reaction occurred. Upon evaporation of the solvent a white solid was obtained. This was recrystallized from acetonitrile–ether, filtered, and dried *in vacuo*. The resulting solid melts at 93–94°. This same product was obtained when varying ratios of pyridine and gallium trichloride were mixed in methylene chloride, although the melting points of the products were slightly different. The elemental analysis given in Table V is the average of three analyses of the complex and corresponds closely to the 2:3 $GaCl_3$:py mole ratio.

When excess pyridine was added to gallium tribromide solution in methylene chloride, a vigorous reaction occurred. Evaporation of the solvent left a white solid, which was recrystallized from methylene chloride. Elemental analysis (Table V) corresponds to the 1:2 $GaBr_3$–py complex, mp 83–84° (lit. mp[27] 88°). In other attempts, addition of pyridine solutions in methylene chloride to gallium tribromide in the same solvent in the mole ratio of 1:1 or 2:1 pyridine–gallium tribromide resulted in the formation of white solids having melting points of 126–127 and 129–130°, respectively. The elemental analysis results (Table V) were very close and correspond to the 2:3 $GaBr_3$–py complex.

Similar experiments with gallium triiodide gave a white solid, which turns yellow on standing for a few hours under vacuum and decomposes on heating to 180°. Elemental analyses were not satisfactory for any proposed composition.

All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Because of the extreme moisture sensitivity of gallium trihalide–acetonitrile complexes, low halide contents were consistently obtained as a result of hydrolysis. A summary of elemental analyses is given in Table V.

The apparatus and procedure for conductance measurements have been described in detail.[35] The infrared spectra of Nujol mulls and thin films of solution were taken with a Beckman Model IR 10 spectrophotometer and a Perkin-Elmer Model 521 spectrophotometer made available by the University of Illinois. For mulls, CsBr and CsI windows were employed. Solution spectra were measured in a 0.1-mm solution cell provided with CsBr windows down to the 300-cm^{-1} region and between polyethylene windows down to the 250-cm^{-1} region.

Proton nmr spectra were obtained at 60 Mc using a Varian A-60 spectrometer equipped with a variable-temperature probe (V-6031) and a variable-temperature control unit (V-6040). The temperature was monitored by measuring the peak separation of methanol. The areas under the peaks were obtained by integration of the signals. Samples for nmr spectra were prepared by weight and all transfers were made in a dry nitrogen atmosphere. Because of the exothermic reaction, acetonitrile was added to the gallium tribromide samples cooled in liquid nitrogen.

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Coordination Compounds of Indium. X. Anionic Indium(III) Halide Complexes

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The compounds obtained from the reaction of substituted ammonium halides (CX) with indium(III) halides in organic solvents are shown to be salts of the type $C[InX_4]$, $C_2[InX_5]$, and $C_3[InX_6]$. Species of stoichiometry C_4InX_7 can be prepared, and the lattices of these apparently also contain InX_6^{3-} anions. Vibrational spectroscopy has been used to investigate the structures of the compounds prepared.

Introduction

Salts of anionic indium halide complexes were first reported a century ago,[2] and a number of species, such as K_3InCl_6 and $NaInCl_4$, have since been described in the literature.[3–5] In 1936, Ekeley and Potratz[6] found that reaction of an indium halide with the corresponding substituted ammonium or sulfonium halides in an organic solvent gives rise to a series of colorless crystalline compounds, which they formulated as double salts, but which are better written as the anionic indium complexes $C[InX_4]$, $C_2[InX_5]$, and $C_3[InX_6]$. Species with the stoichiometry C_4InX_7 were also reported (C = substituted ammonium or sulfonium cation). Crystal structure investigations have confirmed the formulation as anionic complexes[7,8] for $(C_2H_5)_4N[InCl_4]$ and $((C_2H_5)_4N)_2[InCl_5]$. In addition a small number of substituted anionic indium halide complexes are known, although little structural information is available. The anion of the salt $(NH_4)_2[InCl_5(H_2O)]$ has C_{4v} symmetry.[9] Disubstituted anionic species, such as $InCl_4L_2^-$ (L = urea, thiourea)[10] and $InCl_4bipy^-$ (bipy = 2,2′-bipyridyl),[11] have been prepared, but no X-ray structural investigations have been reported.

The object of the present work was to confirm and extend the preparative work on anionic indium halide complexes, to examine the vibrational spectra of these compounds, and to relate the findings to any relevant structural information. The Raman spectra of InX_4^- species in solution have been studied by Woodward and his coworkers,[12] and the vibrational spectrum of $InCl_6^{3-}$ has been reported recently.[13] While the

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