The relative stability of complexes containing substituted aryl groups σ bonded to platinum(II) has been reported to be: 1-naphthyl > *o*-tolyl > *p*-tolyl.[5] The *m*-tolyl derivatives decompose at slightly higher temperatures than the analogous *p*-tolyl compounds indicating that *meta* substitution may result in added stabilization similar to that reported for *ortho*-substituted aryl groups. In the triphenylstibine series of compounds *ortho* substitution decreases thermal stability. This is apparently due to the previously mentioned combined steric effects of the large ligand and the *ortho*-substituted benzene rings.

The reactivity and solubility of the compounds follow the same trends observed from decomposition temperatures, decreasing with *ortho* substitution and increasing size of the stabilizing ligand. The solubility of these compounds in polar chlorinated hydrocarbons follows the order: $C_5H_5N > (C_6H_5)_3P > (C_6H_5)_3As > (C_6H_5)_3Sb$ and *p*-tolyl $\cong$ *m*-tolyl > *o*-tolyl.

Although addition and displacement reactions of compounds of the type L_2PtR_2, where L is pyridine or a tertiary phosphine, with alkyl iodides have been reported,[2,5,9] preliminary investigations indicate that triphenylarsine- and triphenylstibine-stabilized platinum(II) complexes do not react with alkyl iodides.

The infrared spectra of all compounds reported are similar to the spectra of previously described *cis*-triphenylphosphine complexes of platinum(II). The spectra of these compounds are also similar to those of triphenylarsine and triphenylstibine, the main difference being the reduced intensity of the absorption peak at 909 cm^{-1} in the triphenylstibine compounds and the 912-cm^{-1} peak in triphenylarsine compounds. The presence of absorption peaks associated with the substituted aryl groups was also noted.

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Preparations, Far-Infrared Spectra, and Raman Spectra of Pentahaloindium(III) and -thallium(III) Complexes

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The addition of excess tetraalkylammonium halide to indium(III) and thallium(III) halides in a variety of nonaqueous solvents leads to the formation of pentahaloindates and pentahalothallates—*e.g.*, $[(C_2H_5)_4N]_2[InCl_5]$, $[(C_2H_5)_4N]_2[TlCl_5]$, $[(CH_3)_4N]_2[TlCl_5]$, $[C_8H_{18}N_2][TlCl_5]$, and $[C_8H_{18}N_2][TlBr_5]$. Vibrational spectra of $[(C_2H_5)_4N]_2[InCl_5]$ are those expected for a square-pyramidal geometry for $InCl_5^{2-}$, which is known from previous single-crystal X-ray data to have rigorous C_{4v} symmetry in the tetraethylammonium salt. Spectra of the corresponding thallium compound also are indicative of a square-pyramidal geometry for the anion. Similarly, the X-ray powder patterns of the tetraethylammonium pentachlorothallate(III) indicates this salt is isomorphous (and presumably isostructural) with the corresponding indium complex. In the presence of the cation $C_8H_{18}N_2^{2+}$, vibrational spectra indicate irregular geometries for the pentahalo complexes. Therefore it appears probable that the square-pyramidal structure found for the tetraethylammonium salts results from peculiarities of the crystal packing. Raman spectra for nitromethane solutions of $InCl_5^{2-}$ and $TlCl_5^{2-}$ indicate significant dissociation to the tetrahalo complexes, and the intensities may be analyzed in terms of the equilibrium: $[(C_4H_9)_4N][TlCl_4] + [(C_4H_9)_4N]Cl = [(C_4H_9)_4N]_2[TlCl_5]$. In nitromethane or alcohol it is possible that the MX_5^{2-} species are coordinated by the solvent to produce pseudooctahedral complexes.

Introduction

Many five-coordinate halide complexes of group V and IV elements are known. The phosphorus(V) halides readily come to mind and anionic species of the type MX_5^- have been reported for group IV elements such as silicon, germanium, and tin. In fact, it appears that where both four- and six-coordinate complexes are known for an element, the preparation of intermediate five-coordinate species should only require discovery of the necessary experimental conditions.

There is an extensive literature[2,3] on four- and six-coordinate thallium and indium halide complexes, prepared principally by classical methods from aqueous solutions. Also, a series of complexes $MCl_5H_2O^{2-}$ (M = Tl, In) is known, and in the case of thallium the interesting binuclear species $Tl_2Cl_9^{3-}$ has been prepared. Of importance to the present work is a series of double salts[4] containing $InCl_3$ and $InBr_3$, with formulas like $[R_4N]_nX \cdot InX_3$ (n = 1–4). Recently, a different

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[1] Alfred P. Sloan Fellow.

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[3] P. Pascal, "Nouveau Traite de Chimie Minerale," Vol. VI, Mason et Cie, Paris, 1961.

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preparation of $[(C_2H_5)_4N]_2[InCl_5]$ was reported,[5] but the constitution of the anion was not discussed. While this work was in progress, two reports appeared on the preparation of alkylammonium pentachlorothallate salts[6] but no structural data were given. A particularly important development, which occurred during the present work, was the X-ray single-crystal structure determination on $[(C_2H_5)_4N]_2[InCl_5]$.[7] The purpose of our investigation was systematically to consider the preparation of five-coordinate halide complexes of thallium and indium and study the vibrational spectra of those compounds. Some of the present results have appeared in a communication.[8]

Experimental Section

General Information.—Microanalyses for carbon, hydrogen, and nitrogen were carried out by Miss Hilda Beck of this department. Halide and metal analyses were performed by the authors using standard gravimetric procedures or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weight determinations were performed on a Mechrolab Model 302 vapor pressure osmometer. Infrared spectra were obtained for Nujol mulls between polyethylene plates, using a Beckman IR 11 instrument. Raman spectra were obtained for compressed pellets on an instrument which employs He–Ne laser excitation (6328.17 Å) and a SPEX 1400 II double monochromator.[9] The 90° geometry was used for the illumination of all samples. X-Ray powder patterns were obtained with nickel-filtered Cu Kα radiation, using a 114-mm diameter Debye–Scherrer camera. Alkali halides were used as internal calibrants.

Tetrahydrofuran or acetonitrile solutions of thallic chloride were made by passing chlorine through thallous chloride suspensions in these solvents. Excess chloride was removed by a rapid stream of nitrogen. Thallic bromide solutions were prepared by adding bromine dropwise to stirred suspensions of thallous bromide in tetrahydrofuran or acetonitrile. The presence of water in the samples was checked by investigating their ir spectra in the ranges (1500–1700 cm^{-1}) and (2900–3500 cm^{-1}) using a Beckman IR-9.

Tetraethylammonium Pentachlorothallate(III).—A solution of thallic chloride prepared from thallous chloride (3.60 g) and acetonitrile (50 ml) was filtered and added to one of tetraethylammonium chloride (6.5 g) in acetonitrile (50 ml). The solution was evaporated to ~50 ml and cooled in ice. The white precipitate was recrystallized from 2% $[(C_2H_5)_4N]Cl$–CH_3CN solution (30 ml) to give cubic crystals which were filtered off, washed with ether, and air dried; yield, 4.54 g (47%). *Anal.* Calcd for $C_{16}H_{40}N_2Cl_5Tl$: C, 29.93; H, 6.28; N, 4.36; Tl, 31.83; Cl, 27.61. Found: C, 29.68, 30.14; H, 5.99, 6.50; N, 4.35, 4.47; Tl, 31.64; Cl, 27.58. The molecular weight in ethanol at 37° was 215 (7.66 mM) and 180 (4.12 mM); the calculated value is 214 for a 2:1 electrolyte. An identical product may be prepared from methylene chloride solution.

Tetraethylammonium Pentachloroindate.—This salt may be prepared from $InCl_3$ plus $[(C_2H_5)_4N]Cl$ in ethanol,[4] methylene chloride,[7] or acetonitrile.[8] Also a pure product may be prepared conveniently by the interaction of $[(C_2H_5)_4N][InCl_4]$ with $[(C_2H_5)_4N]Cl$ in acetonitrile. In a typical preparation 0.79 g (1.9 mmol) of $[(C_2H_5)_4N][InCl_4]$ in 20 ml of acetonitrile was added to 0.31 g of $[(C_2H_5)_4N]Cl$ dissolved in 5 ml of acetonitrile. Square platelike crystals began to form in a few minutes. The product was collected by suction filtration and washed with $(C_2H_5)_2O$. *Anal.* Calcd for $C_{16}H_{40}N_2Cl_5In$: C, 34.78; H, 7.30; N, 5.07; Cl, 32.08; In, 20.77. Found: C, 34.90; H, 7.52; N, 5.20; Cl, 32.28; In, 20.59; mp 264–267° dec. The molecular weight in ethanol at 37° is 132 at 6.79 mM concentration, 164 at 13.4 mM, and 178 at 21.7 mM; the calculated value for a 2:1 electrolyte is 184.

Tetramethylammonium Pentachlorothallate(III).—In a typical preparation thallic chloride, prepared from thallous chloride (3.60 g) in acetonitrile (30 ml), was added to tetramethylammonium chloride (5.0 g) in methanol. The ice-cold mixture was washed with a little ether and air dried; yield, 7.4 g (83%). The air-dried product contained some water, as judged by infrared spectra. This was removed in a vacuum desiccator containing $Mg(ClO_4)_2$. *Anal.* Calcd for $C_8H_{24}N_2Cl_5Tl$: C, 18.12; H, 4.57; N, 5.29; Tl, 38.57; Cl, 33.40. Found: C, 18.51; H, 4.71; N, 5.26; Tl, 38.24; Cl, 33.42.

N,N′-Dimethyl(triethylenediammonium) Pentachlorothallate(III).—Filtered solutions of N,N′-dimethyl(triethylenediammonium) chloride (0.90 g) in methanol (250 ml) and thallic chloride—prepared from thallous chloride (1.0 g)—in tetrahydrofuran (20 ml) were mixed, and after evaporation to *ca.* 100 ml, the white product was filtered off, washed with ether, and air dried; yield, 1.33 g (60%). *Anal.* Calcd for $C_8H_{18}N_2Cl_5Tl$: C, 18.34; H, 3.46; N, 5.35; Cl, 33.83; Tl, 39.02. Found: C, 18.70; H, 3.63; N, 5.34; Cl, 33.09; Tl, 40.16. Attempts to recrystallize this complex were hampered by its low solubility in methanol.

N,N′-Dimethyl(triethylenediammonium) Pentabromothallate(III).—A solution of thallic bromide, prepared from thallous bromide (2.84 g), in tetrahydrofuran (20 ml) was added to N,N′-dimethyl(triethylenediammonium) bromide (3.3 g) in methanol (120 ml), and the mixture was evaporated to about 80 ml. The crude material was stirred with methanol (80 ml), and the deep-yellow product was filtered off, washed with ether, and air dried; yield, 4.79 g (64%). *Anal.* Calcd for $C_8H_{18}N_2Br_5Tl$: C, 12.88; H, 2.43; N, 3.75; Br, 53.55; Tl, 27.39. Found: C, 13.00; H, 2.19; N, 3.62; Br, 53.10; Tl, 28.94. The molecular weight in ethanol at 37° was 262 (2.07 mM); that expected for a 1:1 electrolyte was 373.

Raman Spectra of Solutions and Equilibrium Studies.—Raman spectra of tetraethylammonium and tetrabutylammonium chlorothallate solutions in nitromethane were studied. For equilibrium measurements, two solvent bands at 481 and 556 cm^{-1} were used as internal standards for Raman intensity measurements. A number of solutions of different concentrations of $[(C_4H_9)_4N][TlCl_4]$ in CH_3NO_2 were run to obtain a value for the intensity of $\nu_1(TlCl_4^-)$ referred to the two solvent bands. Spectra were obtained of solutions containing added $[(C_4H_9)_4N]Cl$ and the relative intensity obtained above was used to determine the concentration of $TlCl_4^-$ present in the solution. From this and the originally known amounts of $[(C_4H_9)_4N][TlCl_4]$ and $[(C_4H_9)_4N]Cl$, equilibrium constants were calculated.

Tetrabutylammonium tetrachlorothallate used in these experiments was prepared by a procedure similar to that of Cotton, Johnson, and Wing;[10] mp 132°; lit.[10] 115–116°.

Results and Discussion

Preparations.—Ekeley and Potratz[4] prepared $[(C_2H_5)_4N]_2[InCl_5]$ in ethanol and suggested that it could be recrystallized from this solvent. However, repetition of this work showed that without the presence of excess chloride, recrystallization gives $[(C_2H_5)_4N][InCl_4]$, the melting point of which Ekeley and Potratz incorrectly attribute to $[(C_2H_5)_4N]_2[InCl_5]$. In our work, acetonitrile was used as the reaction medium since it gives purer products. Excess chloride was still necessary to prevent the precipitation of the MCl_4^- (M = In, Tl) salts.

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TABLE I

FAR-INFRARED AND RAMAN SPECTRA (CM^{-1}) OF $[(C_2H_5)_4N]_2[InCl_5]$ AND $[(C_2H_5)_4N]_2[TlCl_5]$

$[(C_2H_5)_4N]_2[InCl_5]$		$[(C_2H_5)_4N]_2[TlCl_5]$		Tentative assignments[c]		
Ir	Raman	Ir	Raman	ν_n	Symmetry	Expected activity
295 sh	294 s[a]	*Ca.* 285 sh, br	275 vs[a]	ν_1	A_1	Ir and Raman
282 s	287 sh[b]	255–250 vs	260 sh[b]	ν_7	E	Ir and Raman
272 s		245 sh		ν_2	A_1	Ir and Raman
	194 w		171 vw	ν_4	B_1	Raman
	167 m		153 w	ν_6	B_2	Raman
150 sh, vbr		138 sh		ν_8	E	Ir and Raman
141 s	*Ca.* 140 sh?	123 s	*Ca.* 120 sh?	ν_3	A_1	Ir and Raman
	123 m	116 sh	113 mw	ν_5	B_1	Raman
	106 m	95 w	99 mw	ν_9	E	Ir and Raman

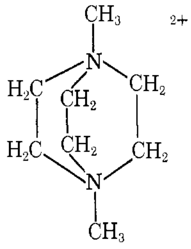
[a] In nitromethane solution this band appears to be polarized. [b] In nitromethane solution this band appears to be depolarized. [c] Based on C_{4v} square-pyramidal symmetry.

Tetramethylammonium salts were prepared from methanol or ethanol since $[(CH_3)_4N]Cl$ is insoluble in acetonitrile. Surprisingly, $[(CH_3)_4N]_2[TlCl_5]$ is the preferred product, even when a large excess of thallic chloride is present. By contrast, the tetrabutylammonium cation leads to the crystallization of only $[(C_4H_9)_4][TlCl_4]$ from acetonitrile solutions which contain excess chloride. Recently, methylene chloride was used[7] to recrystallize $[(C_2H_5)_4N]_2[InCl_5]$ for an X-ray diffraction study and we have found this to be a suitable solvent for the preparation of $[(C_2H_5)_4N][TlCl_5]$.

It appears that the formation of $[(C_2H_5)_4N]_2[TlCl_5]$ is aided by the use of solvents with low dielectric constants such as methylene chloride (and thionyl chloride[4]), compared with alcohols and acetonitrile. The difference may be due to variations of the solubility product with solvent. In addition, the lower dielectric constant media may suppress dissociation to MCl_4^- and Cl^-.

Preparations in the bromide system using alcohols or acetonitrile with $[(C_2H_5)_4N]Br$ or $[(CH_3)_4N]Br$ gave light yellow or cream-colored products of variable composition. Far-infrared spectra show these compounds to contain the $TlBr_4^-$ ion, as is also suggested by their colors. When $[(C_2H_5)_3NH]Br$ and $[C_2H_5NH_3]Br$ were used, only starting material was obtained.

In a recent review,[11] Basolo has summarized many cases in which a large unstable complex is stabilized by a counterion of similar size and the same charge number. For instance, thallium can be precipitated quantitatively from hydrochloric acid solution as $[Co(NH_3)_6][TlCl_6]$,[12a] and $[Co(NH_3)_6][TlBr_6]$ is easily prepared in the same way.[12b] A similar procedure[13] was used to prepare several hexachlorometalates including $[Co(pn)_3][InCl_6]$ (pn = 1,2-propanediamine). Accordingly, we attempted the preparation of TlX_5^{2-} salts by using the N,N′-dimethyl(triethylenediammonium) cation (DMTEA; see below), which forms halide salts that are soluble in many organic solvents. Addition of thallic bromide in tetrahydrofuran to a methanol solution of $[DMTEA]Br_2$ yields a yellow solid precipitate which has the composition $[DMTEA][TlBr_5]$. The analogous chloride complex was also prepared in the same way from methanol with no necessity for the presence of excess chloride. Attempts to prepare TlI_5^{2-}-containing products by adaptations of the above procedures were unsuccessful with TlI_4^- salts always being the result.



DMTEA

Spectra of Solids.—Raman and infrared spectral data for most of the solid complexes are given in Tables I and II and display Raman spectra are presented in Figure 1. Initially we were puzzled by the spectra of the tetraethylammonium salts since the number of bands, their positions, and their activity in the infrared and Raman spectra were all anomalous for the most logical structure—a trigonal bipyramid. A complex of this geometry should display eight fundamentals:

TABLE II

FAR-INFRARED AND RAMAN SPECTRA (CM^{-1}) OF $(CH_3)_4N^+$ AND $DMTEA^{2+}$ SALTS OF TlX_5^{2-} [a]

$[(CH_3)_4N]_2[TlCl_5]$	$[DMTEA][TlCl_5]$		$[DMTEA][TlBr_5]$	
Ir	Ir[b]	Raman[c]	Ir	Raman
282 sh	281 sh	279 vs	209 sh	
	276 sh		192 vs	196 m
262 vs, br	261 s	255 sh		189 m
244 s, br	243 s			169 vs
		195 w	134 m	
	171 wm		114 s	
	167 wm		111 s	
		155 m	108 s	
140 sh	136 s, br		87 m	102 m, br
123 s	121 w, sh	121 m		87 mw
117 s		109 vw		76 m, br
		96 m		61 vw
		52 s		48 s
		41 w		33 m

[a] DMTEA is $C_8H_{18}N_2^{2+}$, the N,N′-dimethyl(triethylenediammonium) ion. [b] A medium weak band at 303 cm^{-1} is attributed to ν_3 of a $TlCl_4^-$ contaminant. [c] A shoulder at 309 cm^{-1} is attributed to ν_1 of a $TlCl_4^-$ contaminant.

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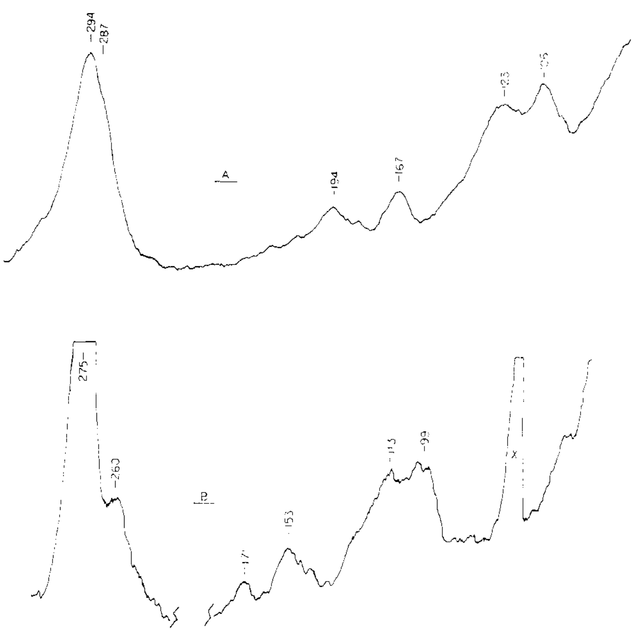

Figure 1.—(A) Raman spectrum of $[(C_2H_5)_4N]_2[InCl_5]$ solid. (B) Raman spectrum of $[(C_2H_5)_4N]_2[TlCl_5]$ solid.

three (ν_1, ν_2, and ν_8) are exclusively Raman active, two (ν_3 and ν_4) are exclusively infrared active, and three (ν_5, ν_6, and ν_7) are active in both infrared and Raman spectra. Furthermore, the order of these frequencies for a variety of trigonal-bipyramidal molecules (*e.g.*, $SbCl_5$)[14] is ν_5 (E′ in-plane stretch) > ν_3 (A_2'' out-of-plane stretch) > ν_1 (A_1' in-plane stretch) > ν_2 (A′ out-of-plane stretch), and these stretching frequencies are generally well separated from the deformation frequencies. Thus, eight fundamentals are expected with the highest two being exclusively infrared active. By contrast, the spectrum of $[(C_2H_5)_4N]_2[InCl_5]$, Table I, has nine bands, of which the two highest are both infrared and Raman active. Thus the activity of these highest bands, as well as other details of the spectra, indicate the ion is not a trigonal bipyramid. A resolution of this dilemma is afforded by the recent single-crystal X-ray structure determination of $[(C_2H_5)_4N]_2[InCl_5]$ which shows that the anion is a square pyramid with fourfold symmetry required by the space group.[7]

For lack of a closer analog, the vibrational frequencies of the square-pyramidal BrF_5 molecule may be used as a guide to the assignments for the indium and thallium complexes. While certain features of the assignments for BrF_5 may be open to contention, there is general agreement that the two highest frequencies may be assigned to ν_1 (A_1) and ν_7 (E), both of which are infrared and Raman active.[15] Other details of the spectrum which agree with the C_{4v} symmetry are the observation of nine vibrational frequencies and the activity of the observed bands. This last feature is brought out more clearly in Table I where tentative assignments are given on the assumption that the frequencies in $InCl_5^{2-}$ fall in the same order as those in BrF_5. The results are quite reasonable; although several bands which should appear in both infrared and Raman spectra are found by only one of these techniques, there are no direct violations of the selection rules.

The vibrational spectra for $[(C_2H_5)_4N]_2[TlCl_5]$ are remarkably similar to those of the corresponding indium salts (Table I). However, an apparent discrepancy with the selection rules exists for the shoulder at 116 cm^{-1} in the infrared spectrum which, if assigned to ν_5, should only be Raman active. Also agreement between the ν_1 and ν_7 bands in infrared and Raman spectra is not as close as for the indium salts and ν_7 appears to be split in the infrared spectrum. Despite these complications the $TlCl_5^{2-}$ spectra give a good over-all fit to that expected for a square pyramid. The very great similarity between these $InCl_5^{2-}$ and $TlCl_5^{2-}$ spectra is more clearly brought out in Figure 1.

The relationship of the thallium salt to the indium salt is also demonstrated by X-ray powder patterns. Our preparations of $[(C_2H_5)_4N]_2[InCl_5]$ yield powder patterns which may be indexed by using the tetragonal unit cell parameters reported by Brown, Einstein, and Tuck:[7] $a = 9.37$ and $c = 14.13$ Å. Similarly the thallium salt may be indexed by assuming a tetragonal unit cell with slightly larger dimensions, $a = 10.0$ and $c = 15.7$ Å. Thus it appears that the two compounds are isomorphous and presumably isostructural. In summary, both the spectral and X-ray data indicate that $TlCl_5^-$ (in $[(C_2H_5)_4N]_2[TlCl_5]$) has the square-pyramidal structure, which is unusual for complexes that contain a central ion with an outer d^{10} electronic configuration. This structure is a requirement of the space group for $[(C_2H_5)_4N]_2[InCl_5]$ and presumably a similar situation exists for the analogous $TlCl_5^{2-}$ salt. Therefore, it is of interest to examine spectroscopic data for these ions in combination with other cations where the packing may result in different geometries.

As shown in Table II the $DMTEA^{2+}$ salts of $TlCl_5^{2-}$ and $TlBr_5^{2-}$ display 12 bands above 60 cm^{-1} (those appreciably below this frequency are probably lattice modes). This is the number of bands expected for highly unsymmetric MX_5 species, and it is concluded that packing in the $DMTEA^{2+}$ salts is responsible for this low symmetry.

By contrast, the infrared spectrum of $[(CH_3)_4N]_2[TlCl_5]$ (Table II) is quite similar to that of the tetraethylammonium salt (Table I); therefore the anion in the tetramethylammonium salt is probably square pyramidal. We conclude that these pentahalo complexes are quite sensitive to their environment and in the case of the tetraethyl- and tetramethylammonium cations the packing fortuitously leads to square-pyramidal geometries. This interpretation is in harmony with observations on other five-coordinated species which indicate high flexibility for this coordination number.[16,17]

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Spectra of Solutions.—Qualitative features of the solution Raman spectra for $TlCl_5^{2-}$ and $InCl_5^{2-}$ indicate dissociation of these complexes. For example, a saturated solution of $[(C_2H_5)_4N]_2[TlCl_5]$ in nitromethane shows two strong peaks of nearly equal intensity at 310 and 277 cm^{-1}, both highly polarized. Comparison with spectra of solid compounds indicates that these are due to $TlCl_4^-$ (ν_1) and $TlCl_5^{2-}$, respectively. These assignments are consistent with the observation that only one band, at 279 cm^{-1}, remains after a large excess of $[(C_2H_5)_4N]Cl$ is added to the solution.

To elucidate the nature of a higher halide complex in solution, quantitative equilibrium experiments were carried out with tetrabutylammonium chloride and tetrachlorothallate in nitromethane. Equilibrium constants were calculated from the intensities of ν_1 for $TlCl_4^-$ for five solutions which ranged from 0.53 to 0.29 *M* nominal $TlCl_4^-$ concentration and from 0.45 to 0.16 *M* nominal Cl^- concentration. Attempts were made to fit the data with one-step equilibria which yield $Tl_2Cl_9^{3-}$, $TlCl_6^{3-}$, $Tl_2Cl_{10}^{4-}$, or $TlCl_5^{2-}$, respectively. Only the last of these gave reasonably constant values of K, such that for

$$TlCl_4^- + Cl^- = TlCl_5^{2-} \qquad (1)$$

the equilibrium constant is $4.6 \pm 1.0\ M^{-1}$ at 26 ± 1°.

Similarly, molecular weight measurements in ethanol at 37.3° indicate that dissociation is occurring. For $[(C_2H_5)_4N]_2[TlCl_5]$ an apparent molecular weight of 215 was obtained for a $7.66 \times 10^{-3}\ M$ solution while a value of 180 was obtained at 4.12×10^{-3} nominal molarity; the formula weight is 642. The corresponding indium compound yields values of 178 at 2.17×10^{-2} nominal molarity and 132 at $6.79 \times 10^{-3}\ M$ whereas the formula weight is 553. Apparently, the more concentrated solutions, which yield a van't Hoff *i* factor of 3, represent two $(C_2H_5)_4N^+$ plus MCl_5^{2-} and the more dilute solutions correspond to a shift to the left for equilibrium 1.

Both Raman and molecular weight data indicate the formation of MCl_5^{2-} complexes in solution. However, the question as to whether or not these are solvated to form six-coordinated species is not easily answered. The nitromethane solution spectrum of $[(C_4H_9)_4N]_2[TlCl_5]$ in the presence of $[(C_4H_9)_4N]Cl$ contains a weak polarized line at 309 cm^{-1} due to $TlCl_4^-$ and a strong polarized line at 277 cm^{-1} with an apparently depolarized shoulder at 261 cm^{-1}. The agreement between these bands and those for solid $[(C_2H_5)_4N]_2[TlCl_5]$ is remarkable. A similar close correspondence is observed between the solution spectrum of $InCl_5^{2-}$ and the spectrum of $[(C_2H_5)_4N]_2[InCl_5]$ solid. (Owing to interference by the solvent, it is not possible to obtain deformation frequencies.) The correspondence between the solution and solid-state spectra indicates similar species are involved. Coordination by the solvent cannot be ruled out because the available evidence indicates that additional coordination has relatively little influence on $InCl_5^{2-}$ and $TlCl_5^{2-}$ frequencies. For example, Spiro observed a strong stretching frequency at 270 cm^{-1} for $Cs_2[TlCl_5H_2O]$ which is only 7 cm^{-1} below the frequency which we observe for $TlCl_5^{2-}$ in nitromethane solution.[18] Similarly, Woodward and Taylor observed a band at 295 cm^{-1} for In(III) in aqueous HCl, and they postulated that this might represent $InCl_5^{2-}$.[19] However $InCl_5H_2O^{2-}$ rather than $InCl_5^{2-}$ is the pentahalide species crystallized from aqueous solution.[2,3] It is not necessary for the composition of a complex in the solid state to reflect the composition of the major species in solution; however it would be surprising for the nonaquated form to predominate in solution in equilibrium with the aquated species in the solid state. Therefore, it is likely that the species which Woodward and Taylor observed was $InCl_5H_2O^{2-}$. If this is true, the $InCl_5H_2O^{2-}$ complex displays a negligible frequency shift from $InCl_5^{2-}$ in nitromethane solution or in $[(C_2H_5)_4N]_2[InCl_5]$. Thus it is possible that the MCl_5^{2-} moieties are solvated in nitromethane solution to produce pseudooctahedral complexes which display M–Cl stretching frequencies characteristic of C_{4v} species.

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