remarkable. The tentative conclusion we draw from these comparisons is that electron transfer between cluster ions has available a favorable mechanism that cannot operate for the nonsymmetrical reactions. In this connection it has been shown[21] that the formation of polymolybdate anions from monomer units is also a very rapid process.

Acknowledgment.—We are grateful to Professor A. F. Voigt, for use of the scintillation counter for the chlorine-36 tracer experiments, and to Professor R. E. McCarley, for helpful comments and fruitful discussion.

[21] O. Glemser and W. Höltje, *Angew. Chem. Intern. Ed. Engl.*, **5**, 736 (1966).

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Coordination Compounds of Thallium(III). III. The Vibrational Spectra of Several Anionic and Neutral Complexes of Thallium(III) Chloride and Iodide and the Nature of These Species in the Solid State and in Polar Solvents

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Several new anionic and neutral complexes of thallium(III) chloride and iodide have been prepared. These include $(C_2H_5)_4NTlCl_3I$, $(C_2H_5)_4NTlCl_4B$, $TlCl_3 \cdot 1.5pyz$, $(TlX_3)_2 \cdot terpy$, $TlCl_3 \cdot terpy$, and $TlI_3 \cdot py$, where X = Cl or I, B = 2,2′-bipyridyl or 1,10-phenanthroline, pyz = pyrazine, terpy = 2,2′,2′′-terpyridyl, and py = pyridine. Molecular weight measurements in acetone and acetonitrile show that these and other complexes of thallium(III) [$TlCl_3 \cdot 2py$, $TlCl_3 \cdot 3\gamma$-pic, and $TlCl_3 \cdot 2DMSO$] are appreciably dissociated in polar media. $TlCl_3 \cdot 3\gamma$-pic, $TlCl_3 \cdot 2py$, $TlCl_3 \cdot 2DMSO$, and $TlX_3 \cdot bipy$ behave as weak electrolytes in these two solvents, whereas $(TlX_3)_2 \cdot terpy$ are typical 1:1 electrolytes. The above solution data together with the far-infrared and Raman (for $TlCl_3I^-$ and $TlCl_3 \cdot 2DMSO$) spectra of the solid complexes indicate the structures: $TlCl_3X^-$ (X = Br or I), pseudo-tetrahedral; TlX_4B^- (X = Cl or Br, B = bipy or phen), *cis*-MX_4L_2 type structure; $TlCl_3 \cdot 3\gamma$-pic, *cis*-$TlCl_3N_3$; $TlCl_3 \cdot 1.5pyz$, *trans*-$TlCl_3N_3$; $(TlX_3)_2 \cdot terpy$, $[TlX_2 \cdot terpy]^+[TlX_4]^-$; $TlCl_3 \cdot 2DMSO$, *trans*-trigonal bipyramid; $TlCl_3 \cdot 2py$, $TlCl_3 \cdot bipy$, and $TlCl_3 \cdot phen$, halogen-bridged dimers or polymers. Comparisons are made where possible with the analogous indium(III) halide systems.

Introduction

In contrast to the considerable amount of data which has recently been accumulated on the acceptor properties of the indium(III) halides[1-4] and other salts, *e.g.*, nitrates and perchlorates,[5,6] relatively little work has been carried out on the analogous thallium(III) halide systems. Infrared and Raman spectral studies[4,7-9] have been used as a guide to the structure of adducts of indium(III) chloride, bromide, and iodide and complex halides of the type $[InX_{4+n}]^{(1+n)-}$, where n = 0, 1, or 2. The development of a convenient method for the *in situ* preparation of thallium(III) chloride[10] has resulted in renewed interest in the chemistry and stereochemistry of thallium(III) halide systems. Following the work of Spiro[11-13] and Johnson and Walton[1] on the Raman and infrared spectra of $[TlX_{4+n}]^{(1+n)-}$, it is now possible to establish the presence or absence of these particular species in other systems. In the absence of a single-crystal structure determination on any adduct of the indium(III) or thallium(III) halides, these spectroscopic techniques would seem to offer at present the most rewarding means of studying the nature of these species.

To investigate further the reactivity of the thallium(III) halides and the structure and stability of the resulting complexes, detailed molecular weight, conductivity, and far-infrared spectral studies (500–33 cm^{-1}) have been carried out. During this work several new complexes of thallium(III) chloride and iodide were isolated.

Experimental Section

All reagents and solvents, with the exception of pyridine-2-carboxaldehyde 2-pyridylhydrazone (abbreviated PAPHY), were commercially available. The above named compound was prepared as described by Geldard and Lions.[14]

Preparation of Compounds.—The same method as that described previously[1,10] was used to prepare complexes of thallium(III) chloride; *i.e.*, thallous chloride, suspended in acetonitrile, was oxidized with chlorine and the appropriate reagent was then added to this solution. $(C_6H_5)_4AsTlCl_4$, $(C_2H_5)_4NTlX_4$ (X = Cl or Br), $TlCl_3 \cdot 2py$, $TlCl_3 \cdot 2DMSO$, $TlCl_3 \cdot bipy$, and $TlCl_3 \cdot phen$ were prepared as before.[1,10]

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[1] Part II: B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, **5**, 49 (1966).

[2] A. J. Carty and D. G. Tuck, *J. Chem. Soc., Sect. A*, 1081 (1966).

[3] A. J. Carty, *Can. J. Chem.*, **45**, 345 (1967).

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[5] A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 6012 (1964).

[6] D. G. Tuck, E. J. Woodhouse, and P. Carty, *J. Chem. Soc., Sect. A*, 1077 (1966).

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[8] L. A. Woodward and M. J. Taylor, *ibid.*, 4473 (1960).

[9] L. A. Woodward and P. T. Bill, *ibid.*, 1699 (1955).

[10] F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

[11] T. G. Spiro, *ibid.*, **4**, 731 (1965).

[12] T. G. Spiro, *ibid.*, **4**, 1290 (1965).

[13] T. G. Spiro, *ibid.*, **6**, 569 (1967).

[14] J. F. Geldard and F. Lions, *ibid.*, **2**, 270 (1963).

TABLE I

ANALYTICAL DATA FOR THALLIUM(III) HALIDE COMPLEXES

Compound	Color	% C		% H		% N	
		Found	Calcd	Found	Calcd	Found	Calcd
$(C_2H_5)_2NH_2TlCl_4$	White	11.50	11.42	2.94	2.89	3.36	3.33
$[(C_2H_5)_2NH_2]_2TlCl_5$	White	17.92	18.12	4.69	4.56	5.11	5.29
$(C_2H_5)_4NTlI_4$	Orange	11.46	11.41	2.37	2.39	1.66	1.66
$(C_2H_5)_4NTlCl_3Br$	White	18.68	18.45	3.87	3.87	2.62	2.69
$(C_2H_5)_4NTlCl_3I$	Yellow	16.84	16.92	3.60	3.55	2.40	2.47
$(C_4H_9)_4NTlCl_3I$	Yellow	29.32	28.26	5.90	5.34	2.18	2.06
$(C_2H_5)_4NTlCl_4$(bipy)	White	33.57	34.18	4.40	4.46	6.43	6.64
$(C_2H_5)_4NTlCl_4$(phen)	White	35.09	36.58	4.00	4.30	5.98	6.40
$(CH_3)_4NTlBr_4$(bipy)	Pale yellow	21.92	22.28	2.92	2.67	5.32	5.57
$TlCl_3$·1.5pyz	White	16.76	16.72	1.46	1.40	9.81	9.75
$TlCl_3$·terpy	White	32.54	33.12	2.09	2.04	7.74	7.72
$(TlCl_3)_2$·terpy	White	21.38	21.07	1.41	1.30	4.97	4.92
$(TlI_3)_2$·terpy	Orange	12.97	12.83	0.86	0.79	3.04	3.00
TlI_3·bipy	Orange	15.49	16.20	1.08	1.09	3.53	3.78
TlI_3·phen	Orange	18.75	18.82	1.11	1.05	3.69	3.66
TlI_3·py	Red-orange	9.86	9.04	0.91	0.76	2.10	2.11
$(C_6H_5)_4AsInCl_4(py)_2$	White	51.21	51.16	3.69	3.79	3.55	3.51

$TlCl_3$·3γ-pic.—The stoichiometry of this complex[1] was confirmed (*i.e.*, 1:3 rather than the more usual 1:2). *Anal.* Calcd for $C_{18}H_{21}N_3Cl_3Tl$: C, 36.63; H, 3.59; N, 7.12. Found: C, 36.43; H, 3.52; N, 7.08.

$(C_2H_5)_4NTlI_4$.—This salt was prepared from $(C_2H_5)_4TlCl_4$ by the usual halide-exchange procedure[10] and recrystallized from acetone–ether.

$(C_2H_5)_4NTlCl_3Br$, $(C_2H_5)_4NTlCl_3I$, and $(C_4H_9)_4NTlCl_3I$.—Acetonitrile solutions of thallium(III) chloride were treated with the appropriate alkylammonium halide using 1:1 mole ratios of reactants. The solvent was removed *in vacuo* leaving the appropriate crystalline salt. The crude products were recrystallized from 1:1 acetone–ethanol as white ($TlCl_3Br^-$) or yellow ($TlCl_3I^-$) needles.

$(C_2H_5)_2NH_2TlCl_4$ and $[(C_2H_5)_2NH_2]_2TlCl_5$.—These salts were prepared using a technique similar to that described above using reactants in 1:1 and 1:2 mole ratios, respectively. They were recrystallized from chloroform and acetonitrile–chloroform, respectively.

$(C_2H_5)_4NTlCl_4$(bipy), $(C_2H_5)_4NTlCl_4$(phen), and $(CH_3)_4NTlBr_4$(bipy).—The reaction of the appropriate tetrahalothallate(III) with 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) in acetonitrile gave clear solutions which, on addition of chloroform and ether, gave the required crystalline complex. The reaction mixture was filtered, and the insoluble complex was washed with chloroform and ether and dried *in vacuo*.

$TlCl_3$·terpy and $(TlCl_3)_2$·terpy.—These complexes crystallized rapidly from acetonitrile when solutions of thallium(III) chloride and 2,2′,2′′-terpyridyl were mixed in the correct mole ratios. They were washed with acetonitrile and ether and dried *in vacuo*.

These two complexes had different solubility properties, the former being virtually insoluble in all common organic solvents, whereas the latter complex was somewhat soluble in acetonitrile and acetone, particularly on warming.

$(TlI_3)_2$·terpy.—A 0.175-g $(TlCl_3)_2$·terpy sample was treated with an aqueous acetone solution of sodium iodide (0.22 g) and the reaction mixture was refluxed until a clear orange solution resulted. Water was then added until precipitation of the bright yellow complex was complete. The insoluble product (0.26 g) was filtered off and washed with water and ether and dried *in vacuo*.

The *same* complex was formed when $TlCl_3$·terpy was treated with an aqueous solution of sodium iodide.

TlI_3·bipy, TlI_3·phen, and TlI_3·py.—Treatment of $TlCl_3$·bipy, $TlCl_3$·phen, and $TlCl_3$·2py using the above procedure gave their iodide analogs. The pyridine complex was recrystallized from acetone or ether as orange-red needles which were slightly soluble in benzene and chloroform. It was not possible to isolate this latter complex completely free from impurities, and repeated recrystallizations failed to give the pure complex. The reason for this is not clear. Note: the analytical data for TlI_3·py (Table I) refer to the purest sample isolated, on which *all* characterization studies were carried out.

When $TlCl_3$·2py was allowed to react with sodium iodide under *prolonged reflux*, yellow crystals separated. These were found to contain no organic residue and are almost certainly thallium(I) iodide.

$TlCl_3$·1.5pyz (pyz = Pyrazine).—This white insoluble complex precipitated immediately as the reactants were mixed and was washed with acetonitrile and ether.

$(C_6H_5)_4AsInCl_4(py)_2$.—Indium(III) chloride was dissolved in acetonitrile and tetraphenylarsonium chloride and excess pyridine were added to the warm solution. After 3 days at room temperature the clear reaction mixture deposited the crystalline complex, which was filtered off and washed with acetonitrile and ether.

Analyses.—Carbon, hydrogen, and nitrogen analyses were carried out by A. Bernhardt, Germany, or the microanalytical laboratory in this department. Analytical data for all of these complexes are shown in Table I.

Physical Measurements.—Conductivities were measured in acetonitrile (Spectrograde) or acetone at 22°. Molecular weight measurements were carried out in these two solvents using a Gallenkamp semimicro ebulliometer.

Infrared spectra were recorded as Nujol mulls on Perkin-Elmer 337 (4000–400 cm^{-1}), Grubb-Parsons DM4 (500–200 cm^{-1}), and Beckman IR11 (250–33 cm^{-1}) spectrophotometers. The Raman spectra of solid $TlCl_3$·2DMSO and $(C_2H_5)_4NTlCl_3I$ were recorded on a Cary Model 81 laser spectrophotometer. The Beckman IR11 and Carey 81 spectrophotometers were made available by the kind permission of Professor I. R. Beattie, University of Southampton.

Results and Discussion

The Reactivity of Thallium(III) Chloride.—Previously,[1,10] the *in situ* preparation of thallium(III) chloride in acetonitrile has been used as a convenient route for the preparation of complexes of the thallium(III) halides. Using this method, the new complexes $TlCl_3$·1.5pyz, $(TlCl_3)_2$·terpy, $TlCl_3$·terpy, $(C_2H_5)_4NTlCl_3I$, $(C_4H_9)_4NTlCl_3I$, $(C_2H_5)_2NH_2TlCl_4$, and $[(C_2H_5)_2NH_2]_2TlCl_5$ have been prepared. The isolation of the latter complex shows that by the choice of a suitable cation, halothallates, other than TlX_4^-, can be prepared by this method. We have also confirmed our earlier isolation[1] of $(C_2H_5)_4NTlCl_3Br$ and $TlCl_3$·3γ-pic. The γ-picoline complex is interesting in that together with $TlI_3 \cdot 3(C_6H_5)_3PO$[10] it shows the stoichiometry TlX_3L_3; neutral *monodentate* ligands, *e.g.*, pyridine and DMSO, invariably react to form TlX_3L_2.

Triphenylphosphine, triphenylarsine, and pyridine-2-carboxaldehyde 2-pyridylhydrazone (PAPHY)[14] react with acetonitrile solutions of thallium(III) chloride to give pale yellow powders, which contain no coordinated ligand and are almost certainly thallium(I) chloride. This behavior is in contrast to the stability of indium(III) halides toward phosphines[2] and PAPHY[4] and probably reflects the ease with which the reduction thallic (d^{10}) → thallous ($d^{10}s^2$) occurs, typical of nontransition metal $5d^{10}$ systems.

Cotton, *et al.*,[10] found that the reaction of $TlCl_3 \cdot 2(C_6H_5)_3PO$ with sodium iodide gave $TlI_3 \cdot 3(C_6H_5)_3PO$. Using the same technique $TlCl_3 \cdot$bipy and $TlCl_3 \cdot$phen react to give $TlI_3 \cdot$bipy and $TlI_3 \cdot$phen, respectively, complexes which have been isolated previously by Sutton.[15] On the other hand, $TlCl_3 \cdot$2py gave a complex of composition approximating to $TlI_3 \cdot$py, which was soluble in a variety of polar and nonpolar solvents. $(TlI_3)_2 \cdot$terpy was formed when either $(TlCl_3)_2 \cdot$terpy or $TlCl_3 \cdot$terpy were allowed to react with sodium iodide. The failure of $TlCl_3 \cdot$terpy to give $TlI_3 \cdot$terpy is at first sight surprising but may simply be a reflection on the higher lattice energy and greater insolubility of the 2:1 complex $(TlI_3)_2 \cdot$terpy compared to $TlI_3 \cdot$terpy.[16] In view of the isolation of $TlI_3 \cdot 3(C_6H_5)_3PO$, the instability of $TlI_3 \cdot$terpy is unlikely to be due to steric factors.

The above reactions illustrate the wide range of stoichiometries shown by the thallium(III) halides and the absence of a correlation between the number of molecules of coordinated ligand and the steric requirements of the ligand.[17] This contrasts with the behavior of the indium(III) halides where more regular trends have been noted.[2]

Attempts to carry out iodide-exchange reactions on $TlCl_3 \cdot 3\gamma$-pic and $TlCl_3 \cdot$2DMSO resulted in reduction and formation of thallium(I) iodide.

In a previous paper[4] the isolation of $(C_6H_5)_4AsInCl_4$(bipy) confirmed the ease with which indium(III) forms species of the type $[InCl_4L_2]^-$, as previously noted by Tuck and Woodhouse[18] for L = thiourea and urea. In the present work the analogous pyridine complex $(C_6H_5)_4AsInCl_4(py)_2$ has been isolated, whereas γ-picoline and pyrazine react with acetonitrile solutions containing excess tetraphenylarsonium chloride and indium(III) chloride to yield the previously reported complexes $InCl_3 \cdot 3\gamma$-pic the $InCl_3 \cdot$1.5pyz. Addition of 2,2′-bipyridyl and 1,10-phenanthroline to acetonitrile solutions of $(C_2H_5)_4NTlCl_4$ gave the complexes $(C_2H_5)_4NTlCl_4B$, whereas pyridine, γ-picoline, and triphenylphosphine oxide failed to react under similar conditions. The isolation of $(CH_3)_4NTlBr_4$(bipy) shows that under suitable conditions both indium(III) and thallium(III) form mixed halide–ligand anionic species in addition to the more usual complex halides $MX_{4+n}^{(1+n)-}$.

In all cases the infrared spectra (4000–650 cm^{-1}) of the complexes were characteristic of cation and ligand absorptions and showed the absence of solvent (acetonitrile) molecules. In particular, $TlCl_3 \cdot$1.5pyz had a spectrum virtually identical[19] with that of $InCl_3 \cdot$1.5pyz[4] and characteristic of pyrazine bonded through both nitrogen atoms,[20] indicating that these complexes are polymeric with the local structure MCl_3L_3 around the central metal atom. Also, the spectra of $InCl_3 \cdot$terpy,[4] $TlCl_3 \cdot$terpy, and $(TlX_3)_2 \cdot$terpy were similar, indicating the similar bonding characteristics of the ligand in these three complexes.

Molecular Weight and Conductivity Studies.—Prior to detailed spectroscopic measurements on the complexes described in the present work, it was considered worthwhile to investigate the properties of several of these complexes in solution to ascertain whether spectral measurements in solution would be meaningful.

The conductivity of thallium(III) halide species in polar solvents has usually been restricted to measurements at *one concentration only*.[1,10] In view of the likelihood of appreciable ionic dissociation in such solvents as acetonitrile,[21] it is essential that, when possible, concentration range studies should be carried out. In Figure 1 the molar conductances of several 1:1 electrolytes (in acetone or acetonitrile) are plotted as a function of $\sqrt{C_m}$. For these complexes, deviations from the Onsager law[22] are small, and their behavior is characteristic of 1:1 electrolytes in these solvents.[23,24]

Cotton, *et al.*,[10] reported that $TlCl_3 \cdot 2L$ (L = DMSO or $(C_6H_5)_3PO$) dissolves in acetonitrile to give solutions in which negligible ionic dissociation occurs. $TlCl_3 \cdot$2DMSO is also very soluble in acetone, and a solution of this complex ($C = 16.0 \times 10^{-3}$ *M*) when freshly prepared had $\Lambda_m = 13$ ohm^{-1} cm^2. This solution was stable for *ca.* 1 min, after which its conductance increased rapidly over the next 4 min until it became stable at $\Lambda_m = 50$ ohm^{-1} cm^2. This behavior is convincing evidence of the caution which must be exercised in relating conductivity data to the solid-state species. However, from these and previous conductivity measurements[10] it is clear that $TlCl_3 \cdot$2DMSO is nonionic in the solid state, although ionic dissociation occurs in acetone, with the possible formation of species of the type $[TlCl_{3-x}(C_3H_6O)_x \cdot 2DMSO]^{x+}, xCl^-$.

Concentration range data for several complexes of thallium(III) are shown in Figure 2 and may be

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(15) G. J. Sutton, *Australian J. Chem.*, **11**, 120 (1958).

(16) These two species may have the structures $[TlX_2(terpy)]^+[TlX_4]^-$ and $[Tl(terpy)_2]^{3+}[TlX_6]^{3-}$, respectively (see later). In view of the nonexistence of TlI_6^{3-}, the 1:1 complex would be expected to be unstable and to decompose to its 2:1 analog, which contains the stable TlI_4^- anion.

(17) For example, compare $TlCl_3 \cdot$2py, $TlCl_3 \cdot 2(C_6H_5)_3PO$, $TlI_3 \cdot$py, and $TlI_3 \cdot 3(C_6H_5)_3PO$.

(18) D. G. Tuck and E. J. Woodhouse, *Chem. Ind.* (London), 1363 (1964).

(19) Spectrum in the range 1300–400 cm^{-1}: 1193 vw, 1167 s, 1122 s, 1103 vw, 1088 vw (doublet), 1046 s, 821 m–s, 790 m, 618 vw, ~510 w, br, 449 s.

(20) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962).

(21) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

(22) $\Lambda_0 - \Lambda_e = (a\Lambda_0 + b)\sqrt{C} = A\sqrt{C}$, where *C* is the equivalent concentration. Alternatively, Λ_e may be replaced by Λ_m, where *C* is now the molar concentration.

(23) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(24) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 929 (1967).

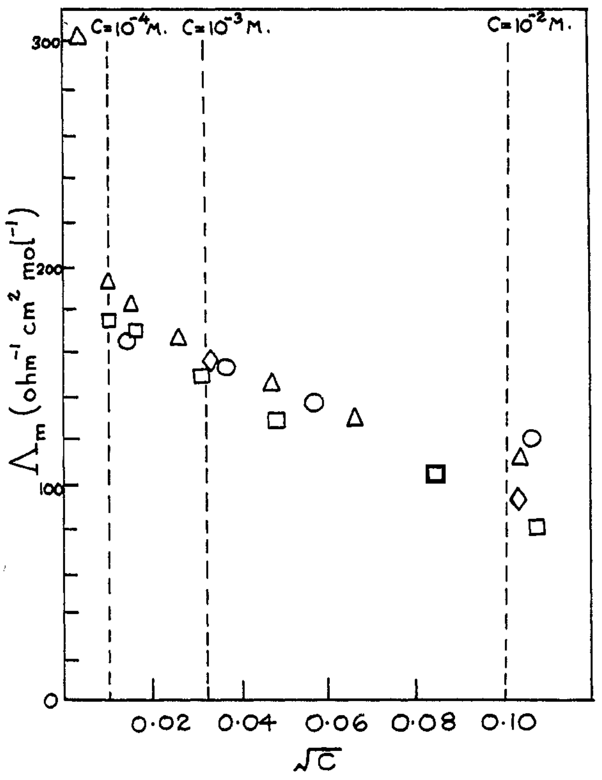

Figure 1.—Conductivity data for several halothallates(III): $(C_2H_5)_4NTlCl_4$ in CH_3CN, △; $(C_2H_5)_4NTlI_4$ in acetone, □; $(C_2H_5)_4NTlCl_3Br$ in CH_3CN, ○; $(C_2H_5)_4NTlCl_4$(bipy) in CH_3CN, ◇.

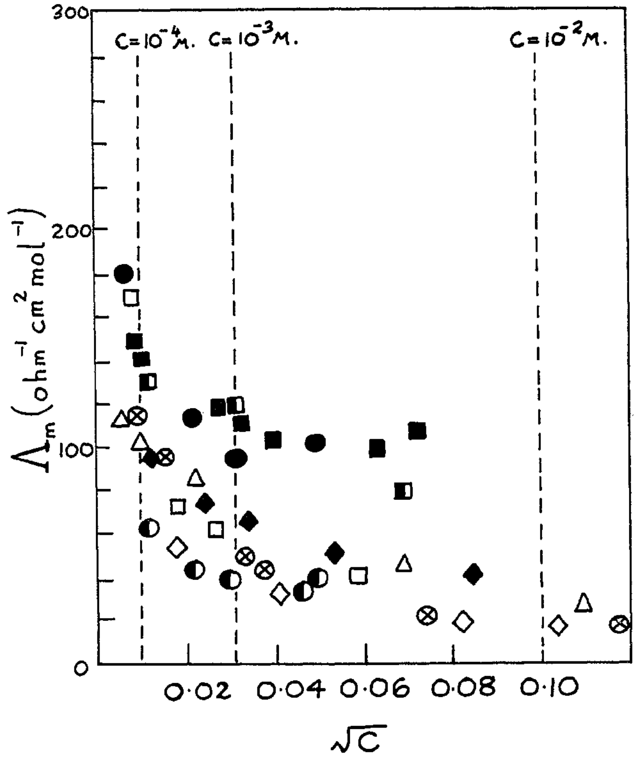

Figure 2.—Conductivity data for adducts of thallium(III) chloride and iodide: $TlCl_3\cdot 2py$ in CH_3CN, △; $(TlCl_3)_2\cdot$terpy in CH_3CN, ■; $TlCl_3\cdot 2py$ in acetone, ⊗; $(TlCl_3)_2\cdot$terpy in acetone, ◧; $TlCl_3\cdot 3\gamma$-pic in acetone, ◇; $(TlI_3)_2\cdot$terpy in CH_3CN, ●; $TlCl_3\cdot$bipy in CH_3CN, ◐; $TlI_3\cdot$py in acetone, ◆; $TlI_3\cdot$bipy in CH_3CN, □.

compared with those for the known 1:1 electrolytes (Figure 1). $TlCl_3\cdot 2py$ and $TlCl_3\cdot 3\gamma$-pic form essentially nonconducting solutions in acetone, although the conductances of these solutions increased markedly for C_m less than $\sim 10^{-3}$ M, characteristic of weak electrolytes. Similar behavior is shown by acetonitrile solutions of the pyridine complex and $TlX_3\cdot$bipy ($X = Cl$ or I). Even if we assume that the former complex is $[TlCl_3\cdot 2py]_2$, *i.e.*, a structure such as $[TlCl_2(py)_4]^+$-$[TlCl_4]^-$ is possible, concentration range studies again show behavior characteristic of a weak electrolyte thus apparently ruling out an ionic structure.

Data for the complexes $TlX_3\cdot$bipy are of particular interest. Sutton[15] proposed that $TlX_3\cdot B$, where B = 2,2′-bipyridyl or 1,10-phenanthroline, are ionic $[TlX_2B_2]^+[TlX_4]^-$ on the basis of conductivity and molecular weight measurements in nitrobenzene, whereas the conductivities of acetonitrile solutions of $TlX_3\cdot$bipy (Figure 2) indicate that they are weak electrolytes. If our data are recalculated on the basis of the above ionic structure, then the Λ_m values are still much less than for 1:1 electrolytes such as $(C_2H_5)_4NTlX_4$ (Figure 1). Sutton also commented[15] that reaction of these 2,2′-bipyridyl complexes with triphenylmethylarsonium chloride gave $(C_6H_5)_3CH_3AsTlX_4$, which was considered[15] as confirmation of the presence of the TlX_4^- anions in these complexes. However, this observation in fact only shows that the TlX_4^- anions are products of this reaction and not necessarily present in the *solid-state* species. Thus, it was found in the present work that tetraethylammonium chloride reacted with $TlCl_3\cdot 2py$, which is nonionic in the solid state, to yield $(C_2H_5)_4NTlCl_4$, a reaction analogous to that observed for $TlX_3\cdot$bipy.

In the concentration range 10^{-2} to 10^{-3} M, the complexes $(TlX_3)_2\cdot$terpy and $TlI_3\cdot$py show molar conductivities characteristic of 1:1 electrolytes in acetonitrile;[23,24] below 10^{-4} M, significant deviation from Onsager law behavior occurs. The structures $[TlX_2\cdot\text{terpy}]^+[TlX_4]^-$ and $[TlI_2(py)_2]^+[TlI_4]^-$ (*i.e.*, $n = 2$) in solution would be consistent with such behavior although this does not necessarily imply that the *solid-state* species are the same.

It is clear that conductivity measurements on thallium(III) halide species are most meaningful in the concentration range 10^{-2} to 10^{-3} M. Also the above results, taken in conjunction with the single concentration data for $TlX_3\cdot 2(C_6H_5)_3PO$ ($X = Cl$ or Br) and $TlCl_3\cdot$phen,[10] indicate that with the possible exception of $(TlX_3)_2\cdot$terpy and $TlI_3\cdot$py most other adducts of the thallium(III) halides are nonionic in the solid state.

The molecular weights of several of the more soluble thallium(III) halide complexes were measured ebullioscopically in acetone or acetonitrile (Table II). In all instances the complexes appeared to be dissociated (on the basis of their monomeric formulations) in these media,[25] irrespective of whether they appeared to be

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(25) These molecular weight measurements do not of course distinguish between dissociations of the types $TlX_3\cdot nL \rightleftharpoons TlX_3\cdot(n-1)L + L$ and $TlX_3\cdot nL \rightleftharpoons [TlX_2\cdot nL]^+ + X^-$, as do the conductivity measurements.

TABLE II

MOLECULAR WEIGHT DATA FOR ADDUCTS OF THE THALLIUM(III) HALIDES

Compound	Solvent	Wt of sample/ 15 ml of solvent, g	Mol wt	
			Found	Calcd for monomer
$TlCl_3 \cdot 2py$	Acetone	0.0863	258	469
$TlCl_3 \cdot 2py$	Acetone	0.4150	275	469
$TlCl_3 \cdot 2py$	Acetone–pyridine	0.0824	261	469
$TlCl_3 \cdot 3\gamma$-pic	Acetone	0.0670	250	590
$TlCl_3 \cdot 2DMSO$	Acetone	0.0882	194	467
$TlCl_3 \cdot 2DMSO$	Acetone	0.1740	223	467
$(TlCl_3)_2 \cdot$terpy	CH_3CN	0.0756	281	644
$(TlCl_3)_2 \cdot$terpy	CH_3CN	0.1736	382	644
$TlI_3 \cdot py$	Acetone	0.0979	287	664
$TlI_3 \cdot py$	Acetone	0.1625	306	664

ionic or nonionic from conductance measurements. This is in contrast to the behavior of $TlCl_3 \cdot 2DMSO$ and $TlCl_3 \cdot 2(C_6H_5)_3PO$ in sulfolane,[10] in which they are monomeric or ionic dimers. The former is favored on the basis of conductivity measurements.

TABLE III

VIBRATIONAL FREQUENCIES (500–33 CM^{-1}) OF $TlCl_3X^-$ AND $TlCl_4^-$

Compound	Medium[b]	Cation vibrations[c]	M–X, M–Cl, and lattice vibrations[c]
$(C_2H_5)_4NTlCl_4$	Nujol mull, I	464 w, 380 w	~295 sh, 285 s, 108 s, 50 m
$(C_2H_5)_2NH_2TlCl_4$[a]	Nujol mull, I	420 mw, 401 w	~300 s, vbr, ~270 s, vbr
$(C_2H_5)_4NTlCl_3Br$	Nujol mull, I	464 w, 380 w	292s, br, 204 ms, 106 s
$(C_2H_5)_4NTlCl_3Br$[a]	CH_3CN, I	. . .	~288 s
$(C_2H_5)_4NTlCl_3I$	Nujol mull, I	464 w, 380 w	283 s, 164 ms, 152 w, 106 s, ~72 sh
$(C_2H_5)_4NTlCl_3I$[a]	CH_3CN, I	. . .	~285 s
$(C_2H_5)_4NTlCl_3I$	Crystals, R	. . .	302 s, 291 s, 282 sh, 164 s, 151 s, 141 w, 97 sh, ~77 m
$(C_4H_9)_4NTlCl_3I$[a]	Nujol mull, I	. . .	~286 s, br

[a] Measurements in the range 500–200 cm^{-1} only. [b] I = infrared; R = Raman. [c] Intensities are relative: w, weak; m, medium; s, strong; sh, shoulder; br, broad.

Far-Infrared and Raman Spectra. (a) Complex Halides $TlCl_3X^-$.—The Raman and infrared spectra of TlX_4^- are consistent with[1,12,13,26] their expected tetrahedral structures.[27] The isolation of the salts of the $TlCl_3Br^-$ and $TlCl_3I^-$ anions permitted a comparison of the vibrational spectra of related tetrahedral (TlX_4^-) and pseudo-tetrahedral (TlX_3Y^-) species as the symmetry is lowered from T_d to C_{3v}. An incomplete infrared spectral study of $(C_2H_5)_4NTlCl_3Br$ has been briefly mentioned previously,[1] but with the exception of a few Raman measurements on mixed halo species $[MX_{4-n}Y_n]^{m-}$ in solution,[28] such investigations are comparatively rare.

The spectral data for the anionic species are shown in Table III, and the Raman spectrum of $(C_2H_5)_4NTlCl_3I$ is illustrated in Figure 3. The highest energy band of $TlCl_3X^-$ (~290 cm^{-1}) is the same in the solid state and in solution, indicating the absence of any significant reaction with the solvent.

Spiro[12,13] has reported the infrared and Raman spectra of $(C_6H_5)_4AsTlCl_4$, enabling a comparison to be made with $(C_2H_5)_4NTlCl_4$ whose infrared spectrum has been recorded down to 33 cm^{-1} (Table III). The doublet at ~290 cm^{-1} is due either to a partial lifting of the degeneracy of ν_3 (F_2 symmetry) of a tetrahedral species or to the appearance of the Raman-active ν_1 mode (A_1 symmetry) on the higher energy side of ν_3. The very strong band at 108 cm^{-1} is assigned to the bending mode ν_4 (F_2 symmetry) and is thus significantly higher in frequency (by ~30 cm^{-1}) than the corresponding mode in $(C_6H_5)_4AsTlCl_4$. The weaker band at ~50 cm^{-1} is either a lattice mode or ν_2 (Raman active only) activated in the crystal. For $TlBr_4^-$, a similar marked dependence of ν_4 on the cation is apparent from the work of Spiro.[13]

To check further the effect of the cation upon the spectrum of $TlCl_4^-$, this anion was isolated as its diethylammonium salt and its infrared spectrum was recorded down to 200 cm^{-1}. In this instance ν_3 was unusually broad (Figure 4) and appears to be at least a doublet. Clearly, the $TlCl_4^-$ anion is appreciably distorted in this environment, a result which is in keeping with related work on the far-infrared spectra of several salts of the type $[(C_2H_5)_2NH_2]_2MX_6$.[29] This is attributed to hydrogen bonding of the type $\geqslant N^+{-}H \cdots X{-}M$, between the diethylammonium

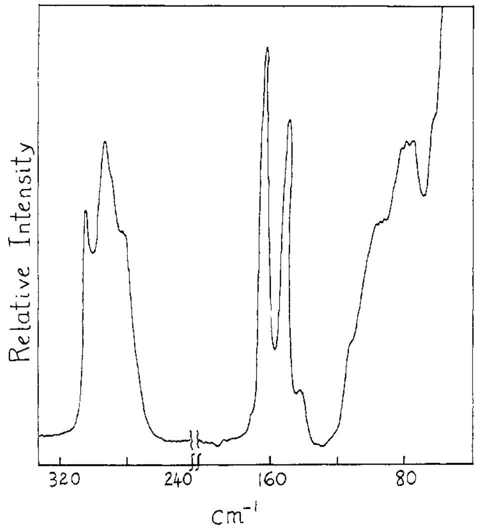

Figure 3.—Raman spectrum of crystalline $(C_2H_5)_4NTlCl_3I$.

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(26) W. R. McWhinnie, *J. Chem. Soc., Sect. A*, 889 (1966).

(27) $(C_6H_5)_4AsTlCl_4$ is isomorphous with[10] $(C_6H_5)_4AsFeCl_4$ which is known to contain tetrahedral $FeCl_4^-$.

(28) See, for example, L. A. Woodward, "Proceedings of the 8th International Conference on Coordination Chemistry," Vienna, 1964, Abstract 2A1, p 15.

(29) R. A. Walton and B. J. Brisdon, *Spectrochim. Acta*, **23A**, 2222 (1967).

TABLE IV

COMPARISON OF THE VIBRATIONAL SPECTRA (CM^{-1}) OF TlX_4^- AND $TlCl_3X^-$

Compound	Assignment[a]					
TlX_4^- (T_d)	A_1 (R) ν_s(TlX)	E (R) δ_d(XTlX)	F_2 (I, R) ν_d(TlX)		F_2 (I, R) δ_d(XTlX)	
TlX_3Y^- (C_{3v})	A_1 (I, R) ν(TlY)	E (I, R) δ(XTlX)	A_1 (I, R) ν(TlX)	E (I, R) ν_d(TlX)	A_1 (I, R) δ(TlX)	E (I, R) ρ_r(TlX_3)
$TlCl_4^-$ [b]	310	60	296		80–108	
$TlCl_3Br^-$	204	. . .	. . .	292	106	. . .
$TlBr_4^-$ [b]	185	~60	~200		50–75	
$TlCl_3I^-$	164	~30 or 77[c]	282	291 302	106	. . .
TlI_4^- [b]	133	. . .	154		~56	

[a] Taken from K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 111. [b] Data taken from ref 13 and from those reported in the present work for $(C_2H_5)_4NTlCl_4$. [c] Either band could be due to this mode; that at ~30 cm^{-1} is at the limit of the measurements and cannot be located exactly.

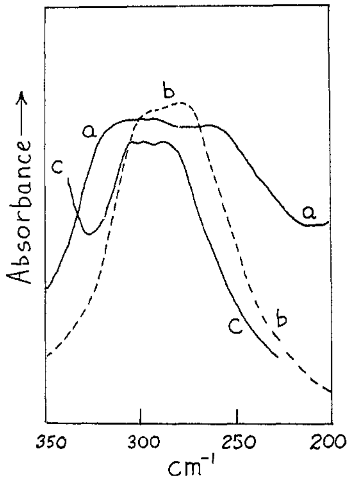

Figure 4.—Far-infrared spectra (350–200 cm^{-1}) of $RTlCl_4$: (a) R = $(C_2H_5)_2NH_2^+$; (b) R = $(C_2H_5)_4N^+$; (c) R = $(C_6H_5)_4As^+$.

cation and the anion, which probably results in significant distortion from regular T_d or O_h symmetry, *in the solid state.*

As the molecular symmetry is lowered from T_d to C_{3v} ($TlX_4^- \rightarrow TlX_3Y^-$), the spectra should become more complex. This is clear from Table IV, where the spectra of TlX_4^- and TlX_3Y^- are compared and the latter are assigned on the basis of their assumed C_{3v} symmetry. One unusual feature of the Raman spectrum is the intense band at 151 cm^{-1} (weak in the infrared spectrum) close to the A_1 thallium–iodine stretching vibration at 164 cm^{-1}. It was originally believed to arise from a deformation mode of the $TlCl_3$ group but, as a referee has pointed out, it is unlikely that the F_2 bending mode of $TlCl_4^-$ could split to give such a high-frequency component. Furthermore, the band is sharp and intense in the Raman spectrum, quite unlike a bending mode.[13] It is apparently not due to an impurity since the electronic spectra of acetonitrile solutions of $TlCl_3I^-$ show the absence of $TlCl_4^-$ and TlI_4^-, for example.[30]

At the present time, the origin of the 151-cm^{-1} band remains obscure although two possible explanations are as follows. It could be an overtone of the 77-cm^{-1} band with enhanced intensity from Fermi resonance with the 164-cm^{-1} band, or, alternatively, a low site symmetry in the crystal may give rise to two A_1 thallium–iodine stretching vibrations (at 164 and 151 cm^{-1}), due to nonequivalent $TlCl_3I^-$ anions within the unit cell.

(b) **$TlCl_3 \cdot 2DMSO$.**—Incomplete spectral data have been reported for $TlX_3 \cdot 2DMSO$ (X = Cl or Br) in an earlier paper.[1] Complete data for $TlCl_3 \cdot 2DMSO$ are now available (Table V) and its Raman spectrum is shown in Figure 5.

TABLE V

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENT OF $TlCl_3 \cdot 2DMSO$

Nujol mull (I)	Crystalline powder (R)	Single crystal (R)	Assignment
418 s	. . .	~418 w, br	"ν(Tl–O)"
332 s	337 w	334 w	ν_{23}(DMSO)
309 s, br	314 m	313 m	ν_d(Tl–Cl)
298 s, br	293 s	290 s	ν_s(Tl–Cl)
. . .	. . .	242 w	?
~215 w, sh	. . .	. . .	?
183 m	. . .	. . .	π($TlCl_3$)
130 m	. . .	. . .	δ_d(ClTlCl) and/or lattice modes
~112 sh	~120 sh, br	~120 sh, br	
99 m	~75 m	74 m	Lattice mode?

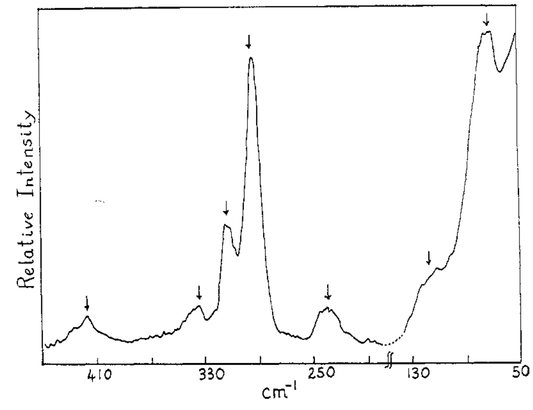

Figure 5.—Raman spectrum of a single crystal of $TlCl_3 \cdot 2DMSO$.

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(30) The electronic spectra of these and other complex halides are being investigated in detail and will be the subject of a separate communication.

TABLE VI

VIBRATIONAL FREQUENCIES (CM^{-1}) OF NITROGEN-DONOR COMPLEXES OF THALLIUM(III)[d]

Compound	Ligand vibrations	ν(Tl–X)	δ(Tl–X)	Other bands
$TlCl_3 \cdot 1.5pyz$[a]	444 s	290 s, 274 mw, 229 m	...	...
$TlCl_3 \cdot 3\gamma$-pic[a]	473 m	255 s, 235 sh	...	206 w?
2,2′,2′′-terpyridyl	416 sh, 400 s	...	...	...
$(TlCl_3)_2 \cdot$terpy	429 w, 400 mw	318 s, 308 sh, 277 sh, 270 s	109 s, 91 m	254 m, 166 m, 159 sh
$(TlI_3)_2 \cdot$terpy	420 m, 396 m, 305 w	186 m, 150 m, 138 m	...	241 w, 164 m
$TlCl_3 \cdot$terpy[a]	431 w, 402 mw, 339 vw	285 s, 248 s	...	...
$TlCl_3 \cdot 2py$	415 m	268 m, 253 m, 224 m	144 m, 125 m, 100 m	184 mw, 173 mw
$TlI_3 \cdot py$	415 mw	176 s, 168 s, 155 ms, 136 m[b]	59 m	73 w?
$TlCl_3 \cdot$bipy	414 m, 360 vw	292 s, 272 s, 243 s, 230 s, 223 sh	133 sh, 122 m, 110 m, 90 m	168 m, 154 m, 61 m, 46 w
$TlI_3 \cdot$bipy	424 mw, 407 m, 350 vw	156 s, ~140 sh	...	214 mw
$TlCl_3 \cdot$phen	422 m	292 s, 267 s, 257 s, 246 sh, 234 sh	122 m, 105 m	150 m
$(C_2H_5)_4NTlCl_4$(bipy)[a]	422 w, 409 m, 350 vw	267 m, 235 s, 212 w	...	...
$(C_2H_5)_4NTlCl_4$(phen)[a]	415 m	265 m, 236 s, 224 sh	...	...
$(C_2H_5)_4NTlBr_4$(bipy)[a]	410 m	<200	...	...
$(C_6H_5)_4AsInCl_4(py)_2$[a]	453 s, 429 m, 353 s, 341 s	255 s[c]	...	...

[a] Measurements down to 200 cm^{-1} only. [b] Some of these bands may be associated with ν(Tl–py). [c] ν(In–Cl). [d] Nujol mulls.

Oxygen-bonded dimethyl sulfoxide complexes of transition and nontransition metal halide complexes have a band or bands near 400 cm^{-1} in their infrared spectra assigned to "ν(M–O)."[31] The strong band at 418 cm^{-1} in the spectrum of $TlCl_3 \cdot 2DMSO$ is accordingly assigned to "ν(Tl–O)," whereas the band at 332 cm^{-1} is the internal ligand vibration ν_{23}.[32]

Since $TlCl_3 \cdot 2DMSO$ is a nonelectrolyte and a monomer in sulfolane,[10] we might expect its infrared spectrum to be characteristic of five-coordinate thallium(III). This is apparently the case since ν(Tl–Cl) in this complex is at a higher frequency than the corresponding modes in neutral six-coordinate thallium(III) complexes (see later).[33] From the data in Table V this molecule can be assigned a trigonal-bipyrimidal structure of approximate D_{3h} symmetry,[34] with a planar $TlCl_3$ grouping.

The broad band at ~300 cm^{-1} in the infrared spectrum appears to be a closely spaced doublet; a lowering in symmetry from D_{3h} may permit ν_{sym} (Tl–Cl) to become infrared active. The origin of the weak bands at 215 (infrared) and 242 (Raman) cm^{-1} is unknown. The 183-cm^{-1} band could be the out-of-plane $TlCl_3$ deformation mode since it should be infrared active but Raman inactive. For a planar MX_3 grouping the order of decreasing energies is $\nu_{antisym}$ (M–X) > out-of-plane MX_3 def > in-plane ClTlCl def, *i.e.*, $\nu_3 > \nu_2 > \nu_4$,[35] consistent with the assignment for $TlCl_3 \cdot 2DMSO$. However, the presence of several unassigned absorption bands makes this assignment tentative and other five-coordinate structures cannot be ruled out.

(c) Nitrogen Adducts of Thallium(III) Chloride and Iodide.—The far-infrared spectral data for these complexes are shown in Table VI. Like its indium(III) analog,[4] $TlCl_3 \cdot 1 \cdot 5pyz$ has three absorption bands (between 300 and 200 cm^{-1}) which are assigned to the three infrared-active Tl–Cl stretching vibrations of a *trans*-octahedral $TlCl_3N_3$ chromophore. On the other hand, the highest band of $TlCl_3 \cdot 3\gamma$-pic is at 255 cm^{-1}, confirming it to be a six-coordinate complex and consistent with a *cis*-octahedral $TlCl_3N_3$ species, if we assign the bands at 255 and 235 cm^{-1} to the two infrared-active ν(Tl–Cl) modes (symmetry $A_1 + E$) predicted for such an isomer.[36] The difference in frequency between the highest ν(Tl–Cl) of the *trans* and *cis* isomers (~35 cm^{-1}) is exactly that noted[4] between the related $InCl_3L_3$ isomers, *e.g.*, *trans*-$InCl_3 \cdot 1 \cdot 5pyz$ and *cis*-$InCl_3 \cdot 3py$. Thus the band positions are considered to be a more reliable guide to the type of isomer isolated rather than the number of bands observed.

The 2,2′,2′′-terpyridyl complexes of thallium(III) chloride and iodide are particularly interesting since both 1:1 and 2:1 complexes can be isolated depending upon the halide. Conductivity measurements on acetonitrile solutions of $(TlX_3)_2 \cdot$terpy indicate that these complexes are 1:1 electrolytes in solution, so that they might have the structure $[TlX_2(terpy)]^+$-$[TlX_4]^-$ in the *solid state.* Molecular weight measurements (Table II) are also consistent with this structure. If so, then their far-infrared spectra should provide evidence to confirm or refute this suggestion. Below 80 cm^{-1} (Table VI) neither complex showed other than a few weak absorptions, but in the regions 320–250 and 190–90 cm^{-1} (Figure 6) the spectra

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(31) B. F. G. Johnson and R. A. Walton, *Spectrochim. Acta*, **22**, 1853 (1966).

(32) W. D. Horrocks, Jr., and F. A. Cotton, *ibid.*, **17**, 134 (1961).

(33) It should be noted that this decrease in ν(M–X) as the coordination number increases is well established, but this can only be used for diagnostic purposes when comparisons are made between similarly charged species of differing coordination numbers.

(34) This symmetry refers to the $TlCl_3O_2$ skeleton; the nonlinearity of the $>S{=}O \rightarrow Tl$ bonds will result in the lowering of this ideal symmetry, but it is not yet possible to establish the over-all molecular symmetry since there is no information on the relative positions of the ligand methyl groups.

(35) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 90.

(36) Since the infrared spectra (down to 200 cm^{-1}) of $TlCl_3 \cdot 2py$ and $TlBr_3 \cdot 2py$[1,26] do not reveal absorptions which can be assigned to ν(Tl–py), it seems likely that the related ν(Tl–N) modes of $TlCl_3 \cdot 1.5pyz$ and $TlCl_3 \cdot 3\gamma$-pic also occur below 200 cm^{-1}.

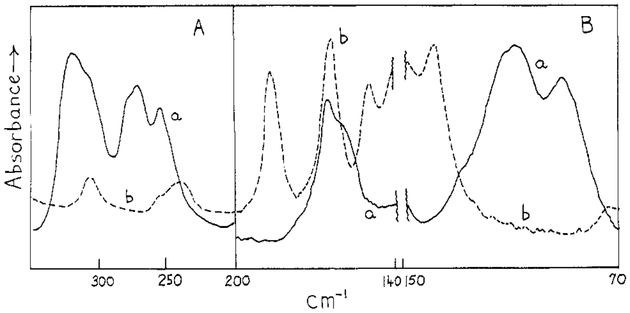

Figure 6.—Far-infrared spectra of $(TlX_3)_2\cdot$terpy: (A) 350–200 cm^{-1} (DM4) and (B) 200–70 cm^{-1} (IR11); (a) X = Cl and (b) X = I.

(cm^{-1}) may be convincingly assigned on the basis of this proposed ionic structure as shown below. The

X	$\nu(Tl–X_2)^+$	$\nu_3(TlX_4^-)$	$\delta(Tl–X_2)^+$	$\nu_4(TlX_4^-)$
Cl	318, 308	277, 270	109	91
I	186	150, 138	~72?	~60?

bands at ~160 cm^{-1}, which are common to both complexes, arise either from a ligand mode or from "ν (Tl–N)." The assignments for the TlX_4^- anions (ν_3 and ν_4) follow from the work of Spiro,[12,13] and for the TlX_2^+ grouping from the increase in ν(Tl–X) and δ(Tl–X) which is anticipated as the positive charge on the species increases. Thus Spiro[11] reports that the Raman-active ν_1 symmetric stretching mode decreases in the series $TlCl^{2+} > TlCl_2^+ > TlCl_3 > TlCl_4^-$, with ν_1 for $TlCl_2^+$ at 320 cm^{-1} close to ν(Tl–Cl) for $[TlCl_2(terpy)]^+$. The main ambiguity about this assignment is that ν_3 for $TlCl_4^-$ is unusually low, compared with ν_3 for $(C_6H_5)_4AsTlCl_4$ and $(C_2H_5)_4NTlCl_4$ at ~290 cm^{-1}. However, in the region 340–250 cm^{-1}, the spectrum of $(TlCl_3)_2\cdot$terpy in acetonitrile shows bands at 311 (sh) and 293 cm^{-1}, which are probably $\nu(TlCl_2)^+$ and $\nu_3(TlCl_4^-)$, respectively. The latter band is close to that reported[26] for $(C_6H_5)_4AsTlCl_4$ in acetonitrile, so that in the solid state ν_3 $(TlCl_4^-)$ is apparently cation sensitive, being lower in $[TlCl_2(terpy)]^+[TlCl_4]^-$ than in $(C_6H_5)_4AsTlCl_4$. Alternative but seemingly less convincing assignments are doubtless possible.

The spectrum of $TlCl_3\cdot$terpy was recorded down to 200 cm^{-1} and the bands at 285 and 248 cm^{-1} were assigned to ν(Tl–Cl) of octahedral thallium(III). However, the structures $[TlCl_3\cdot terpy]$, analogous to that proposed for $InCl_3\cdot$terpy,[4] and $[Tl(terpy)_2]^{3+}[TlCl_6]^{3-}$ cannot be distinguished in the present study since the $TlCl_6^{3-}$ anion has[13] infrared-active Tl–Cl vibrations at 294 and 246 cm^{-1}, close to those reported for this 1:1 complex. Unfortunately, the insolubility of this complex in polar media prevented a solution of this problem from conductivity measurements. This insolubility may in itself favor the nonionic $[TlCl_3\cdot terpy]$ structure. If this complex does have the ionic structure, then the reaction of thallium(III) halides with 2,2′,2″-terpyridyl may be represented

$$TlX_3 \longrightarrow [TlX_2(terpy)]^+[TlX_4]^- \longrightarrow [Tl(terpy)_2]^{3+}[TlX_6]^{3-}$$

Conductivity studies and the far-infrared spectrum of $TlCl_3\cdot 2py$, which has its highest ν(Tl–Cl) mode at 268 cm^{-1}, rule out the structures $[TlCl_2(py)_2]^+Cl^-$, $[TlCl_2(py)_2]^+[TlCl_4(py)_2]^-$, $[TlCl_2(py)_4]^+[TlCl_4]^-$, and five-coordinate $[TlCl_3\cdot 2py]$. It seems likely that this molecule is a halogen-bridged dimer or polymer in the solid state, with a six-coordinate structure. The following assignments seem reasonable: $\nu(Tl–Cl)_{terminal}$ 265 and 253 cm^{-1}; $\nu(Tl–Cl)_{bridging}$ 217 cm^{-1}; ν(Tl–py) 184 and 173 cm^{-1}; δ(Tl–Cl) 142, 125, and 100 cm^{-1}.[37]

In many ways the spectrum of $TlCl_3\cdot$bipy is reminiscent of $TlCl_3\cdot 2py$, except that it is rather more complex and has ν(Tl–Cl) at a higher frequency than does $TlCl_3\cdot 2py$. Also, the complexity of the spectra and conductivity measurements (Figure 2) would almost certainly rule out the structures $[TlCl_2(bipy)_2]^+Cl^-$, $[Tl(bipy)_2]^{3+}[TlCl_6]^{3-}$, $[TlCl_2(bipy)_2]^+[TlCl_4]^-$, and five-coordinate $[TlCl_3\cdot bipy]$. Thus a structure similar to that proposed for $TlCl_3\cdot 2py$ seems likely. Similar conclusions apply to the 1,10-phenanthroline complex $TlCl_3\cdot$phen.

In contrast to the complexity of the above spectra, $TlI_3\cdot$bipy (Table VI) has a remarkably simple spectrum with ν(Tl–I) at 156 cm^{-1} (shoulder at ~140 cm^{-1}), but no further prominent bands other than a medium-weak absorption at 216 cm^{-1} and several weak bands below 80 cm^{-1}, which are probably due to δ(Tl–I) and/or lattice modes. This would suggest a structure different from its chloride analog, possibly five-coordinate $[TlI_3\cdot bipy]$, but since we cannot rule out the possibility that accidental band degeneracies give rise to a deceptively simple spectrum further speculation is not justified at present.

(d) **Anionic $MX_4L_2^-$ Species.**—$(C_6H_5)_4AsInCl_4(py)_2$ has a single strong band at 255 cm^{-1}, assigned to ν(In–Cl), confirming the $InCl_4(py)_2^-$ as having a *trans*-octahedral MX_4L_2 structure; for such a species one metal–halogen stretching vibration is predicted (E_u symmetry).[38] $(C_2H_5)_4NTlCl_4B$, where B = 2,2′-bipyridyl or 1,10-phenanthroline, should show a similar band pattern to that reported previously for $(C_6H_5)_4AsInCl_4(bipy)$.[4] For a species *cis*-MX_4L_2, four M–X stretching modes (symmetry $2A_1 + B_1 + B_2$) are predicted.[38] For the anionic thallium(III) chloride complexes of this type, three of the above ν(Tl–Cl) modes are observed, the two strongest being $B_1 + B_2$. It is comparatively rare to observe unambiguously all four bands of a *cis*-MX_4L_2 species since the two A_1 modes are invariably weak and often neither of them can be located.

Concluding Remarks

The tendency of complexes of the thallium(III) halides to undergo dissociation in most solvents in which they are soluble (particularly polar media) results in a restriction of the physical techniques which can be applied to the study of the solid-state species.

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[37] Above 220 cm^{-1} these measurements disagree somewhat with those of McWhinnie,[26] who reported that a Nujol mull spectrum of this complex also had shoulders at 281 and 247 cm^{-1}, which were not located in the present work.

[38] I. R. Beattie, M. Webster, and G. W. Chantry, *J. Chem. Soc.*, 6172 (1964).

In the absence of crystallographic investigations up to the present time, a combination of infrared and Raman spectroscopic measurements on the *solid* complexes seems the most rewarding means of establishing their structure. Thus from the present investigation the thallium(III) halides have been found to form complexes of coordination number four, five, or six, which are ionic, neutral and monomeric, or neutral and polymeric, and they thus resemble the indium(III) halides in their varied acceptor properties. However, in contrast to the latter halides,[2,4] the factors which determine a particular structure and stereochemistry are not yet well understood.

The structure of species such as TlX_3Y^-, $TlCl_3 \cdot 2DMSO$, and $(TlX_3)_2 \cdot terpy$ can apparently be deduced from a study of their vibrational spectra, but it remains for crystallographic investigations to confirm or refute the conclusions of the present work.

Investigations are continuing on the spectroscopic properties of relatively simple thallium(III) halide species.

Acknowledgments.—The author is most grateful to Professor I. R. Beattie for allowing the use of the Beckman IR11 and Cary 81 spectrophotometers. Mr. G. A. Ozin very kindly measured the Raman spectra of $(C_2H_5)_4NTlCl_3I$ and $TlCl_3 \cdot 2DMSO$.

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Compounds of Titanium(III) Chloride from Nonaqueous Solvents

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The magnetic susceptibility of solid $Ti(CH_3CN)_3Cl_3$ was studied over the temperature range 88–300°K. The temperature dependence of the magnetic moments was found to fit Figgis' theory when the parameters $\lambda = 154\ cm^{-1}$, $\Delta = 770\ cm^{-1}$, and $k = 0.7$ were used. Out of an acetonitrile solution of titanium(III) chloride, compounds of composition $Ti(nc)_2Cl_3$, $Ti(en)_3Cl_3$, and $Ti(dien)_2Cl_3$ were obtained. In acetic anhydride or acetic acid slow acetate substitution for chloride occurred. From acetic anhydride solutions compositions of $Ti(Ac)Cl_2$ and $Ti(Ac)_2Cl$ were produced, but no trisubstituted product could be obtained. From a freshly prepared acetic acid solution and cesium chloride, $Cs_2TiCl_5 \cdot CH_3COOH$ precipitated. The magnetic data and infrared data of all these new compounds are reported.

The nonaqueous chemistry of titanium(III) has been little studied. Previous workers[2–10] have prepared unidentate ligand adducts and have reported limited and sometimes conflicting magnetic data. Still fewer studies have been made on titanium(III) compounds with bidentate ligands.[11–15]

Experimental Section

Reagents.—α-Titanium(III) chloride was obtained from Pittsburgh Plate Glass, New Martinsville, W. Va. The total reducing power of the reagent as titanium(III) was 99.9 ± 0.2% and the total titanium after reduction of any titanium(IV) present was 100.3 ± 0.5% titanium(III). Thus, within the limits of the analytical methods, the sample was considered free of titanium(II) and titanium(IV).

Acetonitrile was purified by fractional distillation from phosphorus pentoxide. The major fraction, which distilled at 81°, was collected over calcium hydride and then vacuum distilled (40° (140 mm)) directly off the calcium hydride into a transfer flask.

Acetic acid, dried by refluxing over phosphorus pentoxide for 1 hr, was distilled directly through an 80-cm fractionating column filled with glass helices. The middle fraction was collected in a storage bulb.

Acetic anhydride, to which was added two drops of 60% perchloric acid, was fractionally distilled through a Vigreux column. Only the middle fraction which distilled at 136–138° was collected in a storage bulb.

Nicotinamide (nc) (Eastman Kodak) was recrystallized from methanol before use.

Ethylenediamine (en) was refluxed over sodium hydroxide for 12 hr, fractionally distilled onto sodium metal, and then fractionally distilled off the sodium. The middle fraction was collected in a storage bulb and kept in a refrigerator.

Diethylenetriamine (dien) was dried over barium oxide and distilled through a Vigreux column at less than 1 μ. The fraction distilling at 56° was collected in a storage bulb.

Methods of Synthesis.—Inasmuch as titanium(III) chloride reacts rapidly with oxygen, it was necessary to carry out the syntheses in special all-glass equipment (Figure 1) which was loaded with reagents either in an inert-atmosphere box (water less than 40 ppm, oxygen about 100 ppm), on a vacuum line, or by gravity from a storge bulb interconnected with the partially

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