

Nature of Compounds of Tl(III) Chloride with Oxygen & Nitrogen Bases

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Thallium(III) chloride forms a number of compounds of varying compositions with nitrogen bases such as pyridine, quinoline, α - and γ -picolines, piperidine, benzylamine, triethylamine, phenylhydrazine, triphenylphosphine oxide, 2,2'-bipyridal and 1,10-phenanthroline, pyridine-N-oxide, triphenylphosphine sulphide and triphenylphosphine selenide. From cryoscopic, conductance and IR spectral studies, their structures have been elucidated. Acetyl chloride, acetyl bromide, benzoyl chloride, nitryl chloride, nitrosyl chloride form 1:1 ionic adducts while thiophosphoryl chloride, selenyl chloride, thionyl chloride form 1:1 non-ionic compounds.

THALLIUM(III) chloride is known to form a large number of compounds with oxygen bases. Diethyl ether¹, dioxane^{2,3}, and ethyl alcohol form adducts, $\text{TlCl}_3 \cdot \text{OEt}_2$, $\text{TlCl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ and $\text{TlCl}_3 \cdot \text{EtOH}$ respectively. Carboxylic acids form complexes with Tl(III) chloride by an elimination reaction while glycine^{5,6} forms a compound of composition $\text{TlCl}_3 \cdot 3(\text{NH}_2\text{CH}_2\text{COOH})$. From conductance and vibrational spectral studies, thallium is reported to be penta-coordinated^{7,8} in $\text{TlCl}_3 \cdot 2\text{Me}_2\text{SO}$ while irregular bipyramidal structure⁹ is reported for $\text{TlCl}_3 \cdot 2(\text{n-Bu})_3\text{PO}$. Tetramethylene sulphone is known to form 1:2 compound with it.

Thallium(III) halides are known to form a variety of compounds with organic nitrogen tertiary bases. Meyer⁴, Renz¹¹ and more recently Abbott¹² have reported the preparation of $\text{TlCl}_3 \cdot (\text{Py})_3$. Recently it has been found that the above compound is formed only in the presence of excess of pyridine otherwise $\text{TlCl}_3 \cdot (\text{Py})_2$ results^{7,13,14}. Solution chemistry in acetone rule out ionic formulation for these compounds^{8,14}. IR spectral studies in the solid state rules out penta-coordination for thallium in these adducts^{15,16}. With γ -picoline, the complex $\text{TlCl}_3 \cdot (\gamma\text{-pico})_3$ has a *cis*-hexa-coordinated thallium¹⁴. In the case of 1,10-phenanthroline, compounds of composition $\text{TlCl}_3 \cdot 1\text{Phen.}$, $\text{TlCl}_3 \cdot 2\text{Phen.}$ and $\text{TlCl}_3 \cdot 3\text{Phen.}$ have been reported^{17,18}. The compound $\text{TlCl}_3 \cdot 1\text{Phen.}$ has a polymeric structure, $\text{TlCl}_3 \cdot 2\text{Phen.}$ is ionic in solution while the compound $\text{TlCl}_3 \cdot 3\text{Phen.}$ has a chelate structure. The structure of the compound $\text{TlCl}_3 \cdot 2\text{-bipy}$ has also been a subject of controversy¹⁹. It has been of interest, therefore, to prepare a number of adducts of Tl(III) chloride with nitrogen and oxygen bases and to characterize these based on conductance, cryoscopic and spectral studies.

Acetonitrile (BDH) was kept over activated molecular sieve for 48 hr and then twice distilled over anhydrous calcium chloride. The fraction distilling at 69°/560 mm was collected and kept over molecular sieve before use. Nitrobenzene (BDH) was purified

by distilling over phosphorus pentoxide. Fractions distilling at 208°/650 mm were collected, left over activated molecular sieve (Type 4A, Linde Co.) for 48 hr and distilled. Fractions distilling at 208°/650 mm were collected. It was stored over activated molecular sieve. Thallium(III) chloride was prepared by passing dry chlorine through a suspension of Tl(I) chloride in dry acetonitrile till a clear solution was obtained. It was filtered to remove any insoluble impurity, and made chlorine-free by evacuation under reduced pressure. Most of the preparations were carried out with this solution of Tl(III) chloride but in some cases Tl(III) chloride was actually isolated by removing acetonitrile under reduced pressure.

Organic tertiary bases were purified by distilling them at the appropriate temperature over KOH beads. 2,2'-Bipyridal (BDH, AR) was kept over phosphorus pentoxide in a desiccator for about 48 hr before use. 1,10-Phenanthroline (E. Merck, AR) was kept over 98% sulphuric acid and phosphorus pentoxide for seven days each before use. Triphenylphosphine oxide was prepared by refluxing triphenylphosphine (1.7 g) in glacial acetic acid (20 ml) and hydrogen peroxide solution (5 ml, 30% v/v) on a water-bath for 3 hr. The contents were poured into water and filtered. The precipitate was repeatedly washed with distilled water and finally recrystallized from ethyl alcohol (m.p. 156°C). Pyridine-N-oxide was prepared by the method reported by Ochiai²⁰. Triphenylphosphine sulphide and selenide were prepared by the method reported in literature^{21,22}. Organic solvents were purified by the standard methods. Acid chlorides were prepared and purified by the standard methods.

Complexes with tertiary bases — Complexes of organic tertiary bases were prepared by adding excess of the base to a cold solution of Tl(III) chloride in acetonitrile. Compounds of stoichiometric composition (1:1) were obtained when Tl(III) chloride was taken in excess while those of 1:2 stoichiometry were obtained by taking the two

components in exact ratio. After the addition of the base, the mixture was shaken well for 30 min when solid compounds separated out. In some cases, the solid compounds could only be obtained by adding some inert solvent. The solid compounds so separated were filtered in a dry atmosphere, washed twice with dry carbon tetrachloride and finally with petroleum ether (60-80°) and then dried *in vacuo*. Stoichiometric compositions of the compounds were determined by elemental analysis and are reported in Table 1.

In the case of the adducts with acid chlorides, thallium(III) chloride was isolated from acetonitrile and then mixed with acid chloride in liquid sulphur dioxide (1:1). The mixture was then slowly brought to the room temperature when sulphur dioxide escaped leaving behind crystalline solids. These

compounds were dried *in vacuo* and their compositions established by elemental analysis (Table 2).

Results and Discussion

As pointed out above stoichiometric compositions of the compounds depend upon the experimental conditions. Most of these compounds are moisture sensitive but are quite stable in the dry atmosphere. Walton²³ has also isolated the compounds $TlCl_3$, Py and $TlCl_3 \cdot 2Py$. In the present studies, we report the isolation of another compound with pyridine of the composition $TlCl_3 \cdot 3Py$. All these compounds are soluble in acetonitrile, nitromethane, acetone, formic acid and nitrobenzene. Molar conductance values in acetone are quite low which is in agreement with the earlier observations^{7,8,14} and suggest non-ionic nature of the adducts. However, molar

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES OF Tl(III) CHLORIDE WITH OXYGEN AND NITROGEN BASES

(Observed mol. wts of all the compounds tally with formula weight except in the case of $TlCl_3 \cdot 2Py$ which is dimeric)

Complex	Colour	m.p. (°C)	Reqd (%)			Found (%)			ΛM in nitrobenzene (ohm ⁻¹ cm ² mole ⁻¹)
			Cl	Tl	N	Cl	Tl	N	
$TlCl_3 \cdot Py$	Dark brown	120	27.20	41.71	3.59	26.00	40.62	4.10	29.6
$TlCl_3 \cdot 2Py$	Brown	230	22.69	43.49	5.58	23.46	44.45	6.47	3.9
$TlCl_3 \cdot 3Py$	Dark brown	230	17.70	37.26	7.68	18.20	36.92	7.02	25.8
$TlCl_3 \cdot \alpha$ -pico	do	128	26.30	50.61	3.47	27.01	49.16	3.65	21.0
$TlCl_3 \cdot \gamma$ -pico	Brown	143	26.30	50.61	3.47	26.58	49.46	3.55	22.3
$TlCl_3 \cdot 2\alpha$ -pico	Light brown	118	22.00	41.13	5.40	21.50	40.52	5.01	26.0
$TlCl_3 \cdot 2\gamma$ -pico	Brown	130	22.00	41.13	5.40	21.40	40.22	5.12	25.2
$TlCl_3 \cdot (C_2H_5)_3N$	do	230	25.70	49.64	3.49	24.15	48.26	4.12	3.6
$TlCl_3 \cdot 3(C_2H_5)_3N$	Dark brown	230	17.20	33.27	6.85	18.13	32.01	7.04	24.6
$TlCl_3 \cdot C_6H_5CH_2NH_2$	do	230	25.42	48.90	3.35	26.12	49.31	3.46	21.5
$TlCl_3 \cdot 3C_6H_5CH_2NH_2$	Cream	144	16.00	32.33	6.65	16.87	33.24	7.03	18.6
$TlCl_3 \cdot C_6H_5NH.NH_2$	Light pink	230	25.35	48.80	3.34	26.35	47.70	3.21	20.4
$TlCl_3 \cdot 3C_6H_5NH.NH_2$	Pink	230	16.70	32.17	6.73	17.30	31.61	6.52	16.2
$TlCl_3 \cdot C_9H_7N$	Light brown	230	24.26	46.47	3.19	23.10	45.74	3.01	16.8
$TlCl_3 \cdot 3C_9H_7N$	Light pink	178	15.96	30.58	6.03	14.94	31.46	5.84	19.3
$TlCl_3 \cdot piperidine$	Dark brown	230	27.00	51.64	3.54	27.96	50.79	3.12	5.4
$TlCl_3 \cdot 3piperidine$	Light yellow	230	20.60	36.20	7.43	19.60	35.92	7.02	3.8
$TlCl_3 \cdot C_8H_{12}N_2$	do	170	21.73	41.63	5.71	22.21	40.58	5.16	18.6
$TlCl_3 \cdot 2C_8H_{12}N_2$	Light pink	230	18.30	34.94	9.62	17.85	35.62	10.12	2.6
$TlCl_3 \cdot C_{10}H_8N_2$	Pink	140	26.00	43.78	6.01	25.10	42.68	5.74	12.4
$TlCl_3 \cdot 2C_{10}H_8N_2$	Pinkish white	230	15.44	32.80	9.00	16.64	33.46	8.65	1.8
$TlCl_3 \cdot 2(C_6H_5)_3PO$	Greenish	230	12.26	23.54	49.89*	13.02	24.24	50.61	3.7
$TlCl_3 \cdot (C_6H_5)_3PS$	Lemon yellow	230	15.91	33.77	5.3†	17.60	35.21	5.01	4.6
$TlCl_3 \cdot (C_6H_5)_3PSe$	Yellow	230	16.28	31.36	12.11‡	17.81	30.25	11.76	4.2
$TlCl_3 \cdot 3(C_6H_5)NO$	Light brown	124	15.60	50.37	7.06	17.80	49.36	6.74	19.1

*Per cent carbon. †Per cent sulphur. ‡Per cent selenium.

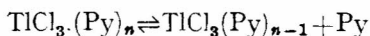
TABLE 2 — CHARACTERIZATION DATA OF THE COMPLEXES OF Tl(III) CHLORIDE WITH ACID HALIDES

(Observed mol. wts of all the compounds tally with formula weight)

Complex	Colour	m.p. (°C)	Reqd. (%)			Found (%)			ΛM in nitrobenzene (ohm ⁻¹ cm ² mole ⁻¹)
			Cl	Tl	C	Cl	Tl	C	
$NO_2Cl \cdot TlCl_3$	Yellow	118	36.23	52.04	3.57†	35.78	52.60	3.28	24.6
$NOCl \cdot TlCl_3$	Pale yellow	152	37.77	54.26	3.72†	37.03	53.78	3.45	20.9
$CH_3COCl \cdot TlCl_3$	Light yellow	136	36.50	52.44	6.17	36.01	51.86	5.85	24.5
$CH_3COBr \cdot TlCl_3$	Pale yellow	106	43.02*	47.11	5.54	42.46	46.72	5.02	18.6
$C_6H_5COCl \cdot TlCl_3$	Yellow	138	31.48	45.23	18.63	30.98	46.04	18.02	22.4
$SeOCl_2 \cdot TlCl_3$	White	78	37.04	42.81	16.58‡	36.78	42.26	17.23	1.8
$SOCl_2 \cdot TlCl_3$	Light yellow	96	41.09	47.49	7.45§	41.59	47.01	7.15	0.9
$PSeCl_3 \cdot TlCl_3$	do	84	44.37	42.50	6.66§	44.87	41.87	6.03	2.4

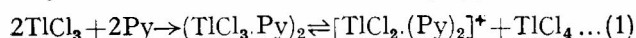
*Total halogen in case of acetyl bromide complex. †Per cent nitrogen. ‡Per cent selenium. §Per cent sulphur.

conductances in nitrobenzene ($\epsilon = 48$) and formic acid ($\epsilon = 68$) of $TlCl_3 \cdot 3Py$ and $TlCl_3 \cdot Py$ show them to be ionic while $TlCl_3 \cdot 2Py$ is non-ionic. Molecular weight determinations in nitrobenzene suggest that the compound $TlCl_3 \cdot 2Py$ is dimeric while $TlCl_3 \cdot 3Py$ and $TlCl_3 \cdot Py$ undergo ionization in this solvent. Our observations in acetone agree with those of Walton²³. Acetone has a low dielectric constant and there is a possibility of extensive ion-pair formation. The possibility of the dissociation of the type in solvents of high dielectric constants



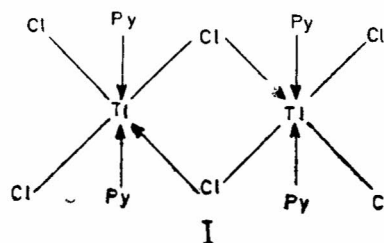
is ruled out as none of the species formed would be conducting.

Further information about the structure of these compounds has been arrived at by IR spectral studies especially in the far infrared region (Table 3). In the compounds $TlCl_3 \cdot Py$ and $TlCl_3 \cdot 3Py$, the absorption bands due to pyridine nucleus undergo changes similar to those which occur on complex formation of pyridine such as $C_5H_5N \cdot HCl$ (ref. 24), $C_5H_5N \cdot CH_3COCl$ (ref. 25), $C_5H_5N \cdot TeCl_4$ (ref. 26) and $C_5H_5N \cdot SeCl_4$ (ref. 27). The bands at 1620, 1520, 1480, 1360, 1265, 1060 and 770 cm^{-1} are due to pyridinium ion. The shift in the absorption bands in all these cases is in the same direction and is nearly of the same magnitude as has been obtained in the case of pyridinium chloride suggesting thereby that pyridine in these compounds is present as pyridinium ion. These observations are consistent with the cryoscopic and conductance studies for these compounds. Further support for this is forthcoming from the IR bands at 318, 308, 282 and 270 cm^{-1} assigned to $\nu Tl-Cl$ modes^{28,29}. But normally these occur at 344 and 332 cm^{-1} . The lowering of these bands is due to the donation of electrons from the nitrogen atom of pyridine to the central thallium atom. The presence of bands at 318, 282 and 270 cm^{-1} due to $\nu Tl-Cl$ suggest a tetrahedral environment round thallium atom in the solid state³⁰. A possible structure involving the formation of $TlCl_4^-$ ions in the solid and solution may be visualized as shown in Eq. (1)



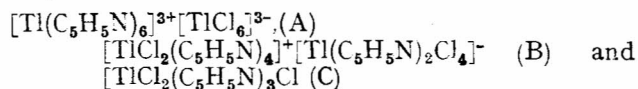
In both the compounds thallium acquires a tetrahedral structure. $\nu Tl-N$ bands are observed at 256 and 248 cm^{-1} in conformity with Walton²³. Absence of splitting of bands indicates absence of distortion in the symmetry or ion-dipole interaction.

The compound $TlCl_3 \cdot 2C_5H_5N$ is a fairly stable compound. It is highly soluble in DMF but has low solubility in nitrobenzene, nitromethane, etc. The molar conductance of $TlCl_3 \cdot 2Py$ in nitrobenzene (3.9 $ohm^{-1} cm^2 mole^{-1}$) shows it to be a non-electrolyte. Molecular weight determinations in nitrobenzene suggest its dimeric structure. There are no bands due to $\nu Tl-Cl$ which could be assigned to pentacoordinated thallium. Bands corresponding to pyridinium ion are absent in the IR spectrum of $TlCl_3 \cdot 2Py$. The bands at 1605, 1592, 1549, 1561, 1490, 1435, 1311, 1250, 1160, 785, 778, 744, 660, 642 and 425 cm^{-1} are due to the coordinated pyridine ring. This supports the non-ionic nature of the compound. $\nu Tl-N$ modes are observed at



256 and 248 cm^{-1} (loc cit) and the $\nu Tl-Cl$ modes at 312 and 308 cm^{-1} , due to terminal $\nu Tl-Cl$. The other bands at 278 and 272 cm^{-1} are due to the bridging metal-chlorine stretching modes as the bridging metal-chlorine stretching modes are expected to lie at lower spectral region as compared with terminal stretching modes³¹. The metal-nitrogen stretching modes are simple as compared to metal-chlorine stretching modes; it suggests that both the bases occupy trans position with respect to each other. A dimeric structure (I) involving chlorine bridging may be postulated.

The compound $TlCl_3 \cdot 3Py$ is quite sensitive to moisture. It is fairly soluble in nitrobenzene, acetonitrile and DMF. Molar conductance values of the millimolar solutions in nitrobenzene show them to be ionic. Following possible formulations (A-C) may be considered:



Formulation (A) can be ruled out on the basis of far IR data since only one $\nu(Tl-Cl)$ mode is expected for $TlCl_6^{3-}$ ions whereas two modes (298 and 268 cm^{-1}) are observed in the present case. Structure (C) can be ruled out on the basis of molar conductance value. The ionic structure (B) may be assigned to the complex with the higher band (298 cm^{-1}) assigned to $\nu Tl-Cl$ of the cation $[TlCl_2(C_5H_5N)_4]^+$ and the lower band (268 cm^{-1}) to $\nu Tl-Cl$ of the anion $[Tl(C_5H_5N)_2Cl_4]^-$. As the $\nu Tl-N$ modes are observed in the same region as $\nu Tl-Cl$ in the octahedral environment, it is therefore not possible to describe the geometry of the molecule. Similar types of description about the nature of the bonding, the type of the ions and the stereochemistry of the molecules may be described for the adducts of α - and γ -picolines, quinoline, triethylamine, benzylamine, piperidine, phenylhydrazine with $Tl(III)$ chloride as they have the same stoichiometric composition and similar ionic properties.

In the case of the compound $TlCl_3 \cdot 3Py \rightarrow O$ molar conductance value of the millimolar solution in nitrobenzene (19.1 $ohm^{-1} cm^2 mole^{-1}$) is quite high suggesting its ionic nature which is also supported by its molecular weight determination. $TlCl_3 \cdot (C_6H_5)_3PS$ and $TlCl_3 \cdot (C_6H_5)_3PSe$ are observed to be non-ionic and monomer. IR spectrum of $TlCl_3 \cdot 3Py \rightarrow O$ shows bands due to $\nu N-O$ at 1240, 822 and 536 cm^{-1} as compared with the ligand bands at 1252, 837 and 544 cm^{-1} , suggesting the coordination of the metal. The other important bands due to $\nu Tl-Cl$ and $\nu Tl-O$ are observed at the same position as in the case of $TlCl_3 \cdot 3Py$. An ionic formulation similar to that proposed for $TlCl_3 \cdot 3Py$

may be suggested for $TlCl_3 \cdot 3C_5H_5NO$. The tendency for the $d\pi-p\pi$ bonding to decrease with decrease in the electronegativity from oxygen to sulphur and then to selenium in triphenylphosphine-, oxide, sulphide and selenide would be balanced by the more efficient overlap in the S-P and Se-P bond and consequently in triphenylphosphine-sulphide and selenide adducts, the lowering of P-S and P-Se stretching frequency would be compensated by the back donation and hence there would not be any significant lowering of these stretching modes. This is what has been observed in the present studies (Table 3). All the important bands of these compounds are included in Table 3. These observations support the non-ionic nature of these compounds.

2,2'-Bipyridal and 1,10-phenanthroline form compounds of composition $TlCl_3 \cdot C_{10}H_8N_2$, $TlCl_3 \cdot C_{12}H_8N_2$ and $TlCl_3 \cdot 2C_{10}H_8N_2$, $TlCl_3 \cdot 2C_{12}H_8N_2$ respectively. All these compounds are slightly soluble in nitromethane and nitrobenzene. Molar conductance values suggest them to be non-ionic. There are four characteristic phenyl stretching modes between 1300 and 1600 cm^{-1} . In bipyridine these are at 1579, 1533, 1448 and 1410 cm^{-1} . On complex formation these consequently shift by about 20-30 cm^{-1} to higher frequency region. Similar observations have been recorded earlier^{32,33}. Two bands at 1058 and 1040 cm^{-1} assigned to in-plane hydrogen bonding modes remain unaffected on complex formation. The ring breathing mode at 991 cm^{-1} is shifted by 24 cm^{-1} to higher region on complex formation. A similar observation has been made for pyridine³⁴. There are also intense bands at 770 and 730 cm^{-1} due to aromatic CH out-of-plane deformation. The fact that these bands do not shift on complex formation suggests a weak interaction between the two

components. In the spectrum of 1,10-phenanthroline, strong bands are observed in the regions 700-900 and 1400-1650 cm^{-1} . The strong bands at 735 and 855 cm^{-1} are due to out-of-plane deformation of CH in the heterocyclic rings and the central ring respectively. The band at 735 cm^{-1} is shifted to 722 cm^{-1} on complex formation while that at 855 cm^{-1} does not shift significantly. This is quite expected as the primary effect of coordination is on the nitrogen atom and the central ring has no nitrogen atom to provide any donor site. A medium intensity band at 990 cm^{-1} present in 1,10-phenanthroline moves to 1010 cm^{-1} on coordination. The bands in the region 1125-1250 cm^{-1} assigned to in-plane CH deformation or possibly ring vibrations move to higher spectral regions. A very strong band at 1418 cm^{-1} resembles the ν_{14} mode of pyridine³³ and it is not disturbed on coordination. The bands at 1448, 1504, 1562 and 1528 cm^{-1} resembling closely those of pyridine move to higher spectral regions on complex formation. It may thus be concluded that in-plane vibrations increase upon coordination whereas out-of-plane vibrations decrease. The other important bands due to $\nu Tl-Cl$ both bridging as well as terminal are observed (Table 3).

Complexes with oxygen donors— With dimethyl sulphoxide and triphenylphosphine oxide, compounds of compositions $TlCl_3 \cdot 2Me_2SO$ and $TlCl_3 \cdot 2Ph_3PO$ are already known wherein five-coordinated thallium has been reported (loc. cit.). Tri-*n*-butylphosphate forms a 1:2 adduct, $TlCl_3 \cdot 2(nBu)_3PO$ with it. Tetra-methylene sulphone also forms a 1:2 adduct $TlCl_3 \cdot 2TMSO$. In the phosphoryl compound $TlCl_3 \cdot 2POCl_3$, coordination takes place through the oxygen atom³⁵.

Adducts with acid chlorides— In the present studies, a number of the adducts of acid chlorides with thallium(III) chloride have been isolated. In some cases, these adducts could be isolated from liquid sulphur dioxide. Nitryl chloride, nitrosyl chloride, acetyl chloride, acetyl bromide and benzoyl chloride form adducts of composition $NO_2Cl \cdot TlCl_3$, $NOCl \cdot TlCl_3$, $CH_3COCl \cdot TlCl_3$, $CH_3COBr \cdot TlCl_3$ and $C_6H_5COCl \cdot TlCl_3$ respectively. Sulphuryl chloride does not form any adduct with it under any experimental conditions but thionyl chloride, selenoyl chloride thiophosphoryl chloride form adducts of composition $SOCl_2 \cdot TlCl_3$, $SeOCl_2 \cdot TlCl_3$ and $PSCl_3 \cdot TlCl_3$ respectively (Table 2). All these compounds are soluble in the parent acid halides, nitromethane, acetonitrile, nitrobenzene and dimethylformamide. Molar conductance values and molecular weight determinations show that the compounds $NOCl \cdot TlCl_3$, $NO_2Cl \cdot TlCl_3$, $CH_3COCl \cdot TlCl_3$, $CH_3COBr \cdot TlCl_3$, $C_6H_5COCl \cdot TlCl_3$ are ionic while the compounds, $SOCl_2 \cdot TlCl_3$, $SeOCl_2 \cdot TlCl_3$, $PSCl_3 \cdot TlCl_3$ are monomeric and non-ionic.

The principle bands of the IR absorption frequencies are given in Table 4. In the case of the adduct $NO_2Cl \cdot TlCl_3$, an intense band at 2298 cm^{-1} is assigned to NO_2^+ ions³⁶. The sharp low intensity band at 3702 cm^{-1} is assigned to combination band $\nu_1 + \nu_3$. If ν_1 is taken as 1398 cm^{-1} from the Raman data of NO_2ClO_4 (ref. 37), then the $(\nu_1 + \nu_2 - 3696 \text{ cm}^{-1})$ is in good agreement

TABLE 3 — PRINCIPAL IR BANDS* OF THE COMPLEXES OF Tl(III) CHLORIDE WITH OXYGEN AND NITROGEN BASES

Compound	Principal bands (cm^{-1})
$TlCl_3 \cdot C_5H_5N$	2720, 1620, 1610, 1520, 1480, 1360, 1265, 1020, 770, 740, 535, 510, 308, 282, 270, 260, 252
$TlCl_3 \cdot 2C_5H_5N$	2750, 1605, 1592, 1579, 1561, 1490, 1435, 1311, 1250, 1160, 785, 778, 744, 660, 642, 425, 312, 308, 256, 248
$TlCl_3 \cdot 2(C_6H_5)_3PO$	2680, 1588, 1576, 1564, 1546, 1488, 1432, 1270, 1208, 1198, 1120, 886, 768, 720, 340, 284, 256
$TlCl_3 \cdot 3(C_2H_5)_3N$	2800, 1420, 1250, 1200, 1110, 1060, 810, 780, 440, 338, 288, 262, 238
$TlCl_3 \cdot 2C_{10}H_8N_2$	2738, 1579, 1553, 1448, 1410, 1058, 1048, 1021, 770, 730, 342, 278, 262, 250
$TlCl_3 \cdot 2C_{12}H_8N_2$	2738, 1562, 1528, 1504, 1448, 1418, 1138, 1010, 855, 722, 338, 310, 268, 246
$TlCl_3 \cdot 3C_5H_5NO$	2930, 1590, 1582, 1455, 1240, 1220, 1145, 1100, 1040, 836, 822, 740, 700, 336, 310, 268, 242
$TlCl_3 \cdot (C_6H_5)_3PS$	2932, 1586, 1580, 1460, 1310, 1184, 1160, 1106, 1100, 1070, 1029, 1000, 755, 695, 504, 488, 338, 312, 270, 246
$TlCl_3 \cdot (C_6H_5)_3PSe$	2930, 1588, 1580, 1458, 1312, 1188, 1158, 1108, 1090, 1065, 1026, 998, 760, 672, 496, 476, 336, 310, 268, 252

*IR spectra were recorded as nujol mulls on Perkin-Elmer double grating infrared spectrophotometers models 337 and 621.

TABLE 4 — PRINCIPAL IR BANDS* OF COMPLEXES OF Tl(III) CHLORIDES WITH ACID CHLORIDES

Compound	Principal bands (cm^{-1})
$NO_2Cl.TlCl_3$	3702, 2298, 596, 312, 296, 272
$NOCl.TlCl_3$	2276, 308, 288, 270
$CH_3COCl.TlCl_3$	2306, 312, 290, 272
$CH_3COBr.TlCl_3$	2300, 308, 288, 268
$C_6H_5COCl.TlCl_3$	2276, 312, 298, 272
$SOCl_2.TlCl_3$	1360, 1106, 876, 562, 324, 296, 286
$SeOCl_2.TlCl_3$	1362, 1096, 856, 646, 558, 318, 294, 284
$PSCl_3.TlCl_3$	1312, 1122, 1056, 776, 654, 536, 306, 286, 276

*See footnote in Table 3.

with the observed value (3702 cm^{-1}). It has been pointed out by Horning and Osberg that such combination bands do occur in the case of the isoelectronic linear carbon dioxide molecule³⁸. The bending mode ν_2 of the nitronium ion has been reported to be at 570 cm^{-1} in $NO_2^+ClO_4^-$ and at 538 cm^{-1} in $NO_2^+NO_3^-$ and for carbon dioxide this absorption band is observed at 660 cm^{-1} (ref. 39). In the present studies this band is observed at 596 cm^{-1} . These observations suggest that nitryl chloride forms nitronium ions with Tl(III) chloride as $NO_2Cl + TlCl_3 \rightleftharpoons NO_2^+.TlCl_4^-$.

The other important bands are due to $\nu Tl-Cl$ modes of $TlCl_4^-$ (Table 4). In the case of $NOCl.TlCl_3$, an intense band at 2276 cm^{-1} indicates the presence of NO^+ ions⁴⁰ while the bands in the lower spectral regions support the formulation of tetrachlorothallate ion. Similarly in the case of $CH_3COCl.TlCl_3$, $C_6H_5COCl.TlCl_3$ and $CH_3COBr.TlCl_3$, all the bands showing the ionic formulations are present as shown in Table 4. It is evident from these observations, that in these adducts, Tl(III) chloride acts as a strong chloride ion acceptor molecule to form tetrachlorothallate ion.

As stated earlier, in the case of the adducts of Tl(III) chloride with thionyl chloride, selenyl chloride and thiophosphoryl chloride, molar conductance values rule out their ionic nature. The $\nu Se-O$ mode at 1170 cm^{-1} in $SeOCl_2$ is shifted to 1106 cm^{-1} in the adduct $SeOCl_2.TlCl_3$, suggesting coordination through oxygen. In the case of thiophosphoryl chloride adduct, as compared to pure thiophosphoryl chloride, the $\nu P-S$ is lowered suggesting coordination through sulphur. Similar observations have been made in the case of the adducts of thionyl chloride. It is apparent from the above studies that acid chlorides such as nitryl chloride, nitrosyl chloride, acetyl chloride and benzoyl chloride are chloride ion donor molecules and form tetrachlorothallate ion with Tl(III) chloride while thionyl chloride, selenyl chloride and thiophosphoryl chloride form adducts with Tl(III) chloride through the oxygen atoms.

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