619. *The Chemistry of Organothallium Compounds. Part I. The Preparations and Properties of Bis(pentafluorophenyl)thallium*(III) *Compounds*

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Bis(pentafluorophenyl)thallium(III) bromide has been prepared from pentafluorophenylmagnesium bromide and thallic chloride, and converted into the corresponding fluoride, chloride, nitrate, acetate, trifluoroacetate, and sulphate. The compounds have low conductances in acetone, and the majority are monomeric. The chloride, bromide, and acetate have low conductances in methanol, but the fluoride, trifluoroacetate, and nitrate are highly ionised. The sulphate is a strong electrolyte in water. In benzene, the chloride and bromide are dimeric. In the solid, the bromide, chloride, and fluoride are probably dimeric, the nitrate contains ionic or weakly co-ordinated nitrate groups, while the sulphate has bridging bidentate sulphate groups.

With 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (*o*-phen), complexes of the type $(C_6F_5)_2$ (bipy or *o*-phen)TlX (X is Cl, Br, NO_3, and $CF_3{\cdot}CO_2$) are formed. Infrared data indicate these probably contain five co-ordinate thallium. The bipyridyl complexes are very weak electrolytes in acetone and molecular weights are consistent with slight ionisation. The phenanthroline complexes are nonelectrolytes and monomeric. In methanol, all complexes are moderately or highly ionised. Representative complexes are monomeric or slightly associated in benzene. An unstable complex, $(C_6F_5)_2py_2TlBr$, has also been prepared.

Complexes of the type $Q[(R_f)_2TlX_2]$ (Q is Ph_4P, Et_4N; X is Cl, Br) have been prepared and are 1 : 1 electrolytes in acetone and methanol. The infrared spectra of the chloro-complexes are consistent with the presence of the tetrahedral $(C_6F_5)_2TlCl_2^-$ ion.

$(C_6F_5)_2TlBr$ reacts with sodium tetraphenylborate, triphenylbismuth, and diphenylmercury with the formation of diphenylthallium bromide.

As part of a study of the factors influencing the formation of covalent metal–metal bonds between (formally) $d^{10}s^1$-metals (Au^0, Hg^I, Tl^{II}, etc.), it has been necessary to prepare compounds of the type R_2TlX (R is aryl or alkyl; X is Cl, Br, I). The known compounds of this class are generally soluble only in very basic solvents such as pyridine and aqueous ammonia, and do not readily give co-ordination derivatives,[1] presumably owing to the stability of the linear R–Tl–R$^+$ ions. Using the pentafluorophenyl group (henceforth termed R_f), bis(pentafluorophenyl)thallium(III) derivatives have been prepared,[2] which have properties very different from those of their known aryl and alkyl analogues.

RESULTS

Three main stoicheiometric classes of bis(pentafluorophenyl)thallium compounds have been established, *viz.* (1) $(R_f)_2TlX$ derivatives, (2) $(R_f)_2$(bipy or *o*-phen)TlX complexes, and (3) $[Ph_4P$ or $Et_4N][(R_f)_2TlX_2]$ complexes. The compounds isolated and the methods of preparation are summarised in Table 1. An unstable complex, $(R_f)_2py_2TlBr$, is formed between $(R_f)_2TlBr$ and pyridine. Complex formation between *o*-phenylenebisdimethylarsine (diarsine) and $(R_f)_2TlBr$ occurs, but the product, probably $(R_f)_2$(diarsine)TlBr, is difficult to obtain pure.

TABLE 1

Bis(pentafluorophenyl)thallium(III) compounds

Type	Examples (X =)	Preparations
$(R_f)_2TlX$	Br	$2R_fMgBr$ * + $TlCl_3 \longrightarrow (R_f)_2TlBr + MgBrCl + MgCl_2$ [a]
	F, Cl, NO_3, OAc, OAc_f	$(R_f)_2TlBr + AgX \longrightarrow (R_f)_2TlX + AgBr$ [b]
	$\frac{1}{2}SO_4$	$2(R_f)_2TlBr + Tl_2SO_4 \longrightarrow [(R_f)_2Tl]_2SO_4 + 2TlBr$ [c]
$(R_f)_2bipyTlX$	Cl, Br, NO_3, OAc_f	$(R_f)_2TlX$ + (bipy or *o*-phen) $\longrightarrow$ $(R_f)_2$(bipy or *o*-phen)TlX [d]
$(R_f)_2$-*o*-phenTlX	Cl, Br, NO_3	
$[Ph_4P][(R_f)_2TlX_2]$	Cl, Br	$(Ph_4P$ or $Et_4N)X + (R_f)_2TlX \longrightarrow [Ph_4P$ or $Et_4N][(R_f)_2TlX_2]$ [e]
$[Et_4N][(R_f)_2TlX_2]$	Cl	

[a] In ether. [b] In polar organic solvents. [c] In aqueous methanol. [d] In ether, methanol, or ethanol. [e] In ether or methanol. OAc_f is trifluoroacetate.

* Ref. 3.

The compounds are soluble in a number of polar organic solvents; *e.g.*, the simple derivatives $(R_f)_2TlX$ (X is Cl, Br, OAc_f, $\frac{1}{2}SO_4$) and the majority of the complexes are soluble in ether. $(R_f)_2TlCl$, $(R_f)_2TlBr$, and most of the complexes are soluble in benzene. $[(R_f)_2Tl]_2SO_4$ is the only derivative soluble in water. This property has been used to prepare the chloride and the fluoride by metathesis from the sulphate.

Conductances and Molecular Weights.—In Table 2 are given molar conductances of the compounds in acetone and methanol, together with corresponding data for dimethylthallium nitrate and acetate; some data for pyridine and aqueous solution are also provided. Molecular weights are given in the Experimental section.

In acetone, the compounds $(R_f)_2TlX$ (X is Cl, Br, NO_3, OAc, OAc_f, $\frac{1}{2}SO_4$) have very low conductances, the majority (X is Cl, Br, NO_3, OAc_f) being monomeric, and the sulphate slightly associated. The acetate is not sufficiently soluble for a molecular weight determination. The conductances of the bromide and chloride are independent of concentration over a tenfold change in concentration and increase slowly with time (Table 2). The latter suggests a slow solvolysis of the Tl–Hal bond. The halogen atoms in these compounds are ionisable, being removed completely when acetone solutions of $(R_f)_2TlCl$ and $(R_f)_2TlBr$ are titrated with silver nitrate. The conductances of $(R_f)_2TlNO_3$ are also nearly independent of concentration, in contrast with the behaviour of dimethylthallium nitrate (Figure 1).

In methanol, the chloride, bromide, and acetate are almost un-ionised, the fluoride is partly ionised, while the nitrate and trifluoroacetate are virtually 1 : 1 electrolytes. Although both $(R_f)_2TlNO_3$, and Me_2TlNO_3 have very low conductances in acetone and are highly ionised in methanol, their behaviour in mixtures of these solvents is different

[1] Coates, " Organometallic Compounds," 2nd edn., Methuen, London, 1960, p. 158.

[2] A preliminary account has been given, Deacon and Nyholm, *Chem. and Ind.*, 1963, 1803.

[3] Nield, Stephens, and Tatlow, *J.*, 1959, 166.

TABLE 2

Molar conductances of bis(organo)thallium(III) compounds, in acetone, methanol, pyridine, and water at *ca.* 20°

Compound	Mol. Cond.	{Concn. 10³M}	Mol. Cond.	{Concn. 10³M}	Mol. Cond.	{Concn. 10³M}	Mol. Cond.	{Concn. 10³M}
		In acetone				In methanol		
$(R_f)_2TlBr$	1·2	(1·71) [a]	1·2	(18·6) [a]	3·1	(1·89)	1·6	(8·54)
$(R_f)_2TlCl$	1·0	(2·16) [a]	0·9	(17·9) [a]	6·4	(2·04)	3·8	(5·84)
$(R_f)_2TlF$		Almost insoluble			39·1	(1·92)	24·2	(6·92)
$(R_f)_2TlNO_3$	2·7	(1·74)	2·5	(10·2)	70·5	(1·98)	59·0	(5·93)
$[(R_f)_2Tl]_2SO_4$	17·9	(1·02)						
$(R_f)_2Tl(OAc)$	0·5	(2·61)			4·1	(1·96)		
$(R_f)_2Tl(OAc_f)$	3·0	(1·75)	2·3	(4·74)	56·8	(1·69)	47·4	(3·62)
$(R_f)_2$bipyTlBr	21·0	(1·36)	17·2	(5·44)	11·9	(1·37)		
$(R_f)_2$bipyTlCl	13·7	(1·32)	10·2	(5·38)	22·0	(1·47)		
$(R_f)_2$-*o*-phenTlBr ...	4·5	(1·26)	3·2	(7·60)	29·0	(1·37)		
$(R_f)_2$-*o*-phenTlCl ...	2·7	(1·63)	1·8	(5·21)	40·0	(1·39)		
$(R_f)_2$bipyTlNO$_3$	12·2	(1·53)	11·5	(2·03)	77·3	(1·51)		
$(R_f)_2$-*o*-phenTlNO$_3$...	5·3	(1·47)	2·5	(7·28)	76·1	(1·53)		
$(R_f)_2$bipyTl(OAc$_f$) ...	8·4	(1·36)	6·0	(5·47)	61·6	(1·65)		
$[Ph_4P][(R_f)_2TlCl_2]$ ...	109	(1·16)	93·6	(4·99)	79·4	(1·22)	74·3	(2·74)
$[Ph_4P][(R_f)_2TlBr_2]$ ...	106	(0·983)	97·3	(3·66)	80·7	(1·16)	70·9	(3·79)
$[Et_4N][(R_f)_2TlCl_2]$ ...	116	(1·51)	111	(2·85)	90·2	(1·37)	85·4	(3·23)
$(R_f)_2py_2TlBr$	3·3	(1·30) [a]						
Me_2TlNO_3	9·3	(0·533)	(*ca.* 4·5)	(*ca.* 3·9)	79·0	(3·91)	68·6	(10·8)
$Me_2Tl(OAc)$	<0·5	(*ca.* 1·6)			58·8	(4·26)		
		In water				In pyridine		
$[(R_f)_2Tl]_2SO_4$	177	(0·716)	167	(1·38)				
$(R_f)_2TlBr$					*ca.* 0·1	(2·46) [a]		
$(R_f)_2TlNO_3$					2·7	(2·18)		
Me_2TlNO_3	94·3	(1·99)	84·2	(13·2)	11·1	(3·64)		

[a] Conductance increases on standing, *e.g.*, for $(R_f)_2TlBr$: Mol. Cond. (10³M). After 45 min., 1·8 (2·09, 18·6). After 14·5 hr., 2·8 (6·31, 12·4). 1 : 1 Electrolytes in acetone and pyridine have Mol. Cond. ~150 at 10^{-3}M; in methanol, Mol. Cond. ~100 at 10^{-3}M. However, the expected values for large ions would be somewhat lower.

(Figure 2). Molecular weights of $(R_f)_2TlBr$ and $(R_f)_2TlCl$ in benzene indicate dimerisation. (This has been confirmed independently for the bromide.)[4] In water, $[(R_f)_2Tl]_2SO_4$ is a 2 : 1 electrolyte, while the nitrate and bromide are nonelectrolytes in pyridine.

The bipyridyl complexes are very weak electrolytes in acetone, and the molecular weights are slightly lower than the calculated values, confirming slight dissociation. The phenanthroline complexes are nonelectrolytes and monomeric.

In benzene, the complexes $(R_f)_2$bipyTlBr, $(R_f)_2$bipyTl(OAc$_f$), $(R_f)_2$-*o*-phenTlCl, and $(R_f)_2$-*o*-phenTlBr are monomeric in *ca.* 1% solution, but slightly associated in more concentrated solution. $(R_f)_2$bipyTl(OAc$_f$) and $(R_f)_2$-*o*-phenTlNO$_3$ are monomeric in chloroform. All these complexes ionise significantly in methanol, their behaviour ranging from weak [$(R_f)_2$bipyTlBr] to 1 : 1 electrolytes (nitrate derivatives). The complexes $Q[(R_f)_2TlX_2]$ (Q is Ph_4P, Et_4N; X is Cl, Br) are 1 : 1 electrolytes in acetone and methanol. Molecular weights in acetone are consistent with this ionisation ($i \sim 1{\cdot}5$—$1{\cdot}9$). Considerable association of the tetraphenylphosphonium compounds occurs in benzene. The complex $(R_f)_2py_2TlBr$ is a nonelectrolyte in acetone, the conductance increasing with time. Accurate molecular weights could not be obtained for this compound. Possibly loss of ligand occurs in solution. The crystalline complex smells of free pyridine.

Mixtures of $(R_f)_2$-*o*-phenTlBr and $(R_f)_2TlBr$ in acetone solution have much higher conductivities than if those of the components were additive (see Experimental section, Table 7). Probably the reaction,

$$(R_f)_2\text{-}o\text{-phenTlBr} + (R_f)_2TlBr \rightleftharpoons (R_f)_2\text{-}o\text{-phenTl}^+ + (R_f)_2TlBr^-, \text{ occurs.}$$

Infrared Spectra.—The infrared spectra of all compounds in the region 2000—450 cm.$^{-1}$ have been recorded, and most have been examined from 2000 to 200 cm.$^{-1}$. Except where

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[4] Fenton, Gillies, Massey, and Randall, *Nature*, 1964, **201**, 818.

bands due to other groups interfere, absorption characteristic of $(R_f)_2Tl$ is observed at 1642—1631, 1520—1506vs, 1488—1471vs, 1385—1370vs, 1101—1075vs, 1082—1064, 1012—1002, 974—962vs, 804—774 (sometimes two bands), 720—715, 613—599, 372—353vs, 324—308, 291—275, and 235—217 cm.$^{-1}$ in the spectra of all bis(pentafluorophenyl)thallium compounds. (The most intense features are indicated vs.) Corresponding bands are found at 1637, 1515, 1497, 1376, 1092, 1082, 1003, 977, 805, 711, 612, 348, 311, 281, and 221 cm.$^{-1}$ in the spectrum of R_fI,[5] which is a satisfactory reference compound for an R_f group attached to an atom of heavy mass. Vibrational assignments are being made for the $(R_f)_2Tl$ group, and will be reported later as part of a wider study of the spectra of organothallium compounds.[6] Accordingly in this Paper the discussion of the infrared spectra is confined to absorption due to ligands other than R_f, anions, and Tl–Hal bonds.

In the spectra of the bipyridyl complexes, bands at 1605—1597, 1597—1592, 1582—1577, 1572—1567, 1445—1439, 1312 or 1311, 1248—1245, 1183—1176, 1161 or 1160, 771—761, 737—734, 648—646, 629—625, and 413 or 412 cm.$^{-1}$, due to bipyridyl, could be distinguished from $(R_f)_2Tl$ absorption. In the nitrate and trifluoroacetate, absorption due to these groups obscured some bipyridyl bands. The absorption due to *o*-phen in the $(R_f)_2$-*o*-phenTlX complexes does not form so consistent a pattern, possibly due to crystal splitting. Bands due to *o*-phen were found at 1631—1626, 1595—1592, 1580, 1451—1449, 1433—1429, 1351—1344, 1224—1222, 1103—1087 (split for X = Cl), 864—843 (two or three bands), 776 or 775(?), 732—721 (split for X = Cl, Br), 642—638, 418 or 417, 278—273(?), and 244—242 cm.$^{-1}$. In the spectrum of $(R_f)_2py_2TlBr$, bands at 1595, 1445, 1215, 1157, 1035, 943, 754, 700, *ca.* 698, 618, and 412 cm.$^{-1}$, due to pyridine, could clearly be distinguished from $(R_f)_2Tl$ absorption, and have counterparts in the spectra of a large number of pyridine complexes.[7] In Table 3, assignments of bands due to the nitrate group in the spectra of pentafluorophenylthallium nitrate compounds and dimethyl- and diphenyl-thallium nitrate are given. These were made by using the reported assignments for ionic and co-ordinated nitrate groups.[8] The assignments of the two lowest frequencies are uncertain and possibly should be reversed.[8b] We prefer those given in Table 3, as the higher is assigned to ν_5 (antisym. bend) and the lower to ν_3 (sym. bend). Bands in the spectrum of $(R_f)_2TlNO_3$ at 1792 and 1779 cm.$^{-1}$ are explicable as the combinations

TABLE 3

Nitrate absorption bands (in cm.$^{-1}$) of some organothallium nitrates [a]

		Compounds				
NO_3^- mode	ONO_2 (type)	$(R_f)_2TlNO_3$	Me_2TlNO_3	Ph_2TlNO_3	$(R_f)_2bipyTlNO_3$	$(R_f)_2$-*o*-phenTlNO$_3$
$\nu_1(A_1')$	$\nu_2(A_1)$	1052w?	1045w, sp	1045w	1041m	1027m
$\nu_2(A_2'')$	$\nu_6(B_2)$	817m 832m [b]	816 [c]	815m	*d*	*d*
$\nu_3(E')$	→ $\nu_1(A_1)$	1357vs, br	1321vs, br	1368vs, br	1299vs, br	1294vs, br
	→ $\nu_4(B_1)$	1403s, br	1361vs, br		1418s, br	1411s, br
$\nu_4(E')$	→ $\nu_3(A_1)$	729m	733s	731 [e]	*d*	*d*
	→ $\nu_5(B_1)$	739m			*d*	*d*
Combination Bands		1792vw, sp 1779vw, sp	1776w, sp	1776w, sp		

[a] Obtained by using Nujol, hexachlorobutadiene, and fluorolube mulls. Intensities: (w) weak, (m) medium, (s) strong, (v) very, (br) broad, (sp) sharp. [b] In acetone solution. [c] Intensity uncertain as superimposed on a Me_2Tl band.[6] [d] Bands obscured by ligand absorption. [e] Not observed directly due to Ph_2Tl absorption. From 1776—1045 (see text).

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[5] Green, unpublished results, 1963. See also, Long and Steele, *Spectrochim. Acta*, 1963, **19**, 1955.

[6] Deacon and Green, unpublished results, 1963, 1964.

[7] Gill, Nuttall, Scaife, and Sharpe, *J. Inorg. Nuclear Chem.*, 1961, **18**, 29.

[8] (*a*) Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222; (*b*) Gatehouse and Comyns, *J.*, 1958, 3965; (*c*) Addison and Gatehouse, *J.*, 1960, 613; (*d*) Buijs and Schutte, *Spectrochim. Acta*, 1962, **18**, 307.

$(\nu_2 + \nu_5)$ and $(\nu_2 + \nu_3)$, respectively, and that of Me_2TlNO_3 at 1776 cm.$^{-1}$ is explicable as 1045 + 733. In Ph_2TlNO_3, $\nu_4(NO_3^-)$ is obscured by other absorptions, but if the band at 1776 cm.$^{-1}$ is interpreted [8c,d] as $(\nu_1 + \nu_4)$, then ν_4 is at 731 cm.$^{-1}$. Assignments for acetate and trifluoroacetate derivatives were made using the reported spectra of sodium acetate [9] and sodium trifluoroacetate,[10] and are given in Table 4. The sulphate bands of $[(R_f)_2Tl]_2SO_4$ are recorded in Table 5, and bands due to Tl–Hal stretching in various pentafluorophenylthallium halide derivatives in Table 6.

TABLE 4

Acetate and trifluoroacetate absorption bands (in cm.$^{-1}$) of some bis(organo)thallium(III) compounds [a]

$(R_f)_2Tl(OAc)$	$Me_2Tl(OAc)$	$(R_f)_2Tl(OAc_f)$	$(R_f)_2bipyTl(OAc_f)$	Assignment
1546sh (or less) *	1541vs	1608vs	1669vs	ν antisym. $-CO_2^-$
1449s, sh	*			CH_3 antisym. def.
1408s	1418vs, br	*	1433s	ν sym. $-CO_2^-$
1353sh *	1335m			CH_3 sym. def.
		1217vs	1206vs	C–F stretch
		1195vs	1192vs	,,
		1185vs	1182sh	,,
		1143m *	1139vs	,,
*	1047sh			Me rock
1009s *	1009m			Me rock
*	933s	873m	846s	ν(C–C)
		809m	759s *	
677s	655vs	734s	728vs	δ (OCO)
610m, br *	641m			$-CO_2^-$ wag (out-of-plane)
		599w	*ca.* 597sh	CF_3 def. in phase
		518w, br	518vw, br	CF_3 def. out of phase
457w, br	454w, br			$-CO_2^-$ rock
		432m, br		CF_3 rock
		283vs	274s	CF_3 rock
	1235w			Unassigned

[a] Obtained using Nujol and hexachlorobutadiene mulls.

* Either impossible to locate due to absorption of other groups, or located by intensity differences between bands in these spectra and those of the corresponding halides, hence position and intensity are uncertain.

TABLE 5

Sulphate bands (in cm.$^{-1}$) of di[bis(pentafluorophenyl)thallium(III)] sulphate

1206s, br	1157vs, br	*ca.* 1111sh	985s	643s, br	636sh	*ca.* 625sh(?)	598m, br [a]
1202m, sh	1156s	*ca.* 1110sh	989s	635m	620sh	590m	*ca.* 435vw(?) [b]

[a] Obtained by using Nujol and hexachlorobutadiene mulls for the region 2000—450 cm.$^{-1}$. [b] In a KCl disc from 2000—400 cm.$^{-1}$.

TABLE 6

Tl–Hal stretching frequencies (in cm.$^{-1}$) of bis(pentafluorophenyl)thallium(III) halide compounds [a]

Compounds				
$(R_f)_2TlF$	$(R_f)_2bipyTlCl$	$(R_f)_2$-*o*-phenTlCl	$[Ph_4P][(R_f)_2TlCl_2]$	$[Et_4N][(R_f)_2TlCl_2]$
318vs, br	238vs, br	224vs, br	264vs, br 232vs, br	269vs, br 248vs, br

[a] Obtained using Nujol mulls.

Group Exchange Reactions.—Bis(pentafluorophenyl)thallium bromide reacts with sodium tetraphenylborate in acetone, with triphenylbismuth, and with diphenylmercury in ether to yield diphenylthallium bromide. It has not been possible to isolate the other product of these reactions except from that with diphenylmercury, from which a mixture

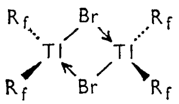
[9] Nakamura, *J. Chem. Soc. Japan*, 1958, **79**, 1411.

[10] (*a*) Klemperer and Pimentel, *J. Chem. Phys.*, 1954, **22**, 1399; (*b*) Robinson and Taylor, *Spectrochim. Acta*, 1962, **18**, 1093.

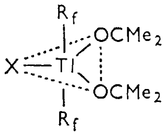
of $(R_f)_2Hg$ and $PhHgR_f$ was obtained. Group exchange also occurs when aqueous solutions of sodium tetraphenylborate and $[(R_f)_2Tl]_2SO_4$ are mixed. Group exchange between organometallic compounds is well known,[11] but aryl–aryl exchange is unusual.

Discussion

The Compounds $(R_f)_2TlX$.—As $(R_f)_2TlCl$ and $(R_f)_2TlBr$ are dimeric in benzene, the compounds are probably dimeric in the solid state [12] with a tetrahedral array of ligands about thallium (I). A similar structure has been suggested for the dimethylthallium methoxide dimer.[13] An ionic structure, as in other R_2TlHal compounds,[1,14] is excluded by the low conductances of the pentafluorophenyl compounds in methanol. A trigonal monomeric structure for the chloride is unlikely due to the absence of a Tl–Cl stretching frequency above 220 cm.$^{-1}$, as the trigonal monomer should have a Tl–Cl vibration above 232 cm.$^{-1}$, the lowest Tl–Cl stretching frequency of $(R_f)_2TlCl_2^-$ (Table 6). Boron trifluoride has both antisym. and sym. B–F stretching modes at higher frequencies than the corresponding modes of BF_4^-.[15]



(I)



(II)

Monomers are formed when $(R_f)_2TlX$ (X is Cl, Br) compounds are dissolved in acetone, indicating the rupture of halogen bridging, perhaps due to co-ordination of acetone [cf. the similar case of $(PhPEt_2,HgBr_2)_2$].[16] A crystalline complex between acetone and $(R_f)_2TlBr$ could not be isolated, but this does not preclude complex formation in solution. Either the tetrahedral species $(R_f)_2(Me_2CO)TlX$ or the five co-ordinate species (II) could be formed. That the latter is possible is indicated by the isolation of $(R_f)_2py_2TlBr$ from a solution of the bromide in pyridine. Structure (II) is favoured, as it would permit the $(R_f)_2Tl$ group to revert to the stable linear C–Tl–C stereochemistry.

Molecular weights of $(R_f)_2TlF$ were not obtained owing to low solubility in suitable solvents. The location of a Tl–F stretching frequency (Table 6) precludes an ionic structure for the crystalline compound. Probably the structure is a fluorine-bridged dimer (cf. (I)], but with strong bridging bonds; otherwise the low solubility of the compound in acetone is difficult to understand, since weak bridging would permit solution *via* monomer formation as with the chloride and bromide. There are insufficient infrared data for fluorine-bridged compounds to indicate whether the observed Tl–F frequency is at a reasonable value for the suggested structure.

$(R_f)_2TlNO_3$ crystallises in at least two modifications characterised by differences in the nitrate absorption bands (see Experimental section). The values in Table 3 are for the form that could be consistently prepared. The splitting of the E' nitrate modes and the weak intensity of the infrared forbidden A_1' mode indicate that the site symmetry of the nitrate group is lowered from D_{3h}. However, it is doubtful whether significant co-ordination of nitrate to thallium occurs, as this is expected to cause much greater splitting of the E' modes. For co-ordinated nitrate,[8a,b] bands are found at 1531—1481, 1290—1253, 1034—

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[11] See, *e.g.*, ref. 1, ch. 1 and p. 157; Haszeldine and West, *J.*, 1956, 3631; 1957, 3880; Maher, Thesis, Imperial College, 1963, and references therein.

[12] It has not yet been possible to obtain suitable crystals for an *X*-ray structure investigation.

[13] Menzies and Walker, *J.*, 1934, 1131.

[14] Crowfoot and Powell, *Z. Krist.*, 1934, **87**, 370.

[15] Nakamoto, " Infra-red Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, pp. 90, 106.

[16] Cass, Coates, and Hayter, *J.*, 1955, 4007.

970, 800—781, 750—736, and 720—705 cm.$^{-1}$. If weak nitrate co-ordination does occur, a structure with bridging nitrates, similar to (I) is possible. Bridging and unidentate nitrate have the same symmetry. The high conductance in methanol is consistent with the view that any nitrate co-ordination must be weak. The data in Table 3 indicate that the site symmetry of nitrate in dimethylthallium nitrate is also lowered from D_{3h}, yet this compound is certainly ionic. The corresponding iodide is ionic,[14] and the nitrate is a strong electrolyte in methanol and water. The infrared spectrum of the crystalline nitrate shows only one C–Tl stretching frequency, which is consistent with the presence of linear Me_2Tl^+ ions.[6] Diphenylthallium nitrate is certainly ionic, as the highest E' mode is not split. The weak absorption due to the infrared inactive A_1' mode (Table 3) is also observed for some other ionic nitrates.[8]

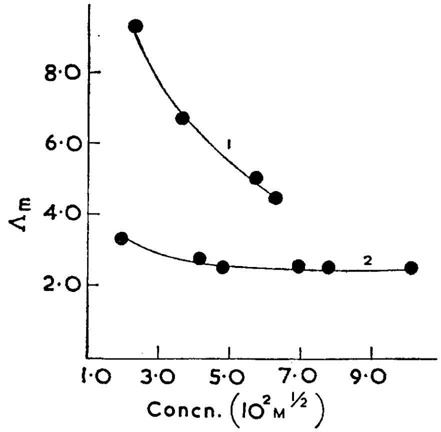


FIGURE 1. Concentration dependence of the conductance of dimethylthallium(III) nitrate and bis(pentafluorophenyl)thallium(III) nitrate in acetone

Curve (1) Me_2TlNO_3; curve (2) $(R_f)_2TlNO_3$

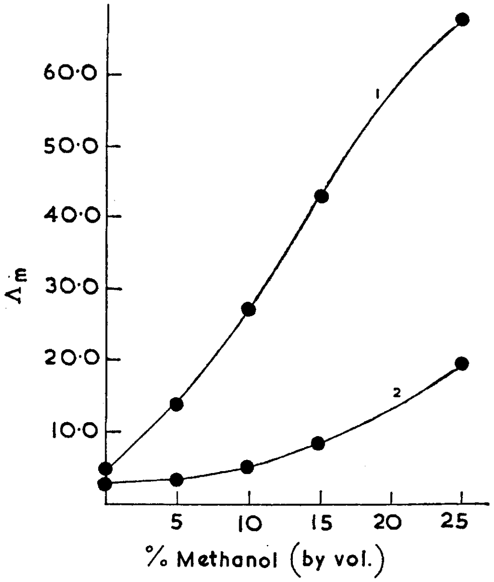


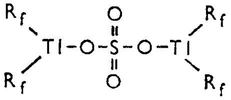
FIGURE 2. The conductance of dimethylthallium(III) nitrate and bis-(pentafluorophenyl)-thallium(III) nitrate in acetone–methanol

Curve (1) Me_2TlNO_3, $3\cdot90 \times 10^{-3}$M; curve (2) $(R_f)_2TlNO_3$, $2\cdot01 \times 10^{-3}$M

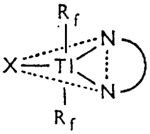
The reasons for the low conductances of Me_2TlNO_3 and $(R_f)_2TlNO_3$ in acetone may not be the same for they have different concentration dependence (Figure 1); the conductance is also affected differently by the addition of methanol (Figure 2). Dimethylthallium nitrate probably exists as ion pairs in acetone, and these are readily separated on addition of methanol. The much smaller effect of adding methanol to acetone solutions of $(R_f)_2TlNO_3$ suggests that retention of acetone by thallium occurs. If an acetone complex analogous to (II) is formed, it would be expected to be nonconducting [cf. $(R_f)_2py_2TlBr$ in acetone]. It would also involve co-ordination of nitrate to thallium. Unfortunately the spectrum of $(R_f)_2TlNO_3$ in acetone is not diagnostic. Only the nitrate band at 832 cm.$^{-1}$ can be distinguished from solvent and $(R_f)_2Tl$ absorption, and lack of reference data for nitrates in acetone makes this valueless.

A likely structure for $[(R_f)_2Tl]_2SO_4$ can be established from consideration of the sulphate absorption bands (Table 5). The sulphate ion (symmetry T_d) gives bands at *ca.* 1100 and *ca.* 600 cm.$^{-1}$, unidentate sulphate (symmetry C_{3v}) bands at *ca.* 1200—1030 (two), *ca.* 970, *ca.* 650—600 (two), and *ca.* 450 cm.$^{-1}$, and bidentate or bridging bidentate sulphate (symmetry C_{2v}) bands at *ca.* 1220—1050 (three), *ca.* 990, *ca.* 650—510 (three), and *ca.* 450 cm.$^{-1}$.[17] The number of sulphate bands observed for $[(R_f)_2Tl]_2SO_4$ indicates C_{2v} symmetry for the sulphate group. Bidentate sulphate is not consistent with the stoicheiometry, hence the sulphate groups are bridging bidentate and the simplest structure likely is (III), with trigonal stereochemistry for thallium. The sulphate ionises in water to give sulphate ions and $(R_f)_2Tl^+$ ions, in which the C–Tl–C skeleton probably reverts to the stable linear arrangement. Three water molecules could also be co-ordinated to give a trigonal bipyramidal stereochemistry.

It is probable that in $(R_f)_2Tl(OAc)$ and Me_2TlOAc, the acetate groups are not unidentate donors. Co-ordination of acetate through one oxygen atom shifts ν (antisym. $-CO_2^-$) to higher and ν (sym. $-CO_2^-$) to lower frequencies than in the free acetate ion, leading to a greater separation (Δ) between these frequencies.[18] For $(R_f)_2Tl(OAc)$, $\Delta \leqslant 138$ cm.$^{-1}$ [ν (antisym.) cannot be located with certainty, but is not higher than the shoulder at 1546 cm.$^{-1}$, and may be lower, hidden under the 1511 cm.$^{-1}$ band of $(R_f)_2Tl$], and for Me_2TlOAc, $\Delta = 123$ cm.$^{-1}$ compared with 157 cm.$^{-1}$ for free acetate ion.[9] The remaining possibilities, ionic, bidentate, or bridging acetate cannot be distinguished on the basis of infrared spectra.[19] As $(R_f)_2Tl(OAc)$ is a nonelectrolyte in methanol, it is unlikely to be ionic in the solid, and the most likely structure is one with bridging acetate groups, similar to (I). Dimethylthallium acetate is highly ionised in methanol (Table 2), hence strong acetate bridging is unlikely in the solid and the compound may be ionic.



(III)



(IV)

Unidentate co-ordination by the trifluoroacetate ion should lead to similar changes in the $-CO_2^-$ frequencies to those found for acetate, but the available evidence is inconclusive.[6,20] Nevertheless the low value of ν (antisym. $-CO_2^-$) in $(R_f)_2Tl(OAc_f)$ (Table 4) compared with 1680 cm.$^{-1}$ for sodium trifluoroacetate [10a] is inconsistent with the presence of unidentate trifluoroacetate. As the compound is highly ionised in methanol, the crystalline compound probably contains ionic or weakly bridging trifluoroacetate ions. The monomeric nature and low conductance of the compound in acetone may be due to the formation of a complex with the solvent [cf. $(R_f)_2TlNO_3$].

The Complexes $(R_f)_2$-(*o*-phen or bipy)TlX.—Absorption due to Tl–Cl stretching is found in the infrared spectra of $(R_f)_2$bipyTlCl and $(R_f)_2$-*o*-phenTlCl (Table 6), hence these complexes, and by analogy the corresponding bromides, probably contain five-co-ordinate thallium. The nitrate absorption bands of the corresponding nitrates show that the symmetry of nitrate is lowered from D_{3h} (Table 3). The splitting between ν_1 and ν_4 is not as great as in many nitrato-complexes,[8] but is large enough to suggest the co-ordination of nitrate and hence the presence of five-co-ordinate thallium. The $-CO_2^-$ stretching frequencies of $(R_f)_2$bipyTl(OAc_f) have a separation of 236 cm.$^{-1}$, which is similar to that for sodium trifluoroacetate,[10a] *viz.* 228 cm.$^{-1}$, and suggests very weak, if any, co-ordination of trifluoroacetate. The monomeric nature of the complexes in various solvents (see Results) is in agreement with the hypothesis of five co-ordination, but the ionisation of the

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[17] Ref. 15, p. 164; Barraclough and Tobe, *J.*, 1961, 1993.

[18] Ref. 15, p. 198; Lever, Lewis, and Nyholm, *J.*, 1962, 5262.

[19] Beattie and Gilson, *J.*, 1961, 2585.

[20] Downs, Ebsworth, and Emeléus, *J.*, 1962, 1254; Baillie, Brown, Moss, and Sharp, unpublished results (Sharp, personal communication).

compounds in methanol, $(R_f)_2(\text{bipy or } o\text{-phen})TlX \rightleftharpoons X^- + (R_f)_2(o\text{-phen or bipy})Tl^+$, shows that the fifth group (X) is not strongly held, especially when X is NO_3 or OAc_f.

The complexes probably have a trigonal bipyramidal shape, the bonding involving $6s6p^36d_{z^2}$ hybridisation of thallium. The electronegative pentafluorophenyl groups lower the $6p,6d_{z^2}$ energy separation, permitting expansion of the co-ordination beyond four, the usual maximum for di(organo)thallium compounds.[1] The effect of the pentafluorophenyl groups can also be explained by using Craig and Magnussen's orbital contraction theory.[21]

If these complexes have a trigonal bipyramidal structure, there are several possible isomers. At this stage the structure (IV) seems most likely, as it has the stable linear C–Tl–C configuration, and the R_f groups occupy the terminal positions which are preferred by electronegative groups in this stereochemistry. As the $<$NMN is usually 90° or less in bipy or *o*-phen complexes, the bond angles in the trigonal plane are unlikely to be 120°.

The relative stabilities of the $(R_f)_2TlX$ and $(R_f)_2(\text{bipy or } o\text{-phen})TlX$ (X is a halogen) compounds in terms of the dissociations

$$(R_f)_2TlX \rightleftharpoons (R_f)_2Tl^+ + X^-$$

$$(R_f)_2(\text{bipy or } o\text{-phen})TlX \rightleftharpoons (R_f)_2(\text{bipy or } o\text{-phen})Tl^+ + X^-$$

in acetone and methanol can be established from their conductances * (Table 2). In acetone the order is $Cl^- > Br^-$ (class A) [22] and in methanol $F^- < Cl^- < Br^-$ (class B).[22] Solvation energies of halide ions have a large effect on the stability sequence of halide complexes.[23,24] Thus, it is possible, as above, that inversion of the stability order may occur with change of solvent. There is some evidence that this occurs for tetrahalomercurate(II) complexes, the stability sequence in acetonitrile and water being class A and class B, respectively.[24] The conductance data also suggest that the *o*-phen complexes are more stable than their bipy analogues in acetone, but that the reverse is true in methanol.

The Complexes $[Ph_4P \text{ or } Et_4N][(R_f)_2TlX_2]$.—The conductances of the compounds in acetone and methanol indicate that the complexes are of the form $[Ph_4P \text{ or } Et_4N]^+[(R_f)_2TlX_2]^-$ (X is Cl, Br), and molecular weights in acetone are consistent with this formulation. The infrared spectrum of each chloro-complex contains two bands attributable to Tl–Cl stretching (Table 6), which is in agreement with the presence of tetrahedral $(R_f)_2TlCl_2^-$ ions. The complexes $[Ph_4P][(R_f)_2TlCl_2]$ and $[Ph_4P][(R_f)_2TlBr_2]$ are shown to be isostructural by *X*-ray powder photography. No other stable anionic complexes of organothallium compounds are known; although the complex $PhTl(CN)_3^-$ has been prepared, it readily decomposes to diphenylthallium cyanide.[25] The stabilisation of anionic bis(pentafluorophenyl)thallium complexes is due to a reduction of the $6s,6p$ energy separation, which increases the stability of four co-ordination relative to two co-ordination. The aggregation of these compounds in benzene is as expected for electrolytes in this medium.[26]

The formation of $(R_f)_2TlBr_2^-$ ions in the reaction between $(R_f)_2$-*o*-phenTlBr and $(R_f)_2TlBr$ (see Results section) suggests that a further series of complexes, *viz.* $(R_f)_2(o\text{-phen or bipy})Tl^+ (R_f)_2TlX_2^-$ (X is Cl, Br) can be prepared, by reaction between two molecules of $(R_f)_2TlX$ and one of bipy or *o*-phen. This is being investigated.

Group Exchange Reactions.—It is reasonable to suggest the following mechanism for these reactions, which is consistent with the observation that $(R_f)_2TlBr$ undergoes aryl/aryl exchange with anionic (Ph_4B^-), neutral $(Ph_3Bi$, and $Ph_2Hg)$, but not with cationic (Ph_4P^+) phenylorganometallics. As the bromine of $(R_f)_2TlBr$ is ionisable, some $(R_f)_2Tl^+$ ions are

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* Except for $(R_f)_2TlX$ in acetone, where the differences between chloride and bromide are too small.

[21] Craig and Magnussen, *Discuss. Faraday Soc.*, 1958, **26**, 116; *J.*, 1956, 4895.

[22] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[23] Pöe and Vaidya, *Nature*, 1959, **184**, 1139; *J.*, 1961, 1023.

[24] Deacon, *Rev. Pure and Appl. Chem. Australia*, 1963, **13**, 189, and refs. therein.

[25] Challenger and Richards, *J.*, 1934, 405.

[26] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3614.

present in solutions of the compound. Electrophilic attack by this cation on a phenyl compound, *e.g.*, Ph_2Hg, would give $(R_f)_2TlPh$.

$$(R_f)_2Tl^+ \;\overset{\curvearrowleft}{+\ Ph}{-}HgPh \rightleftharpoons PhHg^+ + (R_f)_2TlPh \qquad (1)$$

The tris(organo)thallium compound would lose the most electronegative group (R_f) as a carbanion giving R_fTlPh^+, and the carbanion would attach to mercury.

$$\left.\begin{aligned} (R_f)_2TlPh &\rightleftharpoons R_fTlPh^+ + R_f^- \\ R_f^- + PhHg^+ &\rightleftharpoons R_fHgPh \end{aligned}\right\}\text{ or in one step} \qquad \begin{aligned} (2) \\ (3) \end{aligned}$$

Continuation of this process would ultimately give Ph_2Tl^+, which would be precipitated as the bromide, and the insolubility of this compound would drive the reaction to completion, even though the equilibria in steps (1) and (2) and their subsequent analogues may lie to the left. Alkyl/alkyl exchange between R_3Tl compounds (*e.g.*, between Me_3Tl and Et_3Tl),[27] and between R_3Tl compounds and other Group III organometallics [28] is known, while the mechanism of alkyl exchange reactions between mercury and thallium organometallics has been studied.[29]

EXPERIMENTAL

Preparations of Bis(pentafluorophenyl)thallium(III) *Compounds.*—Melting points below 250° are corrected. Molecular weights were determined in AnalaR solvents, at 25°, using a Mechrolab vapour phase osmometer, model 301A. Petroleum has b. p. 30—40°.

Bis(pentafluorophenyl)thallium(III) *bromide.* Thallium trichloride tetrahydrate, prepared as by Cushman,[30] was partially dehydrated *in vacuo* over phosphorus pentoxide, and finally dehydrated in ether solution over molecular sieves. A filtered solution of pentafluorophenylmagnesium bromide [3] (18·1 g., 0·067 mole) in ether (120 ml.) was slowly added with stirring to an ice-cooled solution of thallic chloride [*ca.* 10 g., 0·033 mole; weighed as $TlCl_3,xH_2O$ ($x < 4$)] in ether (60 ml.) in an atmosphere of dry nitrogen. The mixture was then heated under reflux for 1·5 hr. After hydrolysis of the reaction mixture under nitrogen, the ether layer was separated and evaporated, giving *ca.* 10 g. of brown crystals. The required compound, obtained from benzene as fine white needles, was dried at 90°, m. p. 217—220·5° (decomp.) (yield: 5 g., *ca.* 25%) [Found: C, 23·4; Br, 12·8; ionisable Br, 12·8; F, 30·6; Tl, 32·6%; *M* (in acetone), 622 (5·47%), 610 (2·89%); *M* (in benzene), *ca.* 1060 (0·85%), *ca.* 980 (0·63%)—the compound being insufficiently soluble for accurate values. $C_{12}BrF_{10}Tl$ requires C, 23·3; Br, 12·9; F, 30·7; Tl, 33·1%; *M*, 618]. Prolonged heating at 150° caused slow decomposition. The yield of $(R_f)_2TlBr$ based on thallium was increased to *ca.* 45% by using a $R_fMgBr : TlCl_3$ ratio of 8 : 3. The compound was very soluble in acetone, ether, methanol, ethanol, pyridine, and boiling benzene, less soluble in chloroform and cold benzene, and insoluble in cold water.

Bis(pentafluorophenyl)thallium(III) *chloride.* A solution of bis(pentafluorophenyl)thallium bromide (1·24 g., 2·00 mmoles.) in 30 ml. of aqueous methanol (*ca.* 1 : 10; v : v) was shaken with excess of freshly precipitated silver chloride. After 1 hr., the precipitate was filtered off, and the filtrate was evaporated to dryness yielding the required compound (0·99 g., 88%). Recrystallisation from benzene gave fine white needles which, when dried at 90°, had m. p. 239—241° [Found: C, 25·55; ionisable Cl, 6·1; Tl, 35·6%; *M* (in acetone), 589 (3·23%), 556 (1·84%); *M* (in benzene), *ca.* 1070 (0·52%)—the *chloride* being insufficiently soluble for accurate values. $C_{12}ClF_{10}Tl$ requires C, 25·1; Cl, 6·2; F, 33·1; Tl, 35·6%; *M*, 574]. The chloride was also precipitated [m. p. 237·5—239° (benzene) (Found: C, 25·3; Cl, 6·1; F, 33·1%] when aqueous $[(R_f)_2Tl]_2SO_4$ (see below) was treated with aqueous potassium chloride. An excess of potassium chloride did not give high yields, possibly due to the formation of $(R_f)_2TlCl_2^-$ (see below). The solubility properties were similar to those of the bromide.

Bis(pentafluorophenyl)thallium(III) *fluoride.* This was prepared as for the chloride, but by using silver fluoride in methanol (yield 77%). Recrystallised from methanol–benzene, the

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[27] Evans and Maher, *Proc. Chem. Soc.*, **1961**, 208; *J.*, **1963**, 5534.

[28] Maher, Thesis, Imperial College, 1963, and refs. therein.

[29] Hart and Ingold, *J.*, **1964**, 4372.

[30] Cushman, *Amer. Chem. J.*, **1901**, **26**, 505.

fluoride was obtained as a white microcrystalline powder and was dried at 90°; it then had m. p. (decomp.) *ca.* 320° (Found: C, 25·95; F, 37·5. $C_{12}F_{11}Tl$ requires C, 25·8; F, 37·5%). When the preparation was attempted in acetone, the fluoride was coprecipitated with silver bromide. The fluoride (Found: C, 25·85; F, 37·5%) was also precipitated from the reaction between $[(R_f)_2Tl]_2SO_4$ and sodium fluoride in aqueous solution. The yield was not quantitative suggesting slight solubility in water. The compound was soluble in methanol and ethanol, sparingly soluble in acetone, and insoluble in ether and chloroform.

Bis(pentafluorophenyl)thallium(III) *nitrate.* The compound appeared to crystallise in at least two modifications, as the products of several preparations, while giving analyses consistent with the formula $(R_f)_2TlNO_3$, gave infrared spectra in which the positions and intensities of the nitrate bands differed. However, with the following experimental procedure, it was possible consistently to obtain crystals with nitrate bands at 1403s, br, 1357vs, br, 1052w, 817m, 739m, and 729m cm.$^{-1}$. The last absorption was slightly more intense than that at 739 cm.$^{-1}$.

Bis(pentafluorophenyl)thallium bromide (1·24 g., 2·00 mmoles) in acetone (20 ml.) was added to silver nitrate (0·34 g., 2·00 mmoles) in aqueous acetone (10 ml.) containing the minimum amount of water needed to dissolve the silver salt and a few drops of dilute nitric acid. Silver bromide was filtered off. The filtrate was evaporated until crystals appeared. After cooling, water was added to complete precipitation of the product, which was filtered off and washed repeatedly with water (yield 1·00 g., 85%). Recrystallisation from benzene–methylated spirits gave small white plates, m. p. *ca.* 287—289° (decomp.) [Found: C, 24·1; F, 31·8; N, 2·5%; *M* (in acetone), 598 (1·73%), 554 (0·86%). $C_{12}F_{10}NO_3Tl$ requires C, 24·0; F, 31·6; N, 2·3%; *M*, 600). Heating the *nitrate* to 200° did not change the crystalline form. However, after it had crystallised from a boiling aqueous organic solvent (using the minimum amount of organic solvent necessary for initial solution), changes in the nitrate absorption were observed. For example, from boiling aqueous methanol, the crystals (Found: C, 24·1; F, 31·7; N, 2·5%) had nitrate absorption bands at 1425s, br, 1332vs, br, 1049m, 815w, 739m, and a somewhat weaker band at 724m cm.$^{-1}$. The spectrum in the region 4000—2857 cm.$^{-1}$ showed no evidence for OH^- or water. The compound was very soluble in methanol, ethanol, and pyridine, soluble in acetone, sparingly soluble in ether, hot water, or boiling benzene.

Di[bis(pentafluorophenyl)thallium(III)] *sulphate.* Bis(pentafluorophenyl)thallium bromide (2·48 g., 4·00 mmoles) in aqueous methanol (20 ml.) was added slowly with stirring to a solution of thallous sulphate (1·08 g., 2·14 mmoles) in aqueous methanol (50 ml.). The thallous bromide was filtered off. On concentration of the filtrate, more thallous bromide was deposited and was removed by a series of filtrations. The filtrate was then evaporated to dryness *in vacuo*, giving a mixture of the required compound and excess of thallous sulphate. The former was separated by solution in ether, and was precipitated (1·6 g., 69%) by petroleum. Crystallisation from a mixture of di-isopropyl ether, 1,2-dimethoxyethane, and a little methanol (the compound deposited from the hot solution) gave white microcrystals, which were dried at 90°, m. p. *ca.* 285—290° (decomp.) [Found: C, 25·3; F, 32·3; S, 3·4%; *M* (in acetone), *ca.* 1500 (1·05%), *ca.* 1310 (0·54%). $C_{24}F_{20}O_4STl_2$ requires C, 24·6; F, 32·4; S, 2·7%; *M*, 1174). The *sulphate* was very soluble in ether, ethanol, methanol, and water (solutions slightly cloudy), soluble in acetone, and insoluble in petroleum, benzene, di-isopropyl ether, and 1,2-dimethoxyethane. The sulphate dissolved in mixtures of methanol with each of the last three solvents and crystallised from the boiling solutions, but redissolved on cooling. Aggregates were probably present in the cold solution, but were broken down on heating, permitting crystallisation. Attempts to prepare the compound by the silver salt method failed, as the reaction seemed incomplete.

Bis(pentafluorophenyl)thallium(III) *acetate.* This *acetate* was prepared by refluxing the stoicheiometric amounts of the bromide and silver acetate in methanol for 6 hr., a few drops of acetic acid also being added, and was isolated as for the chloride (yield 71%). Recrystallised from ethanol, the compound was obtained as white microcrystals, washed with ether, and dried at 90°, decomp. 233—238° (slight preliminary decomposition 226—233°) (Found: C, 28·2; H, 0·45; F, 32·1. $C_{14}H_3F_{10}O_2Tl$ requires C, 28·1; H, 0·5; F, 31·8%). The compound was soluble in methanol and ethanol, sparingly soluble in acetone, and insoluble in ether and water.

Bis(pentafluorophenyl)thallium(III) *trifluoroacetate.* This *compound* was prepared from the bromide and silver trifluoroacetate in ether (yield 88%). Recrystallisation from ether–petroleum gave white microcrystals, m. p. *ca.* 285—288° (decomp.) [Found: C, 25·75; F, 37·7%; *M* (in acetone), 642 (1·55%). $C_{14}F_{13}O_2Tl$ requires C, 25·8; F, 37·9%; *M*, 651). The compound was soluble in ether, ethanol, methanol, and acetone, sparingly soluble in benzene and chloroform, and insoluble in petroleum.

Bis(pentafluorophenyl)-2,2′-*bipyridylthallium*(III) *bromide*. Solutions of bis(pentafluorophenyl)thallium bromide (0·31 g., 0·50 mmole) and 2,2′-bipyridyl (0·078 g., 0·50 mmole) in ether (10 ml. in each case) were mixed, and the solution was evaporated to dryness. The residue was crystallised from aqueous methanol, yielding the required compound as fine white needles, which after being washed with aqueous methanol and dried at 100°, had m. p. 171·5—172·5° (yield 0·22 g., 58%) [Found: C, 34·3; H, 0·8; Br, 10·3; F, 24·7; N, 3·8%; *M* (in acetone), 664 (1·91%), 602 (0·89%), *M* (in benzene), 858 (2·05%), *ca.* 750 (0·52%). $C_{22}H_8BrF_{10}N_2Tl$ requires C, 34·1; H, 1·0; Br, 10·3; F, 24·6; N, 3·6%. *M*, 774]. The compound was very soluble in ether, methanol, ethanol, acetone, and benzene, and insoluble in water.

Bis(pentafluorophenyl)-2,2′-*bipyridylthallium*(III) *chloride*. This *chloride* was prepared as above and was obtained as fine white needles (yield 57%), m. p. 167·5° [Found: C, 36·4; H, 1·1; Cl, 5·0; F, 25·9%; *M* (in acetone), 656 (1·42%), 627 (1·19%). $C_{22}H_8ClF_{10}N_2Tl$ requires C, 36·2; H, 1·1; Cl, 4·9; F, 26·0%; *M*, 730]. The compound had similar solubilities to those of the bromide.

Bis(pentafluorophenyl)-2,2′-*bipyridylthallium*(III) *trifluoroacetate*. This *compound* was prepared as above and was obtained in 43% yield as small white plates, m. p. 168—169° [Found: C, 36·2; H, 0·8; F, 30·3; N, 3·5%; *M* (in acetone), 721 (1·21%), *M* (in chloroform), 762 (0·65%), *M* (in benzene), 800 (0·76%). $C_{24}H_8F_{13}N_2O_2Tl$ requires C, 35·7; H, 1·0; F, 30·6; N, 3·5%; *M*, 807]. The compound had similar solubility properties to those of the bromide, but the trifluoroacetate was less soluble in benzene.

Bis(pentafluorophenyl)-1,10-*phenanthrolinethallium*(III) *bromide*. This *bromide* was prepared from $(R_f)_2TlBr$ and 1,10-phenanthroline hydrate in a similar manner to the corresponding bipyridyl complex, except that ether–methanol was used as the reaction solvent, and was obtained as fine white needles (yield 80%), m. p. 141—141·5° [Found: C, 35·95; H, 0·8; Br, 10·0; F, 23·7; N, 3·6%; *M* (in acetone), 798 (3·12%), 809 (2·17%), 774 (1·65%), *M* (in benzene), 911 (2·02%), 821 (1·30%). $C_{24}H_8BrF_{10}N_2Tl$ requires C, 36·1; H, 1·0; Br, 10·0; F, 23·8; N, 3·5%; *M*, 798]. The solubility properties were similar to those of the corresponding bipyridyl complex, but the latter was more soluble in benzene.

Bis(pentafluorophenyl)-1,10-*phenanthrolinethallium*(III) *chloride*. This *chloride* was prepared as above, and obtained in 68% yield as fine white needles, m. p. *ca.* 199—204° (decomp.) [Found: C, 38·4; H, 1·1; Cl, 4·7; F, 25·15; N, 3·7%, *M* (in acetone), 771 (1·72%), 764 (1·26%), 721 (1·08%), *M* (in benzene), 849 (2·32%), 736 (1·05%). $C_{24}H_8ClF_{10}N_2Tl$ requires C, 38·3; H, 1·1; Cl, 4·7; F, 25·2; N, 3·7%; *M*, 754]. The solubility properties were similar to those of the bromide.

Bis(pentafluorophenyl)-1,10-*phenanthrolinethallium*(III) *nitrate*. From a similar preparation in ethanol, the *nitrate* crystallised as fine white needles in 68% yield, m. p. 219—220° [Found: C, 37·0; H, 1·15; F, 24·4; N, 5·3%; *M* (in acetone), 768 (1·08%), *M* (in chloroform), *ca.* 720 (0·32%). $C_{24}H_8F_{10}N_3O_3Tl$ requires C, 36·9; H, 1·0; F, 24·3; N, 5·3%; *M*, 780]. The compound was readily soluble in acetone and methanol, and less soluble in ethanol and chloroform.

Bis(pentafluorophenyl)-2,2′-*bipyridylthallium*(III) *nitrate*. From a similar preparation in methanol the compound crystallised as white needles in 76% yield, m. p. 204—205·5° [Found: C, 35·3; H, 1·5; F, 25·3; N, 6·1%; *M* (in acetone), 714 (1·39%). $C_{22}H_8F_{10}N_3O_3Tl$ requires C, 34·9; H, 1·1; F, 25·1; N, 5·55%; *M*, 757]. The infrared spectrum of the product showed a strong band at 3493 cm.$^{-1}$ due to bonded OH and weak bands due to aliphatic C–H stretching, hence the compound contained some methanol. The analyses were not informative in deciding the methanol content {$C_{23}H_{12}F_{10}O_4N_3Tl[(R_f)_2bipyTlNO_3,MeOH]$ requires C, 35·0; H, 1·5; F, 24·1; N, 5·3%}, as the figures favour a methanol-free formulation. The methanol was not removed on prolonged heating at 100°, but the solvent-free compound was obtained as very fine white needles, m. p. 202—204° [Found: C, 34·2; H, 0·9; F, 24·8; N, 5·5%; *M* (in acetone), 690 (1·08%)] on heating the solvate for 3 hr. at 120° *in vacuo* over phosphorus pentoxide. The compound was soluble in acetone, less soluble in methanol, sparingly soluble in ethanol, and insoluble in benzene.

Tetraphenylphosphonium bis(pentafluorophenyl)dichlorothallate(III). Bis(pentafluorophenyl)thallium chloride (0·29 g., 0·50 mmole) and tetraphenylphosphonium chloride (0·19 g., *ca.*

0·50 mmole—the infrared spectrum of the compound showed it to be hydrated) were dissolved in methanol, and a glue was obtained on evaporation to dryness. This slowly crystallised on addition of ether, giving the required compound as small white rods, which were washed with ether, and dried at 60°; they then had m. p. 100—101° (yield 0·31 g., 68%) [Found: C, 45·8; H, 1·7; Cl, 7·9; F, 20·5; P, 3·3%; *M* (in acetone), 599 (2·06%), 559 (1·09%), 534 (0·62%), *M* (in benzene), 1570 (1·13%). $C_{36}H_{20}Cl_2F_{10}PTl$ requires C, 45·5; H, 2·1; Cl, 7·5; F, 20·0; P, 3·3%; *M*, 948]. The compound was soluble in acetone, ethanol, methanol, and benzene, moderately soluble in ether, and insoluble in petroleum.

Tetraphenylphosphonium bis(pentafluorophenyl)dibromothallate(III). Bis(pentafluorophenyl)thallium bromide (0·31 g., 0·50 mmole) and tetraphenylphosphonium bromide hydrate (*ca.* $2H_2O$)[31] (0·24 g., *ca.* 0·50 mmole) were heated in ether (50 ml.). After filtration to remove a little unchanged phosphonium salt, the required compound was precipitated as white microcrystals on the addition of petroleum, and when dried at 60° had m. p. 101·5—102° (yield 0·32 g., 61%) [Found: C, 41·6; H, 1·9; Br, 15·4; F, 18·5; P, 3·1%; *M* (in acetone), 546 (0·54%), *M* (in benzene), 2440 (1·87%), 1930 (1·28%). $C_{36}H_{20}Br_2F_{10}PTl$ requires C, 41·7; H, 1·9; Br, 15·4; F, 18·3; P, 3·0%; *M*, 1037]. The compound had an identical *X*-ray powder photograph, and similar solubility properties to those of tetraphenylphosphonium bis(pentafluorophenyl)dichlorothallate; the bromo-compound was more soluble in ether. The positions of the infrared absorption bands due to the tetraphenylphosphonium ion in the spectra of both compounds (2000—200 cm.$^{-1}$) showed good agreement with the reported data for this ion (2000—400 cm.$^{-1}$)[31] and with a spectrum (400—200 cm.$^{-1}$) of tetraphenylphosphonium iodide.

Tetraethylammonium bis(pentafluorophenyl)dichlorothallate(III). This was prepared in a similar manner but was isolated by slow evaporation to dryness. Recrystallisation from acetone–di-isopropyl ether gave small white rods, which were dried at 50°, and then had m. p. 81—82° (yield 43%) [Found: C, 31·4; H, 2·2; Cl, 10·0; F, 25·0; N, 1·9%; *M* (in acetone), 412 (0·50%). $C_{20}H_{20}F_{10}Cl_2NTl$ requires C, 32·5; H, 2·7; Cl, 9·6; F, 25·1; N, 1·9%; *M*, 739]. The solubility properties were similar to those of the preceding compound. The positions of the absorption bands due to the tetraethylammonium ion in the infrared spectrum (2000—200 cm.$^{-1}$) showed satisfactory agreement with those of a spectrum of tetraethylammonium iodide.

Bis(pentafluorophenyl)dipyridinethallium(III) *bromide*. Bis(pentafluorophenyl)thallium bromide (0·25 g., 0·40 mmole) was dissolved in pyridine (4 ml.). Ether was added, and, after filtration, the solution was evaporated to dryness. Cream microcrystals were obtained on addition of petroleum and were filtered off, washed with petroleum, and dried at 50°; they had m. p. 92—93° (yield 0·07 g., 22%) [Found: C, 33·1; H, 1·2; F, 24·9; Br, 12·4; N, 3·7%; *M* (in benzene), *ca.* 667 (1·09%). $C_{22}H_{10}F_{10}BrN_2Tl$ requires C, 34·0; H, 1·3; F, 24·5; Br, 10·0; N, 3·5%; *M*, 776]. Further crystals were obtained on evaporation of the petroleum filtrate and washings. The compound was slightly unstable, smelling of the free ligand. The molecular weight could not be measured accurately in benzene, as the solutions did not quickly equilibrate in the osmometer. The molecular weight in acetone could not be obtained due to failure of the solutions to equilibrate in reasonable time. Probably loss of pyridine occurred in both solvents. The compound was soluble in ether, benzene, pyridine, acetone, methanol, and ethanol The apparent solubility in petroleum may have been due to the presence of an excess of ligand.

Other Preparations Studied.—Bis(pentafluorophenyl)thallium perchlorate. From the reaction between silver perchlorate and $(R_f)_2TlBr$ in aqueous acetone, white crystals were isolated, presumably $(R_f)_2TlClO_4$, which, after repeated washing with benzene to remove traces of silver perchlorate, were hygroscopic and were not studied further.

Bis(pentafluorophenyl)thallium iodide. An attempt to prepare this compound was unsuccessful. Reaction of the bromide with sodium iodide in acetone did not give a precipitate of silver bromide, a yellow colloidal suspension being obtained. The failure of this reaction is understandable in view of the successful preparation of $(R_f)_2TlX_2^-$ complexes, and $(R_f)_2TlBrI^-$ was probably formed.

Bis(pentafluorophenyl)-o-*phenylenebisdimethylarsinethallium bromide*. A solution of bis(pentafluorophenyl)thallium bromide (0·62 g., 1·00 mmole) and an excess of *o*-phenylenebisdimethylarsine (diarsine) (0·3 ml., *ca.* 1·5 mmole) in ether (20 ml.) was evaporated to small volume and crystals were obtained on addition of petroleum. Recrystallised from ether–petroleum, the required compound was obtained as cream microcrystals, m. p. *ca.* 136° [Found: C, 26·8; H, 1·15; As, 16·6; Br, 8·9; F, 21·4%; *M* (in acetone), 650 (3·06%), 632 (1·76%).

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[31] Deacon, Jones, and Rogasch, *Austral. J. Chem.*, 1963, **16**, 360.

$C_{22}H_{16}As_2BrF_{10}Tl$ requires C, 29·2; H, 1·8; As, 16·6; Br, 8·8; F, 21·0%; *M*, 904]. The products from subsequent attempts to repeat this preparation gave unsatisfactory analyses though the infrared spectra resembled that of the original product. Thus the conditions of formation are not yet understood. The molar conductance in acetone, *ca.* 16 for a *ca.* 10^{-3}M-solution, is not indicative of sufficient dissociation to explain the low molecular weights in this solvent. In methanol, Λ_m (*ca.* 10^{-3}M) is *ca.* 5. The analogous complex of dimethylthallium nitrate could not be prepared. Crystallisation from a solution of the nitrate and diarsine in methanol gave the unchanged nitrate. A complex was probably formed in solution, as the solubility of the nitrate was increased by the presence of the ligand.

Bis(pentafluorophenyl)-2,2′-bipyridylthallium fluoride. Reaction of the stoicheiometric amounts of $(R_f)_2TlF$ and bipyridyl in methanol and evaporation to dryness gave crystals, which on crystallisation from benzene–hexane had m. p. 219—229° (decomp.). The analyses did not conform to those expected for $(R_f)_2$bipyTlF, nor was an alternative stoicheiometry suggested. The infrared spectrum was similar to those of authentic $(R_f)_2$bipyTlX complexes with respect to $(R_f)_2Tl$ and bipy bands, but showed in addition a very strong band at 340 cm.$^{-1}$, probably indicative of Tl–F bonding [cf. 318 cm.$^{-1}$ in $(R_f)_2TlF$].

Dimethylthallium bis(pentafluorophenyl)dichlorothallate. The aim was to prepare a less-soluble derivative than the tetraphenylphosphonium or tetraethylammonium analogues. On addition of the stoicheiometric amount of $(R_f)_2TlCl$ to a suspension of dimethylthallium chloride in methanol, complete solution was achieved, but evaporation to crystallisation gave dimethylthallium chloride. Complex formation undoubtedly occurred in solution, but the stability of the complex was not sufficient to outweigh the lattice energy of dimethylthallium chloride.

The Reaction between Bis(pentafluorophenyl)-1,10-phenanthrolinethallium Bromide and Bis(pentafluorophenyl)thallium Bromide.—The specific conductivities of mixed solutions of $(R_f)_2$-*o*-phenTlBr and $(R_f)_2TlBr$ in acetone, and the expected values if no reaction occurred are given in Table 7.

TABLE 7

$(R_f)_2$-*o*-phenTlBr Concn. (10^3M)	$(R_f)_2TlBr$ Concn. (10^3M)	Conductivity (10^6Ksp. Calc.) *	Conductivity (10^6Ksp. Found)
1·78	3·70	11·6	114
2·83	13·6	26·5	216

* Assuming conductivities of the reactants are additive.

Group Exchange Reactions.—(a) *Between bis(pentafluorophenyl)thallium bromide and sodium tetraphenylborate.* When an ethanol solution (40 ml.) containing $(R_f)_2TlBr$ (0·62 g., 1·00 mmole) and sodium tetraphenylborate (0·17 g., 0·50 mmole) was heated under reflux for 2 hr., a white precipitate slowly formed. This was filtered off and identified as diphenylthallium bromide by infrared spectroscopy (yield 0·32 g., 73%). On evaporation of the filtrate more diphenylthallium bromide was deposited. Decomposition also occurred preventing isolation of the other product.

A similar reaction was observed between sodium tetraphenylborate and $(R_f)_2TlNO_3$ in aqueous ethanol. The precipitated product [Found: C, 35·0; H, 2·8; F, 0·0; N, 4·3. Calc. for $C_{12}H_{10}NO_3Tl(Ph_2TlNO_3)$: C, 34·3; H, 2·4; N, 3·3%] had an infrared spectrum similar to that of authentic diphenylthallium nitrate. Similarly when aqueous solutions of $[(R_f)_2Tl]_2SO_4$ and sodium tetraphenylborate (1 : 1 mole scale) were mixed, a white precipitate slowly formed. The product was identified as $(Ph_2Tl)_2SO_4$ (infrared spectra).

(b) *Between bis(pentafluorophenyl)thallium bromide and triphenylbismuth.* When an ether solution (40 ml.) containing triphenylbismuth (0·29 g., 0·67 mmole) and $(R_f)_2TlBr$ (0·62 g., 1·00 mmole) was heated under reflux for 2 hr., slow precipitation of a pale yellow solid occurred. This was filtered off, and identified as diphenylthallium bromide (infrared spectra). The yellow pyridine-insoluble material, also present in the product, was not further studied. More diphenylthallium bromide deposited from the ethereal filtrate. No other product could be isolated. However, subsequent attempts to prepare the expected tris(pentafluorophenyl)-bismuth, by a different route suggest that the compound decomposes on exposure to the atmosphere.[32]

(c) *Between bis(pentafluorophenyl)thallium bromide and diphenylmercury.* When an ether solution (20 ml.) containing diphenylmercury (0·18 g., 0·50 mmole) and $(R_f)_2TlBr$ (0·31 g.,

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[32] Deacon, Longstaff, Jordan, and Nyholm, unpublished results, 1964.

0·50 mmole) was heated under reflux, a pale yellow precipitate slowly formed. After evaporation to dryness, the residue was extracted with ether, and the procedure was repeated. The insoluble fraction (0·10 g., 45%) was identified as Ph_2TlBr (infrared spectra). After evaporation of the third ether extract, the residue was extracted with petroleum, on removal of which a mixture of bis(pentafluorophenyl)mercury [33] and phenylpentafluorophenylmercury [33] was obtained, m. p. *ca.* 120° (aqueous methanol) (Found: C, 30·7; H, 0·6; F, 29·9; Hg, 38·9. Calc. for $C_{12}F_{10}Hg$: C, 26·9; F, 35·5; Hg, 37·5. Calc. for $C_{12}H_5F_5Hg$: C, 32·4; H, 1·1; F, 21·4; Hg, 45·1%). The composition of the product was confirmed by the infrared spectrum. Sublimation of the product *in vacuo* failed to separate the components.

Dimethylthallium(III) *Compounds*.—A sample of dimethylthallium chloride was provided by Dr. C. Hart of this Department. From this compound the corresponding nitrate and acetate were prepared by the reported method,[34] and were obtained analytically pure on recrystallisation.

Diphenylthallium(III) *Compounds*.—Samples of diphenylthallium bromide and nitrate were provided by Dr. D. Evans of Imperial College.

Analyses.—Thallium was estimated gravimetrically as thallous chromate,[35] or volumetrically, after conversion into the thallous state,[28] by titration with potassium iodate, Andrew's conditions [36] being used. Ionisable halogen was determined by titrating $(R_f)_2TlHal$ in acetone with 0·01M-aqueous silver nitrate, adsorption indicators being used. Microanalyses were by Dr. A. Bernhardt, Mülheim, Germany.

Conductivity Measurements.—Conductivities were measured at *ca.* 20° with a Wayne-Kerr model B221 conductance bridge, using a cell of standard design fitted with bright platinum electrodes. The cell constant was determined with M/1000 aqueous potassium chloride. AnalaR solvents were used. Except where stated otherwise (Table 2), measurements were made within 3 min. of preparing the solutions. The conductivities were steady except for compounds mentioned in Table 2, and for aqueous $[(R_f)_2Tl]_2SO_4$ for which a slight decrease was observed, which was probably due to the slight cloudiness of the solutions (see earlier). It was shown that the time dependence of the conductivities of $(R_f)_2TlBr$ in acetone was not due to electrode phenomena, by using solutions which had been kept without previous contact with the electrodes.

Infrared Spectra.—Spectra were taken of mulls (Nujol, hexachlorobutadiene, and Fluorolube) between potassium bromide and polythene plates, Grubb–Parsons GS2A and DM2 instruments being used. The spectra of solutions between potassium bromide plates (path length: 50 μ) and in potassium chloride discs were recorded with a Unicam S.P. 100/130 spectrophotometer. Because of the possibility of group exchange between co-ordinated anions and the plates,[8] the spectra of nitrates, trifluoroacetates, $(R_f)_2Tl(OAc)$, and $[(R_f)_2Tl]_2SO_4$ were also measured by using plates covered by polystyrene film. Interaction with the plates was found only with $(R_f)_2$(bipy or *o*-phen)$TlNO_3$. With the *o*-phen compound in hexachlorobutadiene, plate attack occurred despite the protective film (possibly the compound is slightly soluble in hexachlorobutadiene), and Fluorolube had to be used. The spectra of the sulphate in mulls and in a disc (Table 5) indicate that group exchange with potassium chloride does not occur on disc formation. The spectrum of $(R_f)_2Tl(OAc)$ in a disc showed good agreement with values obtained for mulls (Table 4). However exchange occurred between dimethylthallium acetate and potassium chloride on disc preparation, shown by the shift of ν (antisym $-CO_2^-$) from 1541 (mull) to 1575 (disc) (cf. 1582 for sodium acetate).[9] Group exchange also occurred during attempts to obtain spectra of solutions. With $(R_f)_2TlNO_3$ the formation of potassium nitrate on the plates was detectable after contact of *ca.* 15 min. between solution and the plates. When the spectrum of $(R_f)_2$bipyTl(OAc_f) was measured in chloroform, exchange with the plates was too rapid for a meaningful spectrum to be obtained.

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