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DERIVATIVES OF PHENYLTHALLIUM(III)
I. THE PREPARATION AND PROPERTIES OF PHENYLTHALLIUM(III) COMPOUNDS

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SUMMARY

The infra-red spectra and conductances of a number of derivatives of the type $PhTlX_2$ are reported. Whereas the phenylthallium dihalides are probably monomeric in the solid state, the carboxylates are polymeric. A number of complexes $PhTlX_2L$ have been prepared, where L is both a unidentate and a bidentate ligand. Properties of $[R_4N][PhTlCl_3]$ and $[R_4N]_2[PhTlCl_4]$ are reported. The NMR spectra of phenylthallium(III) derivatives are discussed.

INTRODUCTION

Although the first phenylthallium(III) derivatives were prepared as long ago as 1930[1,2] little is known about the structures of these derivatives. $PhTlCl_2$ was prepared by the reaction between phenylboronic acid and excess thallic chloride[1]:

$$PhB(OH)_2 + TlCl_3 + H_2O \rightarrow PhTlCl_2 + B(OH)_3 + HCl$$

$PhTlBr_2$ was prepared similarly from $TlBr_3$, but $PhTlI_2$ is unknown. Addition of KI to either the dichloride or dibromide resulted in the rapid formation of iodobenzene. Reaction of $PhTlCl_2$ with the appropriate alkali metal salt produces $PhTl(CN)_2$, $PhTl(CNS)_2$, $PhTl(N_3)_2$ and $PhTl(OH)_2$[2]. Phenylthallium dicarboxylates have been prepared by the reaction of thallium(III) carboxylates and diphenylmercury[3,4] and by reaction of thallium(III) triisobutyrate[5] and tris(trifluoroacetate)[6] with benzene:

$$Ph_2Hg + (RCOO)_3Tl \rightarrow PhHgOOCR + PhTl(OOCR)_2$$
$$C_6H_6 + (RCOO)_3Tl \rightarrow PhTl(OOCR)_2 + RCOOH$$

The compound phenylthallium dioxinate has been prepared and postulated to contain penta-coordinate thallium[7].

The complexes $[Me_4N][PhTlCl_3]$, $[Me_4N]_2[PhTlCl_4]$[8], $K[PhTl(CN)_3]$[2] and $[Ph_4As][PhTlX_3]$ ($X = Cl$, Br, I)[9] have been reported. Complexes (1/1) of $PhTlCl_2$ are known with pyridine[2], Ph_3P[10], and bis(acetylacetone)ethylene diimine[11].

Compounds of the type R_2TlX (R is alkyl or aryl, $X = Cl$, Br, I) are generally soluble only in very basic solvents such as pyridine or aqueous ammonia, and do not readily form coordination derivatives. Phenylthallium(III) derivatives, on the other hand, are readily soluble in many organic solvents and readily form complexes with suitable ligands.

RESULTS

Phenylthallium dichloride is most readily prepared by the reaction of phenyl boronic acid and excess thallium(III) chloride in aqueous solution[1]. Other phenylthallium(III) derivatives can be prepared from the dichloride by metathesis with silver or potassium salts, or by neutralization of $PhTl(OH)_2$ (from $PhTlCl_2$ and NaOH) with the appropriate acid. $PhTl(OOCCF_3)_2$ was prepared by the reaction of thallium(III) tris(trifluoroacetate) and benzene[6]. Complexes of $PhTlCl_2$ and $PhTl(OOCCF_3)_2$ were prepared by reaction of stoichiometric amounts of the reactants, except for $PhTl(Bipy)(OOCCF_3)_2$, where it was found best to use a large excess of bipyridine.

Conductances.

In Table 1 are given molar conductances of the compounds studied, in acetone and methanol. One-to-one electrolytes in acetone have molar conductivities ~150 at 10^{-3} *M* and in methanol, molar conductivities of ~100 at 10^{-3} *M*: the expected values for large ions, however, would be somewhat lower. In acetone, the compounds $PhTlX_2$ ($X = Cl$, $OOCCH_3$ and $OOCCF_3$) have very low conductances: the conductance of the chloride and trifluoroacetate increase slowly with time, suggesting

TABLE 1

MOLAR CONDUCTANCES OF PHENYLTHALLIUM(III) COMPOUNDS IN ACETONE AND METHANOL

Compound	Mol. cond. in acetone				Mol. cond. in methanol			
	Mol. cond.	Concn. (10^3 *M*)	Mol. cond.	Concn. (10^3 *M*)	Mol. cond.	Concn. (10^3 *M*)	Mol. cond.	Concn. (10^3 *M*)
$PhTlCl_2$	4.3	(1.16)	3.5[a] 4.5	(3.89)	35.7	(0.91)	20.6	(3.04)
$PhTl(OOCCH_3)_2$	24.5	(2.00)			16.9	(1.80)		
$PhTl(OOCCF_3)_2$	5.1	(1.26)	3.3[a] 5.1	(2.84)	54.0	(1.21)	44.7	(2.63)
$PhTl(OH)_2$					93.3	(2.15)		
$Ph(Bipy)TlCl_2$	21.8	(0.58)	18.7	(2.44)	45.2	(0.83)	19.9	(2.18)
$Ph(o\text{-}Phen)TlCl_2$	14.0	(0.75)	12.7	(1.22)	37.9	(0.42)	26.9	(1.20)
$Ph(Ph_3PO)TlCl_2$	19.1	(0.63)	16.4	(1.55)				
$Ph(Ph_3P)TlCl_2$	46.9[a] 50.5	(1.56)	35.0[a] 41.1	(3.93)				
$Ph(Py)TlCl_2$	5.2	(1.85)	5.1	(3.10)				
$Ph(o\text{-}Phen)Tl(OOCCF_3)_2$	6.6	(1.13)	6.5	(1.70)				
$[Me_4N][PhTlCl_3]$	120	(1.25)	106	(6.08)	98	(1.00)	68.6	(2.2)
$[Me_4N]_2[PhTlCl_4]$	Insoluble				183	(2.34)	139	(1.2)
$[Et_4N][PhTlCl_3]$	109	(0.58)	117	(3.20)				
$[Et_4N]_2[PhTlCl_4]$	160	(1.0)	148	(2.66)	130	(0.71)	112.8	(2.08)

[a] These conductances increased after 15 min to the second value shown.

a slow solvolysis of the Tl–X bond. The chlorine atom in $PhTlCl_2$ is ionisable, being completely removed when an acetone solution of $PhTlCl_2$ is titrated with silver acetate.

In methanol, the chloride and acetate are partially ionised, and the trifluoroacetate is virtually a 1/1 electrolyte.

The pyridine, bipyridine and phenanthroline complexes are very weak electrolytes in acetone solvent; they ionise significantly, however, in methanol. The compounds $[R_4N][PhTlCl_3]$ and $[R_4N]_2[PhTlCl_4]$ are 1/1 and 2/1 electrolytes respectively.

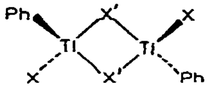
Mixtures of Ph(*o*-Phen)$TlCl_2$ and $PhTlCl_2$ in acetone have about the conductances expected if the components were additive, so that reaction analogous to that observed for (perfluorophenyl)thallium derivatives[12] cannot occur:

$$(C_6F_5)_2(o\text{-Phen})TlBr + (C_6F_5)_2TlBr \rightarrow (C_6F_5)_2(o\text{-Phen})Tl^+ + (C_6F_5)TlBr_2^-$$

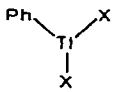
Infrared spectra

A close correspondence is to be expected between the spectra of phenylthallium(III) compounds and that of iodobenzene, which has been assigned in detail[13]. The infrared spectra of $PhTlF_2$, $PhTlCl_2$ and $PhTlBr_2$ are given in Table 2, together with the proposed interpretations. It is convenient to describe the phenyl modes in terms of C_{2v} symmetry of the ring; apart from the use of the preferred choice of axes[14], the notation of the fundamentals is that of Whiffen[13]. The frequencies have the expected similarity to those of diphenylthallium chloride[15] and the phenylmercury halides[16]. The assignments thus require little comment. Of the three X-sensitive (a_1) modes, q, r and t, all involving stretching of the C–Tl bond, the first two only are observed in the region down to 250 cm^{-1}. For iodobenzene, mode q obscures the b_2 β(CH) mode d in the infra-red spectrum: it seems likely that it does so also in the phenylthallium(III) halides. The infra-red spectrum of $PhTlCl_2$ in the region 400–20 cm^{-1} is more difficult to assign (Table 3): vibration frequencies may arise from modes of the Ph–Tl group, from Tl–X vibrations or lattice vibrations. For iodobenzene, the X-sensitive modes t (a_1), u (b_2) and x (b_1) occur at 266, 220 and 166 cm^{-1} respectively, and in PhHgCl they have been assigned at 220, 184 and 180 cm^{-1} respectively. For $PhTlCl_2$ analogous assignments can tentatively be made.

If $PhTlCl_2$ has the dimeric structure (I), the symmetry of the skeleton is C_{2h}. Assignments have been made for a number of dimeric species of D_{2h} symmetry:



(I)



(II)

Al_2Cl_6[17], Ga_2Cl_6[18,19], Ga_2Br_6[19] and Ga_2I_6[19]. The eighteen fundamental vibrations of the C_{2h} skeleton are related to those of the D_{2h} skeleton by the relationship:

TABLE 2

SPECTRA OF $PhTlX_2$
$X = F, Cl, Br, OH; X_2 = (OH)(NO_3)$.

$PhTlF_2$	$PhTlCl_2$	$PhTlBr_2$	$PhTl(OH)_2$	$PhTl(OH)(NO_3)$	Assignment
			3575 m	3520 m	ν(OH)
3060 m	3075 w	3075 w	3065 w	3075 w	ν(CH) a_1 and b_2
	3058 w	3050 w			
		3048 w			
	1958 vw	1948 w			$h+j$
1885 vw	1880 w	1875 w		1792 m	
				1765 m	
1580 w	1562 m	1572 w	1575 m	1570 w	ν(CC), $k(a_1)$
1560 w		1560 vw	1560 w	1560 w	ν(CC), $l(b_2)$
1482 m	1473 s	1480 s	1475 s	1470 sh	ν(CC), $m(a_1)$
1436 s	1439 vs	1435 vs	1433 s	1433 s	ν(CC), $n(b_2)$
				1400 sh	$\nu_3(E')(NO_3)$
				1380 vs	$\nu_3(E')(NO_3)$
	1331 w	1331 w			
1330 w	1312 w	1305 w	1308 w	1328 w	ν(CC), $o(b_2)$
1240 w	1263 w	1263 w	1263 w		β(CH), $e(b_2)$
1170 sh	1170 vw	1171 w	1175 sh		β(CH), $a(a_1)$
1155 m	1155 vw	1151 w	1155 m		β(CH), $c(b_2)$
	1066 vw	1072 w	1078 w		β(CH), $d(b_2)$
		1067 w	1070 sh		X-sens, $q(a_1)$
				1035 sh	$\nu_1(A')(NO_3)$
1022 m	1017 m	1022 m	1022 m	1018 m	β(CH), $b(a_1)$
1001 m	996 s	1001 m	1001 m	995 m	Ring mode, $p(a_1)$
975 w,b	975 vw	975 w,b	975 w,b	980 w	γ(CH), $j(b_1)$
					γ(CH), $h(a_2)$
918 w		910 w		900 w	γ(CH), $i(b_1)$
845 w	857 w	860 w		855 w	γ(CH), $g(a_2)$
				840 sh	$\nu_2(A_2'')(NO_3)$
				829 s	
770 sh	805 vw		765 w	806 w	
				739 s	$\nu_4(E')(NO_3)$
730 vs	730 vs	737 vs	730 vs	732 s	γ(CH), $f(b_1)$
		729 s			
			698 vs		Tl–O–H deform.
692 s	680 vs	690 vs	690 sh	680 s	ϕ(CC), $v(b_1)$
670 sh	672 sh				X-sens, $r(a_1)$
	655 m				
	610 w	620 w	620 w	620 w	α(CCC), $s(b_2)$
			550 w,br	570 sh	Tl–O mode, deform.?
				560 m	
525 w					Tl–F stretch?
500 m					
480 m					
459 m	442 s	461 s	460 s	461 m	X-sens. $y(b_1)$
				442 m	
	342 m				Tl–Cl stretch
	335 m				

TABLE 3

INFRA-RED SPECTRUM OF $PhTlCl_2$ FROM 350 TO 20 cm^{-1}

Peak	Assignment	Peak	Assignment
~342 sh	Tl–Cl stretch	135 sh (?)	
335 s		130 s	
210 sh	*t* X-sens. (a_1)	125 sh	
190 sh (?)		53 w	Lattice modes?
174 sh	*u* X-sens. (b_2)	46 s	
160 s	*x* X-sens. (b_1)	27 m	

where the numbering of the vibrations for the A_2B_6 skeleton is that used by Nakamoto[20]. The infra-red active modes for the C_{2h} structure (a_u and b_u) are thus derived from ν_5, ν_8, ν_9, ν_{10}, ν_{13}, ν_{14}, ν_{16}, ν_{17} and ν_{18} of the D_{2h} case. The ν_{13} vibration is a stretching of the bridging bonds, whereas ν_8 and ν_{16} are stretchings of the terminal bonds: ν_{17} involves stretching of the bridging bonds, but is a more complex vibration. Thus for the $PhTlCl_2$ dimer there should be one bridging Tl–Cl stretch and one terminal Tl–Cl stretch, the terminal stretch probably being at higher frequency than the bridging. For Ga_2Cl_6, the terminal Ga–Cl stretches ν_8 and ν_{16} have been assigned at 420 and 394 cm^{-1} respectively, and the ν_{13} bridging Ga–Cl stretch at 365 cm^{-1}. In the $(C_6F_5)_2TlCl$ dimer, bands at 215 and 130 cm^{-1} have been associated with the bridging Tl–Cl stretches[21]. If $PhTlCl_2$ has a monomeric structure (II), the skeleton has C_{2v} symmetry, and would have a symmetric and antisymmetric Tl–Cl stretch, and three modes involving Tl–Cl bending. If the $CTlX_2$ skeleton is non-planar (C_s symmetry) then there would be the same number of Tl–Cl stretches. The presence of two bands at 342 and 335 cm^{-1}, in the region that can be associated with Tl–Cl terminal stretches, suggests that the compound is probably monomeric in the solid state with a structure (II). This is consistent with the fact that the spectrum of a concentrated solution of $PhTlCl_2$ in methanol (in which $PhTlCl_2$ is monomeric[8]) shows weak features at 330 and 325 cm^{-1}. A more detailed infra-red and Raman study will be published later.

Bands that can be assigned to Tl–Cl stretches above 250 cm^{-1} in various complexes are given in Table 4. Metal–halogen stretching vibrations are expected to move to lower frequency with increasing coordination number of the metal[22].

Assignments for the carboxylate absorption bands in phenylthallium diacetate, bis(trifluoroacetate) and diisobutyrate (Table 5) were made using the reported spectra of sodium acetate[24], sodium trifluoroacetate[25,26] and isobutyric acid[27]. In Table 1 assignments of bands due to the nitrate group in $PhTlOHNO_3$ are given. These were made using the reported assignments for ionic and co-ordinated nitrate groups and for other organothallium nitrates[12]. The sulphate bands of $PhTlSO_4$ are given in Table 6: because the compound is hygroscopic, the spectra obtained may not correspond to a very pure sample.

In the spectrum of $Ph(Bipy)TlCl_2$, bands at 1605, 1592, 1579, 1561, 1490, 1435, 1311, 1251, 1160, 785, 778, 745, 660, 635 and 425 cm^{-1} due to bipyridine could be distinguished from the PhTl absorption. In the trifluoroacetate, absorption due to the $OOCCF_3$ groups obscured some of the bipyridine bands. Bands due to *o*-phenanthroline were found at 1630, 1595, 1570, 1520, 1420, 1349, 1229, 1104, 1094, 865, 855,

TABLE 4

POSSIBLE Tl–Cl STRETCHING FREQUENCIES OF $PhTlCl_2$ COMPLEXES ABOVE 250 cm^{-1}

$PhTlCl_2$	$[Me_4N][PhTlCl_3]$	$[Me_4N]_2[PhTlCl_4]$	Ph(*o*-Phen)$TlCl_2$
~342 sh	305 s	275 sh	285 s,b
335 s	295 sh ?	270 s	
	282 s	260 ?	
Ph(Bipy)$TlCl_2$	**Ph(Py)$TlCl_2$**	**Ph(Ph_3P)$TlCl_2$**	**Ph(Ph_3PO)$TlCl_2$[b]**
295 m	>250[a]	270 m	318 m
		~250	305 m
			~300 sh
			295 sh
			282 m

[a] Continuously falling absorption at 250 cm^{-1}. [b] Ligand and Tl–Cl stretches.

TABLE 5

CARBOXYLATE ABSORPTION BANDS (IN cm^{-1}) OF SOME PHENYLTHALLIUM(III) COMPOUNDS

$PhTl(OOCCH_3)_2$	$PhTl[OOCCH(CH_3)_2]_2$	$PhTl(OOCCF_3)_2$	Ph(*o*-Phen)$Tl(OOCCF_3)_2$	Assignment
1595 s[a]	1605 s	1680 vs	1670 sh	$\nu_{asym}(CO_2)$
1520 s[a]	1505 s	1620 vs	1650 ?	
1445 sh	1430 m			CH_3 asym. def.
1405 m[a]	1410 s	1475 s	1433 s	$\nu_{sym}(CO_2)$
1375 s[a]	1380 s	1415 s		
1325 s	1365 m			CH_3 sym. def.
		1210–1150 vs, b	1235 sh	C–F stretch
			1210 s	
			1180 s	
			1165 s	
			1140 s	
1052 m	1170 m			CH_3 rock
1025 sh	1100 m			
951 m	932 s	870 s	872 m	ν(C–C)
940 m		860 sh	858 sh	
		798 s	845 sh	
739 s[b]	860 s	790 s	803 s	
701 s	765 s	740 sh	738 sh	δ(OCO)
695 s		725 s	725 s[b]	
622 m	630 s			CO_2 wag (out-of-plane)
		602 m	610 w, b	CF_3 def. in phase
		525 m	525 m, b	CF_3 def. out of phase
	540 m			
452 m				CO_2 rock
		425 w	425 w	CF_3 rock

[a] These frequencies agree well with ref. 23. [b] Bands obscured by absorption of other groups.

TABLE 6

SULPHATE BANDS (IN cm^{-1}) OF $PhTlSO_4$

Obtained using Nujol and hexachlorobutadiene mulls.

1175 m	1155 sh	1062 m	610 s	585 s	565 s	450 m

780 and 425 cm^{-1}, in the compound Ph(*o*-Phen)$TlCl_2$. The splitting of the bands in the 1600 and 860 cm^{-1} regions in the bipyridyl and *o*-phenanthroline derivatives respectively, are typical of the coordinated ligand[28]. In the spectrum of Ph(Py)$TlCl_2$, bands at 1610, 1492, 1454, 1245, 1222, 1179, 1142, 1041, 945 (?), 759, and 430 cm^{-1} can be assigned to pyridine.

Bands due to triphenylphosphine oxide in the spectrum of $Ph(Ph_3PO)TlCl_2$ are given in Table 7. Assignments were made by comparison with the spectra of $(C_6F_5)_2Tl(Ph_3PO)Cl_2$ and other complexes[29,30]. The low frequency of the ν(P=O) absorption is consistent with coordination. The band at 405 cm^{-1} may well be associated with the X-sensitive mode *t* of Ph_3PO[30], as it seems to be at too high a

TABLE 7

INFRA-RED SPECTRA OF Ph_3P AND Ph_3PO COMPLEXES OF $PhTlCl_2$

$Ph(Ph_3P)TlCl_2$	$Ph(Ph_3PO)TlCl_2$	Assignment
1588 w	1591 w	ν(CC), $k(a_1)$
1570 w	1580 vw	ν(CC), $l(b_2)$
1485 m	1488 m	ν(CC), $n(b_2)$
1439 s[a]	~1439 s[a]	ν(CC), $n(b_2)$
1330 m	1340 vw	ν(CC), $o(b_2)$
	1319 w	$w+i$ (B_2)
1187 m	1185 sh	β(CH), $a(a_1)$
	1171 vs	P=O stretch
1163 m	1159 s	β(CH), $c(b_2)$
1102 s	1122 vs	X-sens. $q(a_1)$
	1095 m	2 $y(A_1)$
1065 w	1074 m	β(CH), $d(b_2)$
1030 m	1031 m	β(CH), $b(a_1)$
998 m[a]	Obscured	Ring mode $p(a_1)$
983 sh	980 w	γ(CH), $h(a_2)$
851 w 845 w	~858 w[a]	γ(CH), $g(a_2)$
759 s	758 m	γ(CH), $f(b_1)$
752 s	745 sh	
748 s	740 s	
719 vs	Obscured	X-sens. $r(a_1)$
695 sh	702 sh	ϕ(CC), $v(b_1)$
690 s	693 s	
	617 vw	α(CCC), $s(b_2)$
521 vs	545 vs	X-sens. $y(b_1)$
502 vs	539 vs	
	512 w	
Obscured	Obscured	X-sens. $t(a_1)$
	405 w	

[a] Partially obscured by a Ph–Tl mode.

frequency to be a Tl–O stretch. The assignment of the Ph_3P modes in $Ph(Ph_3P)TlCl_2$ again follows those of Deacon and Green. As in a variety of other Ph_3P complexes, the *q* and *r* X-sensitive modes are shifted to higher frequency on complexing (being at 1089, 698 and 602 in the free ligand): the *t*, X-sensitive mode is obscured by a Ph–Tl mode.

NMR spectra

The NMR spectra of phenylthallium(III) derivatives can be treated as 1st order, the coupling of the two thallium isotopes, both of spin $I=\frac{1}{2}$, with the *ortho*-, *para*- and *meta*-protons of the phenyl ring being large. The magnetogyric ratios of the two isotopes are very similar, so that separate ^{203}Tl–H and ^{205}Tl–H couplings are not seen. The NMR spectrum of a solution of phenylthallium(III) perchlorate in D_2O has been reported[31], and the relative signs of the coupling constants measured. Because of the uniform increase in the magnitude of the coupling constants in the series Ph_3Tl, Ph_2Tl^+ and $PhTl^{2+}$, it has been assumed that the Fermi contact term determined the Tl–H coupling constant: there is an increase in both the *s*-character of the Tl–C bond and in the effective nuclear charge z_{eff} of the thallium atom along the series. Both $PhTlCl_2$ and $PhTl(OOCCF_3)_2$ are only partially ionised in methanol solution, whereas phenylthallium(III) perchlorate in D_2O can be assumed to approach $[PhTl(D_2O)_x]^{2+}[ClO_4^-]_2$, so that there will be less *s* character to the Tl–C bonds for the former compounds, and the coupling constant is less. Similarly, for $PhTlCl_2$ in pyridine, where presumably it is strongly solvated (the compound Ph(Py)-$TlCl_2$ can be isolated from solution), the coupling constants are less than in methanol. However, before any detailed explanation of these results is possible, the signs of the coupling constants must be determined: for derivatives of dimethylthallium(III) it has been found that the signs of the Tl–H coupling constants in (Me_2TlOEt) and $(Me_2TlOEt)_2$ are opposite, and no simple explanation of the Tl–H coupling constants is possible on the basis of the Fermi contact term alone[32].

TABLE 8

Tl–H COUPLING CONSTANTS IN PHENYLTHALLIUM(III) DERIVATIVES

Values are for satured solutions at room temperature.

	$PhTl^{2+}$ in D_2O	$PhTlCl_2$ in MeOH	$PhTlCl_2$ in C_5H_5N	$PhTl(OOCCF_3)_2$ in MeOH
ortho	+948	850	812	670
para	+365	323	306	270
meta	+123	110	105.5	80

Mass spectra

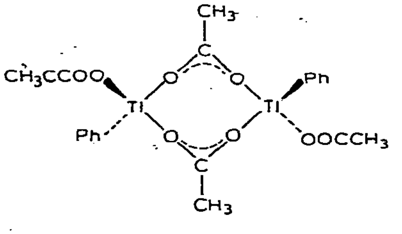
The mass spectra of phenylthallium(III) derivatives are not informative. Thus in the spectrum of $PhTlCl_2$, peaks are observed due to Tl^+, $TlCl^+$, $TlPh^+$, $TlPhCl^+$ and Ph_2Tl^+; no $PhTlCl_2^+$ or $TlCl_2^+$ peaks were observed, and it seems likely that the $PhTlCl_2$ decomposed at the inlet temperature of ~150°.

DISCUSSION

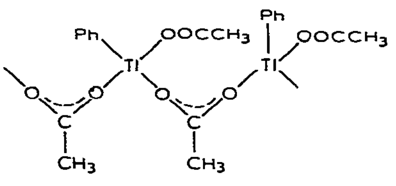
Phenylthallium dichloride is monomeric in MeOH solution[8] and may well be monomeric in the solid state: it is clearly not ionic, however, as Tl–Cl stretches have been recognized. In acetone solution, it is a non-electrolyte. Dimethylthallium chloride adopts a NaCl lattice structure in the solid, and is insoluble in non-polar organic solvents: in the vapour phase, however, dimeric species are present[33]. Both $(C_6F_5)TlCl$ and $(C_6F_5)_2TlBr$ are dimeric in benzene solution, and on the basis of infra-red data, in the solid phase[12]. Phenylthallium dibromide is only slightly soluble in methanol, and the conductivity in that solvent shows that considerable ionisation has occured. No Tl–Br stretch could be detected above 250 cm^{-1}. The location of a Tl–F stretching frequency (Table 1) for $PhTlF_2$ precludes an ionic structure, but monomeric and dimeric species cannot be differentiated on the basis of the present data.

In the phenylthallium(III) carboxylates, there are clearly more than one type of carboxylate group present. Co-ordination of acetate through one oxygen atom shifts $\nu_{asym}(CO_2)$ to higher and $\nu_{sym}(CO_2)$ to lower frequencies than in the free acetate ion, leading to a greater separation between these frequencies[20]. The remaining possibilities (ionic, bidentate or bridging acetate) cannot be distinguished on the basis of infra-red data alone.

In $(C_6F_5)_2TlOOCCH_3$, $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ occur at 1546 (or less) and 1408 cm^{-1} respectively, and the compound has been postulated to be dimeric with bridging acetate groups[12]. If then the bands at 1520 and 1405 cm^{-1} in $PhTl(OOCCH_3)_2$ are assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ respectively of a bridging acetate group, then the bands at 1595 and 1375 cm^{-1} can be assigned to non-bridging acetate groups. The asym. CO_2 stretch is now at higher frequency than that in sodium acetate (1578 cm^{-1}) and the sym. CO_2 stretch is at lower frequency (1414 cm^{-1}) so that the non-bridging acetate groups are probably monodentate, and the simplest structures likely are either the dimer (III) or the polymer (IV). Phenylthallium diacetate is only partially ionised in acetone solution.



(III)



(IV)

The bands at 1505 and 1410 cm^{-1} in the spectrum of phenylthallium diisobutyrate can be associated with $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ of a bridging isobutyrate group, since they occur at 1542 and 1408 cm^{-1} in the dimeric diethylthallium isobutyrate[34]. The separation of the other CO_2 modes is again large (225 cm^{-1}) and probably therefore the non-bridging isobutyrate groups are monodentate, as for the acetate. In methylthallium diisobutyrate, it was suggested that the terminal isobutyrate groups were chelating to give a penta-coordinate thallium[34]: $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ occurred at 1610 and 1390 cm^{-1} respectively, which are very similar to those observed for the phenylthallium(III) compound. In view of the results obtained for phenylthallium diacetate, chelating terminal carboxylate groups now seems rather unlikely.

In phenylthallium bis(trifluoroacetate) two types of carboxylate group are again present. In sodium trifluoroacetate, $\nu_{\text{asym}}(CO_2)$ is at 1680 cm^{-1}. In $PhTl(OOCCF_3)_2$ therefore, the 1680 cm^{-1} band could correspond to a largely ionic terminal $OOCCF_3$ group, and the 1620 cm^{-1} band to a bridging $OOCCF_3$ group, so that the structure is again similar to (III) or (IV), except that the terminal groups are only weakly bound: the compound is highly ionised in methanol, approaching a 1/1 electrolyte. In the complex of phenylthallium bis(trifluoroacetate) with *o*-phenanthroline, only one band could be seen due to $\nu_{\text{sym}}(CO_2)$ so that it is possible that all $OOCCF_3$ groups are equivalent: the compound is thus probably monomeric, with penta-coordinate thallium.

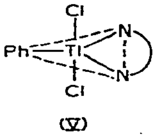
The infra-red spectrum of $PhTl(OH)_2$ (Table 1) clearly shows the presence of an OH group, but gives little other information. The bands at 698 and 550 cm^{-1} could be a Tl–O–H deformation: they are too high to be a Tl–O stretch. The fact that $PhTl(OH)_2$ is appreciably soluble in methanol suggest that the compound can only be partially ionic, and the conductivity in MeOH corresponds to a 1/1 electrolyte. Methylthallium diacetate and KOH react to form MeTlO, rather than $MeTl(OH)_2$[35].

A pure $PhTl(NO_3)_2$ has not been prepared. Both by the reaction of $PhTl(OH)_2$ with nitric acid and by the reaction of $PhTlCl_2$ with silver nitrate in aqueous solution[38], a basic nitrate $PhTl(OH)(NO_3)$ is obtained. The infra-red spectrum of this compound shows the presence of both OH and NO_3 groups. The splitting of the E' (ν_3) nitrate modes and the weak intensity of the infra-red forbidden A'_1 mode indicate that the site symmetry of the nitrate group is lowered from D_{3h} (the splitting of the ν_4 E' vibration may be obscured by the very strong band due to a phenyl fundamental at 732 cm^{-1}). These facts suggest that the nitrate group is coordinated to the thallium atom, and the band at 570 cm^{-1} could be associated with the $Tl–ONO_2$ bond.

A likely structure for $PhTlSO_4$ can be established by consideration of the sulphate absorption bands (Table 6). For a sulphate ion of T_d symmetry, bands would be expected at *ca.* 1100 and *ca.* 600 cm^{-1}, unidentate sulphate, of 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}. The number of sulphate bands observed for $PhTlSO_4$ indicates C_{2v} symmetry for the sulphate group (the band expected in the 990 cm^{-1} region may well be obscured by a Ph–Tl mode): the compound is hygroscopic and light sensitive.

The complexes of $PhTlX_2$

Absorption due to Tl–Cl stretching is found in the infra-red spectra of Ph(*o*-Phen)$TlCl_2$ and Ph(Bipy)$TlCl_2$ (Table 4), hence these compounds probably contain penta-coordinate thallium. If these complexes have a trigonal bipyramidal structure, then there are several possible isomers. The structure (V) seems most likely, as the



(V)

terminal positions are usually occupied by electronegative groups in this stereochemistry. The conductance data shows that some ionisation occurs in solution, and suggests that the *o*-phenanthroline complex is more stable than the bipyridine analogue in acetone, but that they are about equally stable in methanol. It is generally true that complexes of *o*-phenanthroline are more stable than the corresponding 2,2'-bipyridine complexes[36,37]. With $PhTl(OOCCF_3)_2$, the complex with one *o*-phenanthroline precipitates out on mixing methanol solutions of the reactants. To prepare the bipyridine complex however, a large excess of bipyridine is required (although the complex can be prepared from a 1/1 mixture in MeOH by very slow evaporation of solvent).

Vapour pressure measurements[8] suggest that $(Me_4N)(PhTlCl_3)$ and $(Me_4N)_2$- The infra-red spectrum shows Tl–Cl stretching modes. It is a non-electrolyte in acetone solution, and presumably contains tetrahedral thallium. The 1/1 complex between Ph_3P and $PhTlCl_2$ also probably contains tetra-coordinate thallium in the solid state, but in acetone solvent it is extensively ionised. The NMR spectrum of the complex in pyridine solvent shows that the complex has dissociated into Ph_3P and solvated $PhTlCl_2$. Because Ph_3PO has a number of modes in the 400–250 cm^{-1} region, Tl–Cl stretching modes cannot be actually identified, but the number of bands present in the region below 300 cm^{-1} strongly suggest that they are present in the spectrum of $Ph(Ph_3PO)TlCl_2$. The P=O stretching frequency is lower than the value (1195 cm^{-1}) in the free ligand, as expected for coordinated Ph_3PO. The conductivity suggest that some dissociation occurs in acetone solvent.

The complexes $[Me_4N$ *or* $Et_4N][PhTlCl_3]$ *and* $[Me_4N$ *or* $Et_4N]_2[PhTlCl_4]$

Vapour pressure measurements[8] suggest that $(Me_4N)(PhTlCl_3)$ and $(Me_4N)_2(PhTlCl_4)$ in MeOH solution give $(PhTlCl_3)^-$ and $(PhTlCl_4)^{2-}$ ions respectively. This is confirmed by conductivity measurements in acetone and methanol. In the solid state, Tl–Cl stretches are observed at lower frequencies than those in $PhTlCl_2$ and thus $(R_4N)(PhTlCl_3)$ and $(R_4N)_2(PhTlCl_4)$ presumably contain tetra- and penta-coordinate thallium in the solid state.

EXPERIMENTAL

Infra-red spectra were recorded on Perkin–Elmer model 21 double beam spectrometer and on a Perkin–Elmer 457 spectrometer, using Nujol and hexachlorobutadiene mulls, between KBr and polythene plates. Low frequency infra-red spectra were recorded on a RIIC SS 720 interferometer, using polythene discs. NMR spectra were run on a Varian Associates HA 100 Spectrometer operating at 100 MHz for protons, fitted with the standard 5 mm variable-temperature probe. Spectra were scanned by use of the field-sweep mode, using TMS as lock. A frequency meter was used in determining chemical shifts from the solvent. Mass spectra were run on an AEI MS9 instrument which was operated at 70 eV with an ionising current of 100 μA. The spectra were obtained using a direct insertion system. Conductivities were measured at *ca.* 25° with a Phillips conductance bridge, using a cell of standard design fitted with bright platinum electrodes. Except where otherwise stated (Table 1), measurements were made within 2 min of preparing the solutions. The conductances were steady except for compounds mentioned in Table 1.

Phenylthallium dichloride was prepared by the reaction of $TlCl_3$ (45 g) and $PhB(OH)_2$ (6 g) in boiling H_2O (60 ml). The precipitate formed was washed with a little water and recrystallized from MeOH. (Found: C, 20.3; H, 1.8; Tl, 58.6. $C_6H_5Cl_2Tl$ calcd.: C, 20.4; H, 1.4; Tl, 58.0%.)

Phenylthallium bis(trifluoroacetate) was prepared by treating a solution of $Tl(OOCCF_3)_3$ in trifluoroacetic acid with a slight excess of benzene, and refluxing for 10 min. The solution was then refrigerated, and needles of $PhTl(OOCCF_3)_2$ separated. On concentration of the solution, further compound was obtained. It was washed with benzene to remove trifluoroacetic acid and recrystallised from MeOH. (Found: C, 23.8; H, 1.2; Tl, 41.0. $C_{10}H_5F_6O_4Tl$ calcd.: C, 23.7; H, 0.9; Tl, 40.3%.)

$PhTl(OH)_2$ was prepared by addition of aqueous NaOH to a solution of $PhTlCl_2$ in the minimum quantity of MeOH. The white precipitate formed was filtered off and dried *in vacuo* over P_2O_5. It could not be recrystallised. The yield averaged 85% for several preparations. The compound was also prepared from $PhTl(OOCCF_3)_2$ and NaOH. (Found: C, 22.1; H, 2.0; Tl, 64.0. $C_6H_7O_2Tl$ calcd.: C, 22.8; H, 2.2; Tl, 64.8%.)

$PhTlBr_2$ was prepared by treating a suspension of $PhTl(OH)_2$ in MeOH with a concentrated aqueous solution of HBr, until just acid. The white solid was filtered off, washed with a little benzene, and dried *in vacuo*. (Found: C, 15.8; H, 0.9; Tl, 46.0. $C_6H_5Br_2Tl$ calcd.: C, 16.3; H, 1.1; Tl, 46.3%.) The alternative preparation from $TlBr_3$ and $PhB(OH)_2$ is less satisfactory due to the ready disproportionation to Ph_2TlBr and decomposition to TlBr and bromobenzene.

$PhTlF_2$ was similarly prepared from $PhTl(OH)_2$ and aqueous HF in MeOH. The MeOH was then evaporated with a stream of N_2, and the compound dried *in vacuo*. (Found: C, 21.9; H, 1.4. $C_6H_5F_2Tl$ calcd.: C, 22.7; H, 1.6%.)

$PhTl(OH)(NO_3)$ was prepared from $PhTl(OH)_2$ and concentrated nitric acid. (Found: C, 20.7; H, 1.5; N, 3.4. $C_6H_6NO_4Tl$ calcd.: C, 20.0; H, 1.7; N, 3.9%.) The same product was obtained by reaction of $PhTlCl_2$ in aqueous solution with a slight excess of $AgNO_3$[38].

$PhTlSO_4$ was prepared from $PhTl(OH)_2$ and concentrated H_2SO_4 in MeOH The clear solution obtained was concentrated by passage of N_2, and the precipitate then obtained was dried *in vacuo*. The compound was hygroscopic. (Found: C, 18.3; H, 1.7. $C_6H_5O_4STl$ calcd.: C, 19.1; H, 1.3%.)

$PhTl(OOCCH_3)_2$ was best prepared by shaking a solution of $PhTlCl_2$ in MeOH with excess silver acetate for 5 h. Evaporation of solvent and recrystallisation from MeOH gave the compound as a white solid. (Found: C, 30.5; H, 2.8. $C_{10}H_{11}O_4Tl$ calcd.: C, 30.0; H, 2.8%.) A less pure sample of the compound was obtained by treating $PhTl(OH)_2$ with acetic acid: it was found difficult to remove the last traces of acetic acid. Phenylthallium diisobutyrate however was prepared from $PhTl(OH)_2$ and isobutyric acid in benzene. On addition of Et_2O, the compound separated as a white solid and was recrystallised from benzene. (Found: C, 37.3; H, 4.5. $C_{14}H_{19}O_4Tl$ calcd.: C, 36.9; H, 4.2%.)

$Ph(Bipy)TlCl_2$ was prepared by mixing solutions of $PhTlCl_2$ (0.35 g, 1.0 mmole) and 2,2′-bipyridine (0.15 g, 1.0 mmoles) in boiling MeOH and leaving to cool. The solid that then separated was recrystallised from MeOH and dried *in vacuo* over P_2O_5; yield 70%. (Found: C, 35.2; H, 2.5; N, 5.4. $C_{16}H_{13}Cl_2N_2Tl$ calcd.: C, 34.8; H, 2.3; N, 5.8%.)

Ph(Bipy)Tl$(OOCCF_3)_2$ was prepared by mixing PhTl$(OOCCF_3)_2$ (0.51 g) and 2,2'-bipyridine (8-fold excess) in 3 ml boiling MeOH, and leaving to cool. Crystals of the compound separated; yield 50%. (Found: C, 35.8; H, 1.8; N, 3.8. $C_{20}H_{13}F_6N_2O_4Tl$ calcd.: C, 36.2; H, 2.0; N, 4.2%.) The same compound was prepared by dissolving PhTl$(OOCCF_3)_2$ and bipyridine in a 1/1 ratio in a small quantity of MeOH and then leaving the solution to evaporate at room temperature for several weeks: the compound formed as large flat plates.

Ph(*o*-Phen)$TlCl_2$ was prepared from Ph$TlCl_2$ (0.35 g, 1.0 mmole) and *o*-phenanthroline hydrate (0.18 g, 1.0 mmole) in boiling MeOH. On cooling, the compound separated as a white solid and was recrystallised from MeOH. (Found: C, 40.7; H, 2.5; N, 5.2. $C_{18}H_{13}Cl_2N_2Tl$ calcd.: C, 40.6; H, 2.4; N, 5.3%.)

Ph(*o*-Phen)Tl$(OOCCF_3)_2$ was prepared from PhTl$(OOCCF_3)_2$ and *o*-phenanthroline hydrate in MeOH. (Found: C, 38.0; H, 2.0; N, 3.5. $C_{22}H_{13}F_6N_2O_4Tl$ calcd.: C, 38.4; H, 1.9; N, 4.1%.)

Ph(Py)$TlCl_2$ was prepared by dissolving Ph$TlCl_2$ in the minimum quantity of pyridine. Petrol ether was then added, and the white solid formed was recrystallised from MeOH. (Found: C, 30.4; H, 2.2; N, 3.4. $C_{11}H_{10}Cl_2NTl$ calcd.: C, 30.6; H, 2.3; N, 3.2%.)

Ph(Ph_3PO)$TlCl_2$ was prepared by dissolving Ph$TlCl_2$ (0.35 g, 1.0 mmole) and Ph_3PO (0.28 g, 1.0 mmole) in boiling MeOH. The compound separated as a white solid, recrystallised from MeOH. (Found: C, 44.7; H, 3.0. $C_{24}H_{20}OPCl_2Tl$ calcd.: C, 45.6; H, 3.2%.)

Ph(Ph_3P)$TlCl_2$ was prepared by dissolving Ph$TlCl_2$ (1.15 g, 3.0 mmole) and Ph_3P (0.81 g, 3.0 mmole) in 50 ml MeOH, and leaving the solution to stand. Crystals of the compound separated out. (Found: C, 46.5; H, 2.8. $C_{24}H_{20}Cl_2PTl$ calcd.: C, 46.9; H, 3.3%.)

$[R_4N][PhTlCl_3]$ and $[R_4N]_2[PhTlCl_4]$ were prepared by mixing MeOH solutions of R_4NCl (R = Me, Et) and Ph$TlCl_2$ in 1/1 and 2/1 ratio respectively. They were recrystallised from MeOH. $[Me_4N][PhTlCl_3]$ (Found: C, 26.6; H, 3.7; N, 3.2. $C_{10}H_{17}Cl_3NTl$ calcd.: C, 26.0; H, 3.7; N, 3.0%.) $[Me_4N]_2[PhTlCl_4]$ (Found: C, 30.1; H, 5.2; N, 5.0. $C_{14}H_{29}Cl_4N_2Tl$ calcd.: C, 29.4; H, 5.1; N, 4.9%.) $[Et_4N][PhTlCl_3]$ (Found: C, 32.5; H, 4.9; N, 2.8. $C_{14}H_{25}Cl_3NTl$ calcd.: C, 32.4; H, 4.8; N, 2.7%.) $[Et_4N]_2[PhTlCl_4]$ (Found: C, 34.6; H, 5.8; N, 4.4. $C_{18}H_{37}Cl_4N_2Tl$ calcd.: C, 34.4; H, 5.9; N, 4.5%.)

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