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SHORT COMMUNICATION

Complexes of organometallic compounds
XVIII. The preparation and properties of salts of some organothallium(III) complex anions

The formation of anionic chloride and thiocyanate complexes of organothallium(III) cations has been shown previously by paper electrophoretic and anion exchange paper chromatographic investigations[1,2]. The preparation of the solids $[(CH_3)_4N][C_6H_5TlCl_3]$ and $[(CH_3)_4N]_2[C_6H_5TlCl_4]$ followed[3], and the presence of monophenylthallium(III) chloride complex anions, in anhydrous methanol, was demonstrated by osmometric studies[3].

This paper reports further investigations in this area. Salts of anionic halide and thiocyanate complexes of $(CH_3)_2Tl^{III}$ and $(C_6H_5)_2Tl^{III}$, and of anionic halide complexes of $C_6H_5Tl^{III}$, with the cations $(C_6H_5)_4As^+$, $(n\text{-}C_4H_9)_4N^+$, $(C_2H_5)_4N^+$ and $(CH_3)_4N^+$, have been prepared. Information about the species present in anhydrous acetone has been obtained by means of vapor pressure measurements.

Experimental

Pure reagents were used whenever possible, otherwise the reagents were purified through distillation or recrystallization.

$(C_2H_5)_4NBr$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NI$, $(CH_3)_4NCl$ and $(CH_3)_4NBr$ were purchased from C. Erba, Milano. The latter two compounds were purified by dissolution in methanol and precipitation with acetone or ether, or by recrystallization from methanol.

$(C_6H_5)_4AsCl$ was purchased from Fluka, Switzerland. $(C_6H_5)_4AsBr$, $(C_6H_5)_4AsI$ and $(C_6H_5)_4AsSCN$ were obtained by precipitation from aqueous $(C_6H_5)_4AsCl$, on addition of aqueous solutions of the sodium salts of each ligand, and were recrystallized from aqueous ethanol. $(C_6H_5)_4AsCl\cdot HCl$ was prepared as reported elsewhere[4].

The solvents employed (C. Erba) were dried as follows: methanol, with magnesium methoxide; acetone, with K_2CO_3 (after refluxing with $KMnO_4$); ether, with Na/K; n-pentane, with P_2O_5.

The compounds $(CH_3)_2TlI$, $(CH_3)_2TlNO_3$, $(C_6H_5)_2TlCl$, $(C_6H_5)_2TlBr$, $(C_6H_5)_2TlI$ and $C_6H_5TlCl_2$ have been prepared and purified according to methods given in the literature[5]. $(CH_3)_2TlCl$ and $(CH_3)_2TlBr$ have been precipitated by adding aqueous NaCl or NaBr to aqueous $(CH_3)_2TlNO_3$, and recrystallized from water. $(CH_3)_2TlSCN$ and $(C_6H_5)_2TlSCN$ have been prepared by refluxing $(CH_3)_2TlI$ and $(C_6H_5)_2TlBr$ with AgSCN (1 : 1) in methanol; the silver halide was filtered off, and the organothallium thiocyanates were precipitated by adding respectively ether and water.

Preparations of the solid organothallium(III) complexes. These have been generally carried out by adding 15 to 40 ml of anhydrous solvent to a solid mixture, consisting of 0.5–1.0 mmole of an organothallium halide or thiocyanate and of a stoichiometric amount (1 : 1 or 1 : 2) of a tetraorganoammonium or -arsonium salt of the same anion.

TABLE 1

MELTING POINTS AND ANALYTICAL DATA OF ORGANOTHALLIUM(III) COMPLEXES

Compound	*M.p. (°C)*	*C (%) found (calcd.)*	*H (%) found (calcd.)*	*N (%) found (calcd.)*	*Halide (%) found (calcd.)*
$[(C_6H_5)_4As]_2[(CH_3)_2TlCl_3]$	177–181	53.70 (54.22)	4.45 (4.19)		9.34 (9.60)
$[(C_6H_5)_4As]_2[(CH_3)_2TlBr_3]$	194–196	48.12 (48.40)	3.68 (3.74)		18.44 (19.32)
$[(n\text{-}C_4H_9)_4N]_2[(CH_3)_2TlBr_3]$	75–77	43.10 (42.58)	8.29 (8.20)	3.05 (2.92)	24.74 (25.00)
$[(C_6H_5)_4As]_2[(CH_3)_2TlI_3]$	210–211	43.23 (43.46)	3.42 (3.36)		27.63 (27.55)
$[(n\text{-}C_4H_9)_4N]_2[(CH_3)_2TlI_3]$	98–99	37.45 (37.12)	7.08 (7.15)	2.49 (2.55)	34.63 (34.61)
$[(C_6H_5)_4As][(CH_3)_2Tl(SCN)_2]$[a]	165–167	45.21 (45.82)	3.55 (3.57)	3.82 (3.82)	
$[(C_6H_5)_4As][(C_6H_5)_2TlCl_2]$	206–208	53.40 (53.20)	3.94 (3.72)		8.65 (8.72)
$[(CH_3)_4N][(C_6H_5)_2TlCl_2]$	227–231	38.64 (38.16)	4.55 (4.40)	2.85 (2.78)	14.23 (14.08)
$[(C_6H_5)_4As][(C_6H_5)_2TlBr_2]$	199–200	47.69 (47.95)	3.32 (3.35)		17.88 (17.72)
$[(CH_3)_4N][(C_6H_5)_2TlBr_2]$	209–210	31.70 (32.43)	3.52 (3.74)	2.20 (2.36)	26.35 (26.97)
$[(C_2H_5)_4N][(C_6H_5)_2TlBr_2]$	199–200	36.92 (37.03)	4.58 (4.66)	2.18 (2.16)	23.92 (24.64)
$[(C_6H_5)_4As][(C_6H_5)_2TlI_2]$	168–170	43.53 (43.42)	3.00 (3.04)		25.48 (25.49)
$[(C_6H_5)_4As][(C_6H_5)_2Tl(SCN)_2]$[b]	186–188	52.68 (53.19)	3.51 (3.52)	2.99 (3.26)	
$[(C_6H_5)_4As][C_6H_5TlCl_3]$	165–166	46.66 (46.72)	3.27 (3.27)		13.85 (13.79)
$[(C_6H_5)_4As][C_6H_5TlBr_3]$	148–150	39.82 (39.83)	2.78 (2.79)		26.86 (26.50)
$[(C_6H_5)_4As][C_6H_5TlI_3]$	158–159	34.15 (35.45)	2.22 (2.41)		36.90 (36.41)

[a] Sulphur found 8.29%, calcd. 8.74%. [b] Sulphur found 7.19%, calcd. 7.47%.

In this way the dissolution of the solid phase was easily achieved, at room temperature or by gentle warming, even when the reagents (or one of these) were nearly insoluble in the solvent employed. The latter is a typical behaviour due to complex formation in the solution phase.

The procedures used to obtain the solid compounds are summarized as follows:

(*1*) Reaction solvent, anhydrous acetone (hot, if necessary). The product was caused to crystallize by cooling or adding anhydrous pentane and was recrystallized from anhydrous acetone: $[(C_6H_5)_4As]_2[(CH_3)_2TlX_3]$ ($X = Cl, Br, I$), $[(C_6H_5)_4As][(CH_3)_2Tl(SCN)_2]$, $[(C_6H_5)_4As][(C_6H_5)_2TlX_2]$ ($X = Cl, Br, I, SCN$), $[R_4N][(C_6H_5)_2TlBr_2]$ ($R = CH_3, C_2H_5$). (*2*) Reaction solvent, hot ethyl acetate. The product crystallized on cooling and was recrystallized from this solvent: $[(n\text{-}C_4H_9)_4N]_2[(CH_3)_2TlX_3]$ ($X = Br, I$). (*3*) Reaction solvent, hot, anhydrous 1 : 1 acetone/acetonitrile. Recrystallized from anhydrous acetone: $[(CH_3)_4N][(C_6H_5)_2TlCl_2]$. (*4*) Reaction solvent, hot, anhydrous ethanol. Needles were obtained on recrystallization from anhydrous ethanol: $[(C_6H_5)_4As][C_6H_5TlCl_3]$. Use of a sixfold excess of $[(C_6H_5)_4As]Cl$ did not change this stoichiometry. This compound also was obtained by reaction (with C_6H_5–Tl cleavage) of $(C_6H_5)_2TlCl$ and $[(C_6H_5)_4As]HCl_2$ in acetone. (*5*) $[(C_6H_5)_4As][C_6H_5TlX_3]$ ($X = Br, I$) were prepared by taking into account the B-class character of $C_6H_5Tl^{III}$ towards halide ligands: in this respect $C_6H_5Tl^{III}$ behaves as Tl^{III}[6,7]. $[(C_6H_5)_4As][C_6H_5TlCl_3]$ was dissolved in hot methanol, and excess of methanolic KBr or KI (1 : 4) was added. Aqueous methanol was used for the preparation of the bromide complex, while anhydrous methanol was used for the iodide. The complex salts were obtained by cooling. The complex iodide is a yellow solid, which is decomposed by water, with formation of the red-orange compound $[(C_6H_5)_4As][TlI_4]$[7].

The solid organothallium complex salts are white (except $[(C_6H_5)_4As][C_6H_5TlI_3]$) and mostly crystalline. They are generally soluble, or sparingly soluble, in donor solvents (*i.e.*, acetone, the lower alcohols, acetonitrile, etc.) and insoluble in ether and in non-donor solvents (hydrocarbons, benzene, etc.). The melting points and analytical data are reported in Table 1.

Vapor-pressure measurements. These were carried out in anhydrous acetone at 37°, by employing a Mechrolab Osmometer Model 302, and the usual method of treatment of the results[3,8]. The latter are reported in Table 2.

TABLE 2

OSMOMETRIC MEASUREMENTS IN ANHYDROUS ACETONE AT 37° OF ORGANOTHALLIUM(III) COMPLEXES

Compound	*Molar concn.* ($\times 10^2$)	*ΔR readings at the osmometer* Organothallium	Benzil	*i*
$[(C_6H_5)_4As]_2[(CH_3)_2TlCl_3]$	0.83	12.47	4.40	2.83
	0.62	9.52	3.25	2.93
	0.41	6.54	2.20	2.97
	0.21	3.37	1.10	3.06
$[(C_6H_5)_4As]_2[(CH_3)_2TlBr_3]$	1.98	27.52	10.65	2.58
	1.48	21.22	8.05	2.64
	0.99	14.60	5.35	2.73
	0.49	7.49	2.70	2.77
$[(n\text{-}C_4H_9)_4N]_2[(CH_3)_2TlBr_3]$	1.52	21.17	8.10	2.61
	1.08	16.44	5.90	2.79
	0.76	11.34	4.05	2.80
	0.38	5.96	2.12	2.81
$[(C_6H_5)_4As]_2[(CH_3)_2TlI_3]$	0.72	12.01	3.90	3.08
	0.54	9.21	2.90	3.17
	0.36	6.29	1.95	3.22
	0.18	3.38	1.00	3.38

TABLE 2 (*continued*)

Compound	*Molar concn.*	*ΔR readings at the osmometer*		*i*
	(× 10²)	*Organothallium*	*Benzil*	
$[(n\text{-}C_4H_9)_4N]_2[(CH_3)_2TlI_3]$	0.94	13.96	5.00	2.79
	0.70	10.77	3.80	2.83
	0.47	7.40	2.55	2.90
	0.23	3.90	1.25	3.12
$[(C_6H_5)_4As][(CH_3)_2Tl(SCN)_2]$	2.07	20.26	11.10	1.82
	1.55	16.04	8.40	1.91
	1.03	11.23	5.40	2.08
	0.52	6.07	2.80	2.17
$[(C_6H_5)_4As][(C_6H_5)_2TlCl_2]$	0.52	4.35	2.80	1.55
	0.26	2.21	1.40	1.58
	0.13	1.12	0.70	1.60
$[(C_6H_5)_4As][(C_6H_5)_2TlBr_2]$	1.00	7.69	5.40	1.42
	0.75	5.76	4.00	1.44
	0.50	4.23	2.70	1.57
	0.25	2.16	1.35	1.60
$[(CH_3)_4N][(C_6H_5)_2TlBr_2]$	0.42	3.39	2.20	1.54
	0.32	2.63	1.60	1.64
	0.21	1.86	1.10	1.69
$[(C_2H_5)_4N][(C_6H_5)_2TlBr_2]$	0.44	3.42	2.40	1.42
	0.33	2.66	1.80	1.48
	0.22	1.80	1.20	1.50
$[(C_6H_5)_4As][(C_6H_5)_2TlI_2]$	1.00	9.03	5.40	1.67
	0.75	6.97	4.00	1.74
	0.50	4.75	2.70	1.76
	0.25	2.45	1.35	1.81
$[(C_6H_5)_4As][(C_6H_5)_2Tl(SCN)_2]$	0.75	7.88	4.00	1.97
	0.56	6.10	3.00	2.03
	0.37	4.26	2.00	2.13
	0.19	2.24	1.00	2.24
$[(C_6H_5)_4As][C_6H_5TlCl_3]$	2.61	20.11	13.45	1.49
	1.95	15.55	10.05	1.55
	1.30	10.75	6.70	1.60
	0.65	5.53	3.36	1.64
$[(C_6H_5)_4As][C_6H_5TlBr_3]$	0.70	5.91	3.80	1.55
	0.35	3.04	1.90	1.60
	0.17	1.55	0.95	1.63
$[(C_6H_5)_4As][C_6H_5TlI_3]$	0.70	5.90	3.80	1.55
	0.35	3.12	1.90	1.64
	0.17	1.59	0.95	1.67

Discussion

The compounds prepared are salts of organothallium(III) complex anions, which may be reasonably formulated as reported in the Tables on the basis of the stoichiometric data (listed in Table 1) and of the corresponding "*i*" values in anhydrous acetone (reported in Table 2). In fact, in the latter solvent the complex anions $(CH_3)_2TlX_3^{2-}$ (X=Cl, Br, I), $(CH_3)_2Tl(SCN)_2^-$, $(C_6H_5)_2TlX_2^-$ (X=Cl, Br, I, SCN) and $C_6H_5TlX_3^-$ (X=Cl, Br, I) seem to be present as simple monomeric species, together with the cations $(C_6H_5)_4As^+$ and R_4N^+. The alternative hypothesis of no formation of organothallium co-ordination compounds in anhydrous acetone cannot be supported, since we observed that the tetraorganoammonium and -arsonium salts are dissociated in this solvent ($i \sim 1.7$); the number of particles formed per mole of complex would then be at least $n=3$ (*i.e.*, $i \sim 3$) for the compounds 1 : 1 organothallium(III)/ tetraorganoarsonium (or -ammonium) salt, and $n=5$ (*i.e.*, $i \sim 5$) for the 1 : 2 compounds, instead of the respectively found values $n=2$ and $n=3$ (see Table 2).

Several interesting questions now arise, for instance about the co-ordination number of thallium in the prepared complexes. A five-co-ordinate thallium atom could be assumed to be present in the complex anions $(CH_3)_2TlX_3^{2-}$, and a four-co-ordinate one in $(CH_3)_2Tl(SCN)_2^-$, in $(C_6H_5)_2TlX_2^-$ and in $C_6H_5TlX_3^-$, in anhydrous acetone. A solvent-to-thallium co-ordination could obviously take also place in solution phase, so that the above reported co-ordination numbers are only tentatively assigned. On the other hand, while the co-ordination number four for thallium is well-established, the probable existence of five-co-ordinated thallium has been recently reported in complexes of $(C_6F_5)_2Tl^{III}$, Tl^{III} and $C_6H_5Tl^{III}$ [7,9,10,3,5d].

Other questions arising from these investigations concern the nature of the solid phases. The complex $[(CH_3)_4N]_2[C_6H_5TlCl_4]$ was easily prepared[3], while the attempted preparation of the corresponding $(C_6H_5)_4As^+$ derivative was unsuccessful (see under *Experimental*, this paper). Also, attempted preparations of four-co-ordinate halide derivatives of $(CH_3)_2Tl^{III}$ and of the so-called five-co-ordinate derivatives of $(C_6H_5)_2Tl^{III}$ failed.

Structural X-ray investigations are clearly needed, both for the solids and (possibly) in solution phase.

With the aim of possibly answering these and similar questions and in order to obtain a better understanding of the organothallium(III) chemistry, we are carrying out further work. The determination of the electrolytic conductances in organic solvents of the prepared compounds, as well as the determination of stability constants in aqueous solution, are in progress and spectroscopic and structural investigations are planned.

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