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Triphenyltelluronium Haloplumbates (II)

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The paper describes the synthesis and properties of Triphenyltelluronium haloplumbates (II). $[(Ph_3Te)^+]_2[PbCl_4]^{2-}$, $[Ph_3Te]^+[PbBr_3]^-$ and $[Ph_3Te]^+[PbI_3]^-$ type products are obtained by reactions of Ph_3TeX with PbX_2 in presence of HX (X = Cl, Br, I respectively). Conductivity, molecular weight determinations and ^1H nmr data are consistent with their dissociation in dilute solution as Ph_3Te^+ and $PbCl_4^{2-}$ or Ph_3Te^+ and $PbBr_3^-$ or PbI_3^- units. The absence of Te–Pb and Te–X vibrations in the far i. r. spectra of these compounds also supports their formulation as ionic compounds.

INTRODUCTION

Triphenyltelluronium halides, Ph_3TeX (X = Cl, Br, I) are known to form adducts with a number of metal halides[1,2] but characteristics of only a few of them, those with $HgX_2^{3,4}$, $Ti_4^{5,6}X$ and $SnCl_4^{7}$ have been reported in recent years. In this paper we report the study on reactions of Ph_3TeX with PbX_2 in presence of HX and describe some of the properties of isolated products.

EXPERIMENTAL

Tellurium tetrachloride used was of Riedel (Germany) and was purified before use by a standard method[8]. Triphenyltelluronium chloride was prepared by the method reported in the literature[9]. The corresponding bromide and iodide derivatives were obtained by halogen exchange reactions using KBr and KI (which were of BDH, AnalaR quality) in hot water. Lead (II) halides were prepared freshly from lead (II) acetate (BDH, AnalaR) by reacting with dilute aq. HX. Solvents were purified and dried by conventional methods[10,11].

(a) Triphenyltelluronium Tetrachloroplumbate (II) : $[(Ph_3Te)^+]_2[PbCl_4^{2-}]$

A solution of $PbCl_2$ (1.39 g, 5 mmol) in about 5 ml of conc. hydrochloric acid was added to the saturated solution of Ph_3TeCl (3.95 g, 10 mmol) in dry methanol, dropwise and with constant stirring. The resultant solution was then stirred for about 1 h. The white crystalline solid thus obtained was filtered, washed with methanol and benzene (1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca* 73%; M. pt. 234–235°C (dec.).

Alternative method—A saturated solution of $PbCl_2$ (1.39 g, 5 mmol) in hot water was added to saturated hot aqueous solution of Ph_3TeCl (3.95 g, 10 mmol), which resulted in a clear solution and on cooling there was no separation of reactants which otherwise would have separated out on cooling. This solution was concentrated under vacuum (without heating) to about 10 ml. A white crystalline product was obtained, as in first method.

(b) Triphenyltelluronium Tribromoplumbate (II) : $[Ph_3Te]^+[PbBr_3]^-$

A solution of $PbBr_2$ (3.67 g, 10 mmol) in about 15 ml of hydrobromic acid was added to the saturated solution of Ph_3TeBr (4.38 g, 10 mmol) in dry methanol dropwise and with constant stirring. Light pinkish precipitates were formed immediately which were filtered, washed with methanol and benzene (1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca.* 80%. M. pt. 224–225°C (dec.).

(c) Triphenyltelluronium Triiodoplumbate (II) : $[Ph_3Te]^+[PbI_3]^-$

A solution of PbI_2 (4.61 g, 10 mmol) in about 15 ml of hydroiodic acid was added to the saturated solution of Ph_3TeI (4.85 g, 10 mmol) in dry methanol dropwise and with constant stirring. Yellow precipitate was formed immediately which was filtered, washed with methanol and benzene (1 : 1) and dried over P_40_{10} in vacuo. Yield *ca.* 65%. M. pt. 244–245°C (dec.).

The compounds were recyrstallized from cold methanol since in hot, the compounds undergo partial decomposition into Ph_3TeX and PbX_2. The purity of the compounds was checked by TLC. Tellurium contents were determined volumetrically[12(a)] and lead gravimetrically[12(b)] after decomposing the compound with HNO_3. Halogen contents were estimated volumetrically[12(c)] after fusing the compound with Na_2CO_3/NaOH. Carbon and hydrogen contents were estimated from IIT Delhi. The analytical data are compiled in Table 1. Conductance measurements were performed under dry conditions at 30±2° in nitrobenzene, acetonitrile and nitromethane using a conductance bridge and dip type cell with smooth platinum electrode. Molecular weights were determined cryoscopically in nitrobenzene. The ^1H nmr spectra were recorded in DMSO–d_6 solvent using tetramethylsilane as internal reference. The far ir spectra were recorded on polyethylene support from R.S.I.C., IIT Madras.

RESULTS AND DISCUSSION

Ph_3TeCl, when reacted with $PbCl_2$, forms 2 : 1 adduct $[(Ph_3Te)^+]$ $[PbCl_4]^{2-}$, where it transfers its chloride ion to lead (II) chloride which is known to act as halide acceptor[13]. This behaviour of Ph_3TeCl in this reaction is similar to that with other metal halides like HgX_2[3,4], TiX_4[5,5] and $SnCl_4$[7] where Ph_3TeX acts as halide donor and these metal halides as acceptors.

$$2Ph_3TeCl + PbCl_2 \longrightarrow [(Ph_3Te)^+]_2[PbCl_4]^{2-}$$

Similar reactions of Ph_3TeBr and Ph_3TeI with corresponding lead halides could not be performed due to insolubility of $PbBr_2$ and PbI_2 in water and other common organic solvents.

TABLE 1

ANALYTICAL DATA, FOR TRIPHENYLTELLURONIUM HALOPLUMBATES (II)

Compound (empirical formula)	Analysis Found (Calculated)%				
	Te	Pb	X	C	H
$[(Ph_3Te)^+]_2[PbCl_4]^{2-}$ $(C_{36}H_{30}Te_2PbCl_4)$	23.87 (23.93)	18.97 (19.42)	12.84 (13.31)	40.31 (40.50)	2.59 (2.81)
$[Ph_3Te]^+[PbBr_3]^-$ $(C_{18}H_{15}TePbBr_3)$	14.91 (15.83)	24.98 (25.71)	29.32 (29.78)	26.68 (26.80)	1.76 (1.86)
$[Ph_3Te]^+[PbI_3]^-$ $(C_{18}H_{15}TePbI_3)$	13.12 (13.40)	21.29 (21.80)	39.97 (40.20)	10.87 (11.20)	1.49 (1.58)

Also lead (II) halides are soluble in corresponding HX ($X = Cl$, Br, I) yielding $PbCl_4^{2-}$, $PbBr_3^-$ and PbI_3^- ions respectively[13]. When these haloplumbate ions are brought in contact with Ph_3Te^+ ion, there is immediate precipitation of triphenyltelluronium haloplumbates.

$$PbCl_2 + 2HCl \rightarrow PbCl_4^{2-} + 2H^+$$

$$2\ Ph_3TeCl + PbCl_4^{2-} \rightarrow [(Ph_3Te)^+]_2[PbCl_4]^{2-} + 2Cl^-$$

and

$$PbX_2 + HX \rightarrow PbX_3^- + H^+$$

$$(X = Br, I)$$

$$Ph_3TeX + PbX_3^- \rightarrow [Ph_3Te]^+[PbX_3]^- + X^-$$

These adducts are crystalline solids which are fairly stable in dry air but get decomposed in dilute aqueous solution with the separation of PbX_2, like other haloplumbate ions[14]. These compounds are soluble in polar organic solvents but insoluble in non-polar solvents. Also when heated in polar solvents for a long time, these get partially decomposed into reactants.

The molar conductance data in nitrobenzene, nitromethane and acetonitrile suggest the electrolytic behaviour of these adducts. Λ_M values for $[Ph_3Te]^+[PbX_3]^-$ (where X = Br, I) in nitrobenzene and nitromethane are within or close to the expected[15] ranges for 1 : 1 electrolytes containing *ca.* 10^{-3} M of solute and reflect the likely formation in solution of $[Ph_3Te]^+$ and $[PbX_3]^-$ ions. Similarly Λ_M values for $[(Ph_3Te)^+]_2[PbCl]^{2-}$ in nitromethane are within or close to the expected ranges for 2 : 1 electrolytes containing *ca* 10^{-3} M of solute and reflect the likely formation in solution of $2[Ph_3Te]^+$ and $[PbCl_4]^{2-}$. However in nitrobenzene this value is very low which may be due to incomplete dissociation of this compound or interaction of solvent molecules with the solute ions. The molar conductance of all these compounds in acetonitrile is quite low than expected values, which may be due to the reason that in very dilute solutions these haloplumbates decompose to give plumbous halides resulting there by a decrease in conductivity. This may also be mentioned that solution of these compounds in acetonitrile become turbid after sometime, probably due to formation of PbX_2. The molecular weights of these adducts in nitrobenzene are given in Table 2. The data are consistent with the electrolytic nature of compounds as predicted by conductance measurements. However the molecular weights are slightly higher than expected which may be due to ion pair association or incomplete dissociation in nitrobenzene.

TABLE 2

MOLECULAR WEIGHT AND MOLAR CONDUCTANCE DATA FOR TRIPHENYLTELLURONIUM HALOPLUMBATES (II)

Compound	Molar Conductance (*ca.* 10^{-3} M) Λ_M ohm^{-1} cm^2 mol^{-1} Nitrobenzene.	Acetonitrile	Nitromethane	Concentration Range mmol l^{-1}	Average Mole wt (Formula wt.)
$[(Ph_3Te)^+]_2[PbCl_4]^{2-}$	13.1	68.7	140.0	0.7–2.1	597.8 (1066.4)
$[Ph_3Te]^+[PbBr_3]^-$	21.3	52.7	94.0	0.8–2.8	480.0 (805.8)
$[Ph_3Te]^+[PbI_3]^-$	22.3	79.2	78.1	0.7–2.1	530.0 (946.8)

^1H nmr spectra (Table 3) of these compounds show almost similar phenyl proton chemical shifts to be independent of the halogen and therefore it reflects the dissociation of these adducts as $[Ph_3Te]^+$ and $[PbCl_4]^{2-}$ or $[PbX_3]^-$ (X = Br, I).

The far ir spectra of these compounds show the absence of modes which may be assigned as ν_{Te-X}[16–19]. It means that all these compounds contain the discrete triphenyltelluronium ion Ph_3Te^+. All these compounds show very strong bands in the region 263 cm^{-1} to 276 cm^{-1}, which are similar io those assigned to ν_{Te-C} in other phenyl derivatives of tellurium [16–19]. ν_{Te-C} assignments in these compounds which appear at 265, 270 cm^{-1} for $[(Ph_3Te)^+]_2 [PbCl_4]^{2-}$; 263, 271 cm^{-1} for $[Ph_3Te]^+[PbBr]_3^-$ and 263, 276 cm^{-1} for $[Ph_3Te]^+[PbI_3]$, are not significantly different from those reported for the free diphenyltelluride unit[17] and the parent Ph_3TeX^5. Since there is no shift of ν_{Te-C} frequeney towards lower sides, this mean that there is no Te–Pb bond in these compounds. On the basis of absence of Te–Pb and Te–X bonds, it will be suitable to formulate these compounds as ionic compounds, the behaviour which is predicted from above solution studies. The ν_{Pb-X} assignments which are expecied[20,21] in the region 350–70 cm^{-1} can not be made accurately, since a number of phenyl modes[16,17] and lattice modes are also expected in this region and the Pb–X bands may be mixed with these.

TABLE 3

PHENYL PROTON CHEMICAL SHIFTS OF TRIPHENYLTELLURONIUM HALOPLUMBATES (II) IN DMSO-d_6.

Compound	δ ppm₂
$[(Ph_3Te)^+]_2[PbCl_4]^{2-}$	7.38 – 7.86 (bm)
$[Ph_3Te]^+[PbBr_3]^-$	7.32 – 7.84 (bm)
$[Ph_3Te]^+[PbI_3]^-$	7.40 – 7.88 (bm)

bm = broad multiplet.

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