Asian Journal of Chemistry Vol. 7, No. 1 (1995), 196–202

Synthesis and Characterization of (2,3-Dimethyl-4-hydroxyphenyl)tellurium(IV) Halides

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This paper reports the preparation and properties of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV)-halides, R_nTeX_{4-n} (where $X = Cl^-, Br^-, I^-$ and $n = 1, 2$). Conductance and cryoscopic measurements reveal the molecular nature of $RTeCl_3$ and R_2TeX_2 and 1:1 electrolyte-type nature of $RTeBr_3$ and $RTeI_3$ in nitrobenzene, nitromethane and acetonitrile. The ^1H NMR and IR spectra suggest that the halotellurium groups are in *para* position to the —OH group. The far IR spectra reflect the polymeric nature of $RTeX_3$ and monomeric nature having a ψ-trigonal bipyramidal structure of R_2TeX_2 type compounds.

INTRODUCTION

Tellurium tetrachloride is reported[1–6] to yield the hydroxyaryltellurium(IV) chlorides upon reaction with hydroxybenzenes, *viz.*, phenol, catechol, resorcinol, cresols (*ortho-*, *meta-* and *para-*) and chlorophenols (*ortho-* and *meta-*). The corresponding hydroxyaryltellurium(IV) bromides and iodides are also reported[4–6] from these chlorides by halogen-exchange process. We report here, the preparation of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) halides by the reaction of tellurium tetrachloride with 2,3-dimethylphenol and the subsequent reaction of these chlorides with potassium bromide and potassium iodide. Some of the physical and spectroscopic properties of these compounds are described.

EXPERIMENTAL

Tellurium tetrachloride (Riedel, Germany) was purified before use by a standard method[7]. 2,3-Dimethylphenol was obtained from SISCO Research Lab., Bombay (India). Potassium bromide and potassium iodide used were of E. Merck (AnalaR) quality. Solvents were purified and dried by conventional methods[8, 9].

Conductance measurements were carried out in nitrobenzene, nitromethane and acetonitrile at 30 ± 2°C on a Systronics Conductivity Bridge type 305. Molecular weights were determined cryoscopically in nitrobenzene upto the saturation point. The ^{1}H NMR spectra were recorded on a EM-390 90 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 using $SiMe_4$ as an internal reference. Far IR spectra were recorded on Fourier Far IR FIR30 using polyethylene support.

Preparations of (2,3-dimethyl-hydroxyphenyl)tellurium(IV) trichloride

$TeCl_4$ (5.4 g, 20.0 mmol) and 2,3-dimethylphenol (2.46 g, 20.13 mmol) in 80 mL of dry chloroform were refluxed on an oil bath under an atmosphere of dry N_2 for about 14 h until the evolution of HCl ceased. The amount of HCl liberated corresponded to the loss of one equivalent of chlorine atom per mole of $TeCl_4$. Then pet. ether (*ea.* 50 mL) was added dropwise to separate a brown product. This was filtered and washed thoroughtly with benzene to remove the excess of unreacted reactants. It was recrystallized from chloroform to give a brown product.

Preparation of Bis(2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) dichloride

$TeCl_4$ (5.4 g, 20.0 mmol) and 2,3-dimethylphenol (5.0 g, 40.93 mmol) in 100 mL of carbon tetrachloride were refluxed on an oil bath under an atmosphere of dry N_2 for about 52 h until evolution of HCl ceased which corresponded to the loss of two equivalent of Cl atom. Then dry CCl_4 (*ca.* 100 mL) was added to it to separate a light brown coloured product, which was filtered and washed many times with benzene containing a little $CHCl_3$ (90:10) to remove the unreacted reactants and $RTeCl_3$ type product, if any. It was recrystallised from acetonitrile to give a light brown solid.

Preparation of (2,3-dimethyl-4-hydroxphenyl)tellurium(IV) bromides and iodides

The bromo and iodo derivatives of (2,3-dimethyl-4-hydroxyphenyl) tellurium(IV) chlorides were prepared by halogen exchange processes. A general procedure is given below:

A saturated solution of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) chloride in methanol was treated with excess of KBr/KI solution in the same solvent. An immediate darkening of colour followed by separation of KCl was observed. The addition of diethyl ether resulted in complete precipitation of KCl and excess of KBr/KI from the solution. The clear solutions upon concentration under vacuum yielded crystals of (2,3-dimethyl-4-hydroxyphenyl) tellurium(IV) bromide/ iodide. These were recrystallized from ether or chloroform.

The purity of these compounds was checked by TLC. The compounds were analysed for tellurium, halogen, carbon and hydrogen contents as well. The analytical data are given in Table 1.

TABLE–1
ANALYTICAL DATA, MELTING POINTS AND YIELDS FOR (2,3-DIMETHYL-4-HYDROXYPHENYL)TELLURIUM(IV) HALIDES

Compound (R = 2,3-dimethyl-4-hydroxyphenyl (Empirical formula) (Colour)	Analysis % Found (Calcd.)				*M.p. (°C)	†Yield %
	Te	Cl/Br/I	C	H		
$RTeCl_3\cdot$ ($C_8H_9OTeCl_3$) (Brown)	35.44 (35.93)	29.68 (29.99)	26.70 (27.03)	2.10 (2.53)	190–192	80
$RTeBr_3\cdot$ ($C_8H_9OTeBr_3$) (Orange)	25.72 (26.12)	48.70 (49.08)	20.08 (19.65)	1.81 (1.84)	168–170	70
$RTeI_3\cdot$ ($C_8H_9OTeI_3$) (Reddish brown)	19.94 (20.27)	59.99 (60.48)	14.61 (15.25)	1.28 (1.42)	98–100	80
$R_2TeCl_2\cdot$ ($C_{16}H_{18}O_2TeCl_2$) (Light brown)	28.89 (28.93)	15.82 (16.10)	42.86 (43.54)	3.79 (4.08)	140–142	75
$R_2TeBr_2\cdot$ ($C_{16}H_{18}O_2TeBr_2$) (Brown)	23.45 (24.09)	29.64 (30.17)	35.61 (36.24)	3.52 (3.40)	145–147	70
$R_2TeI_2\cdot$ ($C_{16}H_{18}O_2TeI_2$) (Dark brown)	19.98 (20.46)	40.35 (40.69)	30.30 (30.78)	2.81 (2.88)	120–122	80

*Melt with decomposition.

†With respect to $TeCl_4$ for chloro-derivatives and with respect to chloro-derivatives for respective bromo and iodo compounds.

RESULTS AND DISCUSSION

In earlier reports[4–6] on the reactions of tellurium(IV) chloride with hydroxybenzenes it was described that despite the acidic nature of hydroxyl proton, phenols undergo a Friedel-Crafts type condensation reaction with tellurium tetrachloride involving the attack by $TeCl_3^+$ on the position *para* (*ortho-* if *para* position already occupied[5]) to the hydroxyl group in the aromatic ring. The formation of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) trichloride and *bis*(2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) dichloride by the reaction of $TeCl_4$ with 2,3-dimethylphenol also involves the electrophilic attack on the aromatic ring by $TeCl_3^+$ species at a position *para* with respect to the —OH group.

These organyl tellurium chlorides undergo halogen exchange processes when treated with KBr or KI in methanol.

Potassium chloride is much less soluble in methanol as compared to KBr or KI. The organyl tellurium bromides and iodides are soluble in diethyl ether whereas potassium chloride and the organyl tellurium chlorides are insoluble. These facts facilitate the preparation of pure compounds. Compound of the R_3TeCl type was not obtained even when 2,3-dimethylphenol was in excess of the stoichiometrically required amounts. Resorcinol[4] and *m*-cresol[5], however, are reported to yield such product. This may be probably due to steric factors.

The (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) halides are fairly stable in dry air but get hydrolysed in presence of moisture. $RTeX_3$ hydrolyses more readily as compared to R_2TeX_2. In a particular series the order of hydrolysis is $Cl > Br > I$. (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) trichloride is slightly hygroscopic in nature. The compounds are soluble in polar organic solvents but insoluble in non-polar solvents.

The molar conductance data (Table 2) in nitrobenzene, nitromethane and acetonitrile suggest the molecular behaviour of R_2TeX_2 type compounds in solution. This behaviour of R_2TeX_2 type compounds is quite similar to the *bis*(phenyl)tellurium(IV) dihalides[10], *bis*(hydroxyaryl)tellurium(IV) dihalides[4, 5] and other substituted analogues[11]. The molar conductance values for $RTeBr_3$ and $RTeI_3$ are within the expected ranges[12] for 1 : 1 electrolytes in 10^{-3} M solutions indicating the formation of $RTeX_2^+$ and X^- ions in solution ($X = Br^-, I^-$). The conductivity measurements for $RTeCl_3$ suggest that this material is less dissociated. Thus the general behaviour of compounds of the composition of $RTeX_3$ is similar to other such compounds like aminoaryl tellurium(IV) trihalides[13] and hydroxyaryltellurium(IV) trihalides[4–6]. Further, it is observed that the degree of dissociation in a solution containing 10^{-3} M of solute in a series varies in the order $Cl < Br < I$ (except in acetonitrile, where $RTeCl_3 < RTeI_3 < RTeBr_3$).

TABLE–2
MOLAR CONDUCTANCE AND MOLECULAR WEIGHT DATA FOR (2,3-DIMETHYL-4-HYDROXYPHENYL)TELLURIUM(IV) HALIDES

Compound	Molar conductance* (ca. 10^{-3} M) ohm^{-1} Λ_M cm^2 mol^{-1}			Formula weight	Conc. range mmoles/ litre of solvent	Average molecular weight (found)
	Nitrobenzene	Nitromethane	Acetonitrile			
$RTeCl_3$	4.2	35.0	52.0	355.1	2.82–11.26	328.5
$RTeBr_3$	10.2	75.5	177.5	488.5	4.09–10.24	272.7
$RTeI_3$	22.6	89.2	154.8	629.5	3.18–9.53	296.6
R_2TeCl_2	0.2	1.4	3.8	440.9	2.27–9.07	415.3
R_2TeBr_2	0.6	6.3	14.0	529.8	3.78–9.44	503.1
R_2TeI_2	1.6	9.5	19.1	623.7	3.21–9.62	542.9

*Values reported for 1 : 1 electrolyte[12]: nitrobenzene = 20–30, Nitromethane = 75–95, Acetonitrile = 120–160.

The molecular weights of (2,3-dimethyl-4-hydroxy-phenyl)tellurium(IV) halides in nitrobenzene are given in Table 2. The data in general are consistent with the nature of compounds as predicted by conductance measurements. The molecular weights of R_2TeX_2 are slightly lower than the formula weights at concentration less than 5 mM. But at higher concentrations the molecular weights approach the formula weights. The molecular weights of $RTeBr_3$ and $RTeI_3$ are about one half of the formula weights whereas those of $RTeCl_3$ are close to the formula weight and even greater than the formula weight at higher concentration reflecting some polymerisation. This type of behaviour of trichlorides is also reported for other aryl tellurium trichlorides[6, 14, 15]. The dissociation of the $RTeBr_3$ and $RTeI_3$ compounds which behave as 1 : 1 electrolytes in solution decreases with increasing concentration.

Tellurium-halogen frequencies observed in the far IR spectra of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) halides (Table 3) show good agreement with those reported for other aryltellurium(IV) halides[4–6, 13, 14, 16–18]. The $RTeX_3$ type compounds show the presence of bridged halogen atoms, thus reflecting their polymeric nature in the solid state, whereas, the compounds of R_2TeX_3 composition appear to be monomeric in the solid state having a ψ—TBP structure. It is rather difficult to assign the ν_{Te-C} frequency, as a number of phenyl modes are always present in the region (*ca.* 250 cm^{-1}) where ν_{Te-C} is expected[16, 17]. The —OH stretching frequency remains unchanged on forming the (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) halides from the parent compound and confirms the linkage of tellurium to a carbon atom of the aromatic ring rather than the oxygen atom of the hydroxyl group.

TABLE–3
TELLURIUM-HALOGEN FREQUENCIES (cm^{-1}) FOR (2,3-DIMETHYL-4-HYDROXYPHENYL)TELLURIUM(IV) HALIDES

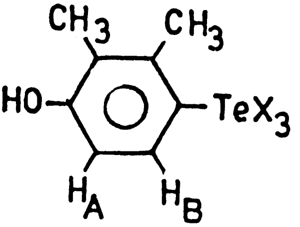
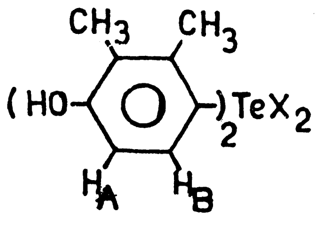
Compound	Cl	Br	I	Assignment
$RTeX_3$	316 m	203 w	168 sh	ν_{Te-X} (terminal)
	285 s	195 m	162 s	
			143 m	
	181 sh	140 m	101 s	$\nu_{Te-X(bridge)} + \delta_{TeX_2}$
	175 m	128 s	95 sh	
	156 s	118 m	86 m	
	143 m	106 m		
	132 m			
R_2TeX_2	285 s	156 m	128 s	$\nu_{sym\ Te-X}$
	256 m	188 s	165 s	$\nu_{asym\ Te-X}$
	139 m	115 m		δ_{TeX_2}
	128 s	104 s		

w = weak, m = medium, s = strong and sh = shoulder.

^1H NMR spectra of (2,3-dimethyl-4-hydroxyphenyl)tellurium(IV) halides (Table 4) showed the aryl proton signals to resonate at lower field than in the parent 2,3-dimethylphenol, thus indicating the deshielding effect of the electron withdrawing halotellurium group. The appearance of two doublets with J = 8–9 Hz in the phenyl proton region indicates the presence of two *ortho* protons on the phenyl ring, indicating thereby the linkage of halotellurium group to a carbon atom *ortho* or *para* to the hydroxyl group. However, the appearance of two distinct type —CH_3 protons at about $\delta_{2.2-2.3}$ ppm, may suggest indirectly the linkage of halotellurium group at the *para* position with respect to —OH group (*ortho* to second methyl group). Methyl protons which are *ortho* to tellurium are deshielded whereas those *ortho* to —OH are shielded because of their electron withdrawing and electron releasing nature respectively. Similarly the phenyl proton which is close to the —OH group (H_A) is most shielded and appears at relatively high field as compared to the other proton (H_B) which appears at low field due to the deshielding effect of the halotellurium group. The hydroxyl protons also appear distinctly at relatively low field. Thus from ^1H NMR studies, it may be concluded that the tellurium is bonded to a carbon atom *para* to the —OH group, which remains intact despite its acidic nature.

TABLE-4

^1H NMR DATA FOR (2,3-DIMETHYL-4-HYDROXYPHENYL)TELLURIUM(IV) HALIDES

Compound	Solvent	Cl	δ ppm Br	I	Assignment
$RTeX_3$	$CDCl_3$	2.18, 2.26	2.22, 2.32	2.22, 2.32	—CH_3
		$6.68, 6.76^{d}$	$6.90, 6.98^{d}$	$6.55, 6.55^{d}$	H_A
		$6.96, 7.06^{d}$	$7.44, 7.52^{d}$	$6.85, 6.95^{d}$	H_B
		8.63	7.90–7.98	7.65	—OH
R_2TeX_2	DMSO-d_6	2,72, 2,40	2.30, 2.42		—CH_3
		$7.03, 7.13^{d}$	$7.04, 7.14^{d}$	*	H_A
		$7.55, 7.63^{d}$	$7.67, 7.75^{d}$		H_B
		7.85–7.90	7.94		—OH

d = doublet

*Spectra not well resolved due to low solubility.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. B.L. Khandelwal, Department of Chemistry, Indian Institute of Technology, Delhi, for getting the infrared and far infrared spectra recorded. One of the authors (SG) is thankful to M.D. University, Rohtak for providing research fellowship.

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(*Received*: 15 March 1994; *Accepted*: 22 June 1994) AJC-837

Medical Chemistry

AFMC INTERNATIONAL MEDICINAL CHEMISTRY SYMPOSIUM (AIMECS–95)

TOKYO, JAPAN

September 3–8, 1995

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