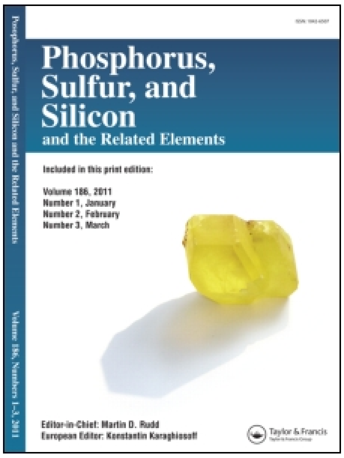

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Studies on 1,10-Phenanthroline Complexes of Some Hydroxyaryltellurium Trihalides

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Studies on 1,10-Phenanthroline Complexes of Some Hydroxyaryltellurium Trihalides

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The synthesis and structural features of some newly synthesized 1,10-phenanthroline complexes of p-hydroxyphenyl- and 3-methyl-4-hydroxyphenyltellurium trihalides (chlorides, bromides, and iodides) are reported. The resulting complexes have been subjected to elemental analyses, conductance and cryoscopic measurements, infra-red and proton magnetic resonance spectral studies. Solution studies reveal the weak to 1:1 electrolyte type behavior of these complexes in solution. Spectral studies indicate the linkage of phenanthroline to the tellurium atom through the nitrogen atoms. Central tellurium atom in these complexes is hexa-coordinated in an octahedral way.

Keywords *p*-Hydroxyphenyltellurium trihalides; 3-methyl-4-hydoxyphenyltellurium trihalides; phenanthroline complexes

INTRODUCTION

Aryltellurium trihalides are known to behave as Lewis acids and form molecular complexes with several nitrogen, oxygen, and sulfur donor bases.[1–14] Tellurium in these complexes is penta- or hexa-coordinated, but the reports on hexa-coordinated complexes are few.[4,9–13] A small number of such compounds are known[6,7] to posses antimicrobial activity, as well. The hydroxyaryltellurium trihalides have two active sites to interact with the nitrogen donor bases: the acidic phenolic proton; and the acceptor tellurium atom. Earlier, we reported[10–13] the complexes of various hydroxyaryltellurium trihalides with pyridine, 2,2′-bipyridyl, piperidine, and thiourea. The present paper describes the synthesis and characterization of 1,10-phenanthroline complexes of hydroxyaryltellurium trihalides derived from phenol and *o*-cresol.

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RESULTS AND DISCUSSION

The formation of *p*-hydroxyphenyltellurium trichloride and 3-methyl-4-hydroxyphenyl-tellurium trichloride by reaction of tellurium tetrachloride with phenol[15,16] and *o*-cresol[15,17] involves the electrophilic substitution of the aromatic ring, by a $TeCl_3^+$ group at a position *para* to the hydroxyl group:

$$R\text{—}H + TeCl_4 \rightarrow RTeCl_3 + HCl. \quad (1)$$

Hydroxyaryltellurium trichlorides undergo halogen-exchange[15–17] when treated with KBr or KI:

$$RTeCl_3 + 3KX \rightarrow RTeX_3 + 3KCl(X{=}Br, I). \quad (2)$$

Reactions of these hydroxyaryltellurium trihalides with 1,10- phenanthroline in 1:1 molar ratio yield $RTeX_3$. Phen type complexes:

$$RTeX_3 + Phen \rightarrow RTeX_3\,.\,Phen. \quad (3)$$

These complexes are colored crystalline solids, fairly stable in dry air, and soluble in polar organic solvents.

Conductance and Cryoscopic Studies

The molar conductance data of ca.10^{-3} M solutions in nitrobenzene, acetone and acetonitrile (Table I) reflect the weak to 1:1 electrolytic behavior of these complexes in solution, presumably due to ionization into $[RTeX_2.Phen]^+$ and X^- ions. Complexes of 3-methyl-4-hydroxyphenyltellurium trihalides appear to be more dissociated than those of *p*-hydroxy phenyltellurium trihalides. Also, the complexes of triiodides appear to be most dissociated and those of trichlorides least dissociated. The lower values of molar conductance than those of 1:1 electrolytes,[18] in some cases, may be due to incomplete dissociation or ion-pair formation.

It has been noted[18] that the concentration ranges selected for such measurements are often arbitrarily chosen and that the method of determination requires the assumption of the molecular weight, which may be erroneous. The complexes that are predicted as 1:1 electrolytes by Λ_M data and have sufficient solubility were, therefore, investigated in acetonitrile over a wider range (1 – 5 mM), and the results subjected to the Onsager Law. Values of equivalent conductance at infinite dilution, Λ_o and $(A + \omega B\Lambda_o)$ are recorded in Table I. A comparison of calculated and experimental values of $(A + \omega B\Lambda_o)$ shows[17,19] the compounds to behave as 1:1 electrolytes. A higher ratio than expected reflects the incomplete dissociation or ion-pair formation. Molecular

TABLE I Molar Conductance, Cryoscopic, and ($A + \omega B\Lambda_o$) Data of Phenanthroline Complexes of Hydroxyaryltellurium Trihalides

R	Complex	Molar conductance Λ_M at ca. 10^{-3} M, $ohm^{-1}\ cm^2\ mol^{-1}$			Formula weight (conc. range, m moles/L	Average Mol. wt. Found	Λ_o (ohm^{-1})	Found Calcd	($A + \omega B\ \Lambda_o$) in acetonitrile	Ratio (found/ calcd.)
		Nitrobenzene	Acetone	Acetonitrile						
p–Hydroxyphenyl	$RTeCl_3$.Phen	14.30	66.41	93.45	507.4 (2.45–3.57)	339.6	—	—	—	—
	$RTeBr_3$.Phen	24.20	116.26	58.62	640.6 (1.75–3.45)	359.3	—	—	—	—
	$RTeI_3$.Phen	19.80	78.90	117.80	781.6 (1.95–3.01)	397.2	132	525.0	329.6	1.592
3-Methyl-4-hydroxyphenyl	$RTeCl_3$.Phen	22.00	66.74	112.81	521.4 (2.32–4.68)	295.5	136	640.0	332.6	1.924
	$RTeBr_3$.Phen	25.30	73.50	62.31	654.6 (2.47–5.75)	328.3	—	—	—	—
	$RTeI_3$.Phen	27.50	96.30	127.23	795.6 (1.09–3.98)	413.7	141	422.2	336.2	1.255

Values ofΛ_M reported[18] for 1 : 1 electrolyte, nitrobenzene = 20–30, acetone = 100–140 and acetonitrile = 120–160.

TABLE II Important IR Spectral Data (cm^{-1}) of Phenanthroline Complexes of Hydroxyaryltellurium Trihalides

R	Complex	$\upsilon_{O—H}$	δ(OH)	$\upsilon_{C=N}$
p-Hydroxyphenyl	$RTeCl_3$.Phen	3400 mb	1380 w 1368 w	1630 w 1614 m
	$RTeBr_3$.Phen	3429 sb	1385 w	1618 m
	$RTeI_3$.Phen	3401 mb	1364 w	1628 m
3-Methyl-4-hydroxyphenyl	$RTeCl_3$.Phen	3306 mb	1390 w 1370 w	1625 w 1616 m
	$RTeBr_3$.Phen	3435 mb	1395 w	1630 w 1613 m
	$RTeI_3$.Phen	3430 mb	1393 w	1626 w

w = weak; m = medium; s = strong; and b = broad.

weights in nitrobenzene (Table I) are much lower than the formula weights, supporting the results of conductance studies.

Infra-Red Spectra

The IR spectra of phenanthroline adducts are quite complex and therefore, an attempt has been made to identify the donor sites of the ligand by comparing the spectra of the complexes with those of parent hydroxyaryltellurium trihalide and phenanthroline.

All the complexes (Table II) show a broad band at about 3400 cm^{-1} (O—H stretching) and at about 1360–1390 cm^{-1} (OH deformation), which reflects the non participation of hydroxyl group of hydroxyaryltellurium trihalides toward bonding with phenanthroline. Several researchers[7–9,20–22] have discussed the IR spectra of phenanthroline and its complexes and have exploited the spectral data for identification of donor sites. In the spectra of phenanthroline complexes, strong bands are expected[20] in three frequency regions namely between 700 and 900 cm^{-1}, between 1125 and 1250 cm^{-1}, and between 1400 and 1650 cm^{-1}. In the spectra of complexes of hydroxyaryltellurium trihalides, the satisfactory assignments of bands in earlier two regions are not possible due to the presence of organyl moiety of $RTeX_3$group. It is the third region that characteristic ring frequencies of phenanthroline occur. The intense bands at about 1500 cm^{-1}, 1590 $cm^{-1}$and 1423 cm^{-1} are reported [20] to move towards higher frequencies on coordination, the 1423 cm^{-1} band being least sensitive. This is the $\upsilon_{C=N}$ band, which most researchers have reported[7–9,21,22] to shift towards higher frequency upon complexation. The complexes of hydroxyaryltellurium trihalides show medium to strong intensity bands around 1610–1630 cm^{-1}, which were not present in the parent hydroxyaryltellurium trihalides. This certainly suggests the linkage of 1,10-phenanthroline molecule to the tellurium atom of $RTeX_3$through the two nitrogen atoms, thus enhancing the coordination number of tellurium to six in these complexes.

Proton Magnetic Resonance Spectra

^1H NMR spectral data for hydroxyaryltellurium trichlorides complexes are presented in Table III.

1,10- Phenanthroline shows[23] four sets of two equivalent protons each at δ 7.62 (a), 7.80 (b), 8.26 (c), and 9.21(d) ppm. Upon complexation with hydroxyaryltellurium trichlorides, these are shifted to downfield side, whereas the aryl protons of hydroxyaryltellurium moiety shift to upfield side. The OH proton of hydroxyaryl group remains intact in the complexes showing its non participation as predicted by IR studies, as well. Although a lot of mixing of signals of protons of phenanthroline and hydroxyaryl groups takes place, yet independent assignments of downfield protons (H_c and H_d) are possible. These results of ^1H NMR spectra suggest the linkage of phenanthroline to the tellurium atom through nitrogen atoms.

On the basis of above spectral evidences, tellurium appears to be hexacoordinated in these phenanthroline complexes, presumably in an octahedral environment. However, in the absence of X-ray studies it is very difficult to assign the exact geometry of the molecules and stereochemical role of the lone pair on tellurium.

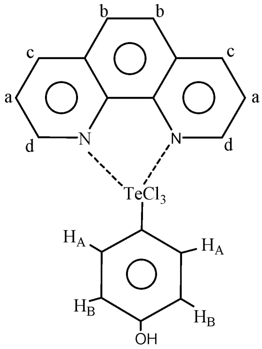
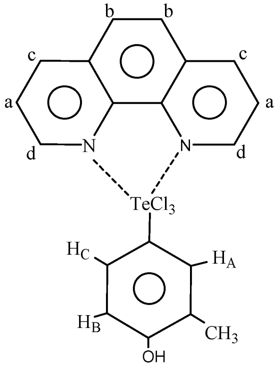
EXPERIMENTAL

All preparations were carried out under an atmosphere of dry nitrogen and the solvents were dried and purified by standard methods [24,25] before use.

Preparation of Hydroxyaryltellurium Trihalides

The *p*-hydroxyphenyltellurium trichloride and 3-methyl-4-hydroxyphenyltellurium trichloride were prepared by reactions of tellurium tetrachloride with phenol and *o*-cresol, respectively.[15–17] The corresponding tribromide and triiodide were prepared by halogen-exchange process using potassium bromide or potassium iodide.[15–17]

TABLE III PMR Spectral Data of Phenanthroline Complexes of Hydroxyaryltellurium Trichlorides in DMSO-d_6

Complex	Chemical shift (δ ppm)	Assignment
	6.84^{d} (2H)	H_B
	$7.82–8.09^{cm}$ (6H)	H_A, H_a, and H_b
	8.58^{d} (2H)	H_c
	9.20^{d} (2H)	H_d
p-$HOC_6H_4TeCl_3$. Phen	9.80^{b} (1H)	OH
	2.31^{s}(3H)	—CH_3 proton
	6.84, 6.98^{b} (1H)	H_B
	$7.70–8.21^{cm}$ (7H)	H_A, H_C, H_a, H_b, and OH
$RTeCl_3$.Phen	8.58^{d} (2H)	H_c
(R = 3-methyl-4-hydroxyphenyl)	9.20^{d} (2H)	H_d

b = broad; d = doublet; cm = complex multiplet; and s = singlet.

Synthesis of 1,10-Phenanthroline Complexes

A saturated solution of 1,10-phenanthroline monohydrate (0.99 g, 5.0 mmol) in about 20 mL dichloromethane was added to a saturated solution of 5.0 mmol (1.64 g, 2.30 g, 3.01 g for p-hydroxyphenyltellurium trichloride, tribromide, triiodide; 1.71 g, 2.37 g, 3.08 g for 3-methyl-4-hydroxyphenyltellurium trichloride, tribromide, and triiodide, respectively) of hydroxyaryltellurium trihalide in about 20 mL dry methanol/

TABLE IV Physical Characteristics and Elemental Analyses of Phenanthroline Complexes of Hydroxyaryltellurium Trihalides

R	Complex (empirical formula)	Color	M.P. °C (dec.)	Yield, %	Elemental analyses found (calcd.) %				
					Te	X	C	H	N
	$RTeCl_3$.Phen	Light pink	188–190	80	24.66	21.23	41.98	2.38	5.22
	($C_{18}H_{13}Cl_3N_2OTe$)				(25.14)	(20.97)	(42.62)	(2.58)	(5.52)
	$RTeBr_3$.Phen	Light green	178–180	80	19.98	37.11	33.26	1.81	4.01
	($C_{18}H_{13}Br_3N_2OTe$)				(19.92)	(37.42)	(33.75)	(2.05)	(4.37)
p-Hydroxyphenyl	$RTeI_3$. Phen	Red	152–155	72	16.10	48.36	27.83	1.36	1.89
	($C_{18}H_{13}I_3N_2OTe$)				(16.33)	(48.71)	(27.66)	(1.68)	(2.04)
	$RTeCl_3$.Phen	Light pink	98–100	90	24.11	20.36	43.28	2.67	5.11
	($C_{19}H_{15}Cl_3N_2OTe$)				(24.48)	(20.40)	(43.78)	(2.90)	(5.37)
3-Methyl-4-	$RTeBr_3$.Phen	Light orange	200–203	85	19.11	36.40	34.21	2.44	4.66
hydroxyphenyl	($C_{19}H_{15}Br_3N_2OTe$)				(19.49)	(36.62)	(34.86)	(2.31)	(4.28)
	$RTeI_3$. Phen	Red	138–141	75	15.80	47.36	28.54	1.67	1.87
	($C_{19}H_{15}I_3N_2OTe$)				(16.04)	(47.85)	(28.68)	(1.90)	(2.01)

chloroform. The contents were refluxed for about 2 h. The solvent was distilled off and the solid thus obtain was extracted with benzene repeatedly and finally with chloroform and then dried over P_4O_{10} in a vacuum dessicator. The complexes were recrystallized from a mixture of methanol and chloroform (50:50).

The purity of these compounds was checked by T.L.C. using silica gel- G. The analytical data and physical properties of the complexes are presented in Table IV.

Analytical Methods and Physical Measurements

Carbon, hydrogen, and nitrogen analyses were obtained microanalytically from sophisticated Analytical Instrumentation Facility, Panjab University, Chandigarh. The tellurium content was estimated volumetrically.[26] Conductivity was measured at 25 ± 2°C with a conductivity bridge type 305 Systronics model and the molecular weights were determined by the cryoscopic method in nitrobenzene up to the saturation point. IR spectra were recorded in the region 4000−400 cm^{-1} at University of Delhi on a SHIMAZDU FTIR - 8300 Spectrometer, using the KBr pellets technique. ^1H NMR spectra were recorded at SAIF, Panjab University, Chandigarh on BRUKER AVANCE II 400 NMR Spectrometer operating at 400.13 MHz in DMSO- $d_6$using tetramethylsilane as an internal reference

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