



SYNTHESIS AND CHARACTERIZATION OF ETHYLENEDIAMINE COMPLEXES OF SOME ARYLTELLEURIUM TRIHALIDES

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ABSTRACT

The synthesis and structural features of some newly synthesized ethylenediamine complexes of aryltellurium trihalides, $R\text{TeX}_3$. EN (R = phenyl, *p*-anisyl, *p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl; X = Cl, Br, I) are reported. The complexes have been subjected to elemental analyses, conductance measurements, molecular weight determination, infrared and proton nuclear magnetic resonance spectral studies. Solution studies reveal their non - electrolyte or weak-electrolyte type behaviour. Spectral studies indicate the linkage of bidentate ethylenediamine molecule to the tellurium atom through the nitrogen atoms; thus, making it hexacoordinated.

Key words: Aryltellurium trihalides, Ethylenediamine, Hexacoordination.

INTRODUCTION

Aryltellurium trihalides are known to behave as Lewis acids and form molecular complexes with several nitrogen, oxygen and sulphur donor bases¹⁻¹⁴. Tellurium in these complexes is penta- or hexa-coordinated, but the reports on hexa-coordinated complexes are quite few^{4,9-13}. A few such complexes are reported^{6,7} to possess bactericidal and fungicidal activities as well. In continuation of our earlier work on the complexes of organytellurium trihalides¹⁰⁻¹⁵ with various N, O and S donors, we hereby report the preparation and properties of some new complexes of aryltellurium trihalides with ethylenediamine.

EXPERIMENTAL

All preparation were carried out under an atmosphere of dry nitrogen and the solvents used were dried^{16,17} and distilled before use.

Preparation of aryltellurium trihalides

Phenyltellurium trichloride, *p*-anisyltellurium trichloride, *p*-hydroxyphenyltellurium trichloride and 3-methyl-4-hydroxyphenyltellurium trichloride were obtained by the reactions of tellurium tetrachloride with triphenyltin chloride¹⁸, anisole^{19,20}, phenol^{21,22} and *o*-cresol^{22,23}, respectively. The corresponding tribromides and triiodides were prepared from respective aryltellurium trichlorides by halogen- exchange processes²¹⁻²⁴.

Preparation of ethylenediamine complexes

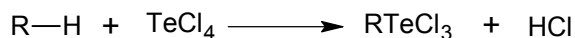
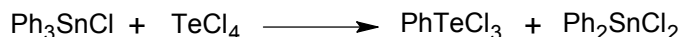
A solution of 5 mmol of ethylenediamine in about 10 mL benzene was added to a saturated solution of 5 mmol of aryltellurium trihalide in ~ 20 mL of dry methanol. The contents were stirred for about 2 h, which resulted in the separation of a solid product. This was filtered, washed with diethyl ether and dried over P₄O₁₀ in a vacuum desiccator. The complexes were recrystallized from dry methanol.

Analytical methods and physical measurements

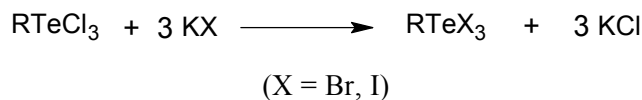
Carbon, hydrogen and nitrogen analyses were obtained microanalytically from Panjab University, Chandigarh. Conductivity was measured at 25 ± 2°C with a conductivity bridge type 305 Systronics model and the molecular weights were determined by cryoscopic methods in nitrobenzene upto the saturation point. Infrared spectra were recorded in KBr pellets in the region 4000 – 400 cm⁻¹ on a Shimadzu FTIR-8300 spectrometer at Delhi University, Delhi and ¹H NMR spectra were obtained from S.A.I.F., Panjab University, Chandigarh on a Bruker Avance II 400 NMR Spectrometer in DMSO-d₆ using TMS as an internal reference.

RESULTS AND DISCUSSION

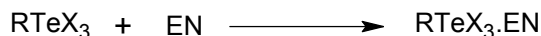
The formation of aryltellurium trichlorides from tellurium tetrachloride¹⁸⁻²³ can be shown as below:



These aryltellurium trichlorides, when reacted with potassium bromide or potassium iodide, are converted into corresponding aryltellurium tribromide or triiodide:



Reactions of these aryltellurium trihalides with ethylenediamine, (EN), yield the 1 : 1 complexes.



These ethylenediamine complexes are light coloured crystalline solids, fairly stable in dry air and soluble in polar organic solvents. The analytical data and physical properties of these complexes are described in Table 1.

Conductance and cryoscopic studies

The solution behaviour of ethylenediamine complexes has been predicted by conductance measurements in nitrobenzene, acetone and acetonitrile and cryoscopic measurements in nitrobenzene upto the saturation point.

The molar conductance, Λ_M values (Table 2) for these complexes are much less than those reported²⁵ for 1 : 1 electrolytes indicating thereby their non-electrolyte or weak-electrolyte type behaviour in solution. The molar conductance values in a particular series generally increases in the order.

$\text{RTeCl}_3 \cdot \text{EN} < \text{RTeBr}_3 \cdot \text{EN} < \text{RTeI}_3 \cdot \text{EN}$, the triiodide complexes being most dissociated. The cryoscopic data for these complexes in nitrobenzene (Table 2) well support the results of conductance measurements.

Infrared spectral studies

The IR spectra of ethylenediamine adducts are quite complex and therefore, an attempt has been made to identify the donor sites of the ligand by comparing spectra of the complexes with those of parent aryltellurium trihalides and ethylenediamine. The most important band of ethylenediamine, which is reported²⁶⁻²⁸ to undergo a significant change upon complexation, is the C – N stretching band. The $\nu_{\text{C-N}}$ appears at $\sim 1060 \text{ cm}^{-1}$ in the parent ligand and it is shifted towards lower frequency in the complexes formed with aryltellurium trihalides, which confirms the bidentate chelating nature of ethylenediamine in these complexes. Similar prediction have been made by Srivastava *et al.*⁶ in $\text{Ph}_2 \text{TeCl}_2 \cdot \text{EN}$.

Table 1: Analytical data, physical properties and yields for ethylenediamine complexes of arytellurium trihalides

RTeX ₃ (R)	Complex (Empirical formula)	Colour (Formula wt.)	Analyses found (calculated) %				M.P., °C (dec.)	Yield (%)
			Te	X	C	H		
RTeCl ₃ (phenyl)	RTeCl ₃ .EN (C ₈ H ₁₃ Cl ₃ N ₂ Te)	Light yellow (371.20)	34.11 (34.38)	28.25 (28.66)	25.39 (25.89)	2.99 (3.53)	7.13 (7.55)	80
RTeBr ₃ (phenyl)	RTeBr ₃ .EN (C ₈ H ₁₃ Br ₃ N ₂ Te)	Dull white (504.50)	24.86 (25.29)	47.24 (47.51)	18.76 (19.05)	2.17 (2.60)	5.37 (5.55)	60
RTeI ₃ (phenyl)	RTeI ₃ .EN (C ₈ H ₁₃ I ₃ N ₂ Te)	Cream (645.50)	19.47 (19.77)	59.35 (59.98)	14.95 (14.89)	2.17 (2.03)	4.13 (4.34)	95
RTeCl ₃ (<i>p</i> -methoxyphenyl)	RTeCl ₃ .en (C ₉ H ₁₅ Cl ₃ N ₂ OTe)	White (401.20)	31.12 (31.81)	26.65 (26.51)	27.35 (26.94)	3.31 (3.77)	6.27 (6.98)	90
RTeBr ₃ (<i>p</i> -methoxyphenyl)	RTeBr ₃ .EN (C ₉ H ₁₅ Br ₃ N ₂ OTe)	Cream (534.50)	23.99 (23.87)	44.44 (44.84)	20.48 (20.22)	2.37 (2.83)	5.10 (5.24)	70
RTeI ₃ (<i>p</i> -methoxyphenyl)	RTeI ₃ .EN (C ₉ H ₁₅ I ₃ N ₂ OTe)	Light yellow (675.50)	19.21 (18.89)	56.58 (56.36)	15.87 (16.00)	2.43 (2.24)	4.34 (4.15)	90
RTeCl ₃ (<i>p</i> -hydroxyphenyl)	RTeCl ₃ .EN (C ₈ H ₁₃ Cl ₃ N ₂ OTe)	Cream (387.20)	32.35 (32.96)	27.65 (27.47)	24.63 (24.82)	3.02 (3.38)	7.00 (7.24)	90
RTeBr ₃ (<i>p</i> -hydroxyphenyl)	RTeBr ₃ .EN (C ₈ H ₁₃ Br ₃ N ₂ OTe)	Light yellow (520.50)	24.78 (24.51)	46.00 (46.05)	18.30 (18.46)	2.67 (2.52)	5.57 (5.38)	80

Cont...

RTeX ₃ (R)	Complex (Empirical formula)	Colour (Formula wt.)	Analyses found (calculated) %				M.P., °C (dec.)	Yield (%)	
			Te	X	C	H			N
RTeI ₃	RTeI ₃ .EN	Yellow	19.43	57.45	14.36	1.43	4.36	220-222	90
(<i>p</i> -hydroxyphenyl)	(C ₈ H ₁₃ I ₃ N ₂ O ₂ Te)	(661.50)	(19.29)	(57.55)	(14.53)	(1.98)	(4.23)		
RTeCl ₃	RTeCl ₃ .en	Light yellow	31.25	26.85	27.11	4.00	5.57	205-207	90
(3-methyl-4-hydroxyphenyl)	(C ₉ H ₁₅ Cl ₃ N ₂ O ₂ Te)	(401.20)	(31.81)	(26.51)	(26.94)	(3.77)	(6.98)		
RTeBr ₃	RTeBr ₃ .EN	Light yellow	24.07	44.35	20.11	2.78	5.35	175-177	60
(3-methyl-4-hydroxyphenyl)	(C ₉ H ₁₅ Br ₃ N ₂ O ₂ Te)	(534.50)	(23.87)	(44.84)	(20.22)	(2.83)	(5.24)		
RTeI ₃	RTeI ₃ .EN	Cream	19.21	56.76	16.31	2.83	3.80	150-153	80
(3-methyl-4-hydroxyphenyl)	(C ₉ H ₁₅ I ₃ N ₂ O ₂ Te)	(675.50)	(18.89)	(56.36)	(16.00)	(2.24)	(4.15)		

Table 2: Molar conductance, molecular weight and infrared data for ethylenediamine complexes of arytellurium trihalides

Compound	Δ_M at ca. 10^{-3} M, $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$		Formula weight	Conc. range, mmol/L	Average mol. wt. found in nitrobenzene	$\nu_{\text{C-N}}$
	Nitrobenzene	Acetone				
RTeCl ₃ .EN (phenyl)	0.55	4.51	44.95	1.61-3.43	366.3	1033 s
RTeBr ₃ .EN (phenyl)	0.65	28.6	*	1.23-4.02	486.4	1006 m
RTeI ₃ .EN (phenyl)	2.31	9.68	*	2.64-7.16	621.8	1035 m
RTeCl ₃ .EN (p-methoxyphenyl)	0.60	2.31	27.5	1.07-3.45	391.6	1010 m
RTeBr ₃ .EN (p-methoxyphenyl)	1.48	31.90	59.2	2.93-3.49	535	1033 vs
RTeI ₃ .EN (p-methoxyphenyl)	17.6	58.30	60.26	1.13-2.84	550.2	1008 s
RTeCl ₃ .EN (p-hydroxyphenyl)	0.55	4.51	*	1.37-2.34	380.6	1034 s
RTeBr ₃ .EN (p-hydroxyphenyl)	0.69	24.20	27.78	2.34-4.16	520.2	1000 m
RTeI ₃ .EN (p-hydroxyphenyl)	8.14	35.20	34.57	2.11-4.97	676.8	1050 m
RTeCl ₃ .EN (3-methyl-4-hydroxyphenyl)	0.66	6.49	40.2	1.00-3.47	387.8	1000 m
RTeBr ₃ .EN (3-methyl-4-hydroxyphenyl)	1.37	48.52	50.43	2.24-4.71	517.8	1006 w
RTeI ₃ .EN (3-methyl-4-hydroxyphenyl)	8.14	66.00	70.82	1.13-4.61	659.3	1005 w

Λ_m reported²⁵ for 1 : 1 electrolyte : nitrobenzene = 20 - 30, acetone = 100 - 140 and acetonitrile = 120 - 160.

* Not soluble; w = weak, m = medium, v = very, s = strong

Thus, tellurium atom in these ethylenediamine complexes acquires a hexacoordination.

¹H NMR spectral studies

Ethylenediamine, H₂N – (CH₂)₂ – NH₂, shows²⁹ two sets of four equivalent protons each at a = 1.19 (4H) and b = 2.74 (4H) δ ppm. The ¹H NMR spectra of ethylenediamine complexes are poorly resolved due to low solubility; the data for two such complexers are given in Table 3.

Table 3. ¹H NMR data for ethylenediamine complexes in DMSO-d₆

Complex	Chemical shift (δ ppm)	Assignment
PhTeCl ₃ . EN	1.27 - 1.37 ^b (4H)	- NH ₂ -
	3.21 ^m (4H)	-CH ₂ (mixed with DMSO-d ₆)
	7.46, 8.21 ^m (5H)	Phenyl
<i>p</i> -HOC ₆ H ₄ TeCl ₃ . EN	1.25 ^b (4H)	-NH ₂
	3.22 ^m (4H)	-CH ₂
	6.96 ^d (9Hz, 2H)	H _B Phenyl
	7.97 ^d (9Hz, 2H)	H _A Phenyl
	8.06 ^b (1H)	-OH

b = broad, d = doublet, m = multiplet

Spectra of *p*-MeOC₆H₄TeCl₃ . EN and RTeCl₃ . EN (R = 3-methyl-4-hydroxyphenyl) not well resolved due to poor solubility.

The –NH₂ and –CH₂- protons in PhTeCl₃.EN and *p*-HOC₆H₄TeCl₃. EN resonate at ~ 1.25 and 3.21 δ ppm, respectively indicating the deshielding of these ligand protons due to shifting of electron density from nitrogen atoms to the tellurium atom. Consequently, the aryl protons of RTeCl₃ appear relatively at upfield side as compared to parent organytellurium trichloride^{3,21,22}. Thus, ¹H NMR spectral studies of these ethylenediamine complexes support the results of infrared spectral studies that tellurium is hexacoordinated in these complexes, presumably in an octahedral environment.

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