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## **Studies on 1, 10- phenanthroline complexes of some diaryltellurium dihalides**

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### **ABSTRACT**

*The synthesis and structural features of some 1, 10-phenanthroline complexes of diaryltellurium dihalides,  $R_2TeX_2 \cdot Phen$  ( $R = p$ -hydroxyphenyl, 3-methyl-4-hydroxyphenyl,  $p$ -methoxyphenyl and  $X = Cl, Br, I$ ) are reported. These 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 behaviour of these complexes in solution. Spectral studies suggest the linkage of phenanthroline to the tellurium atom through the nitrogen atoms. An octahedral environment around the tellurium atom has been suggested.*

**Keywords:** diaryltellurium dihalides, phenanthroline complexes, conductance, cryoscopy, spectral studies.

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### **INTRODUCTION**

Aryltellurium trihalides are known to behave as Lewis acids and form molecular complexes with several nitrogen, oxygen and sulphur donor bases but such reports on diaryltellurium dihalides are relatively less in number [1-13]. It has been reported that Lewis acidity of tellurium atom falls significantly on going from  $RTeX_3$  to  $R_2TeX_2$  [14] A few such compounds are known [1,12] to possess antimicrobial activity as well. In continuation of our work on phenanthroline complexes of organotellurium trihalides [15], we hereby report the synthesis and characterization of 1,10- phenanthroline complexes of some diaryltellurium dihalides.

### **EXPERIMENTAL SECTION**

#### **Materials and Methods**

The chemicals, tellurium tetrachloride (Aldrich), phenol, *o*-cresol, anisole and 1,10 phenanthroline monohydrate (LOBA Chemie) were of reagent grade. The solvents were purified

and dried before use. Bis(*p*-hydroxyphenyl)tellurium dichloride, bis(3-methyl-4-hydroxyphenyl)tellurium dichloride and bis(*p*-methoxyphenyl)tellurium dichloride were obtained by reactions of tellurium tetrachloride with phenol [16], *o*-cresol [17] and anisole [18] respectively. The diaryltellurium dichlorides were converted to corresponding dibromides and diiodides by halogen- exchange processes [16-19] by using KBr or KI in dry methanol.

#### **Preparation of 1, 10-Phenanthroline Complexes**

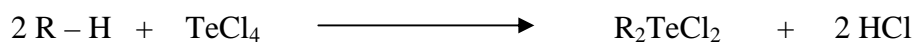
A saturated solution of 1, 10-phenanthroline (0.99 g, 5 mmol) in chloroform (~10 ml) was added with constant stirring to a saturated solution of 5.0 mmol of R<sub>2</sub>TeX<sub>2</sub> in about 20 ml of dry methanol in a R.B. flask. The contents were stirred for about 2-3 h under an atmosphere of dry N<sub>2</sub>. This resulted in the separation of a coloured solid product. This was filtered, washed with chloroform and dried over P<sub>4</sub>O<sub>10</sub> in vacuum desiccator.

#### **Physical Measurements**

The conductance measurements in nitrobenzene, acetone and acetonitrile were performed on a Systronic type 305 conductivity bridge at 25 ± 2° C using a dip type cell with smooth platinum electrodes. The molecular weights were determined cryoscopically in purified nitrobenzene using a Beckmann's freezing point apparatus. The IR spectra (4000-400cm<sup>-1</sup>) were recorded in KBr pellets on a Perkin Elmer Model 2000 FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded on BRUKER AC-300F operating at 299.9486 MHz in DMSO - d<sub>6</sub> using tetramethylsilane as an internal reference. The spectral data were obtained from SAIF, Panjab University, Chandigarh.

## **RESULTS AND DISCUSSION**

Tellurium tetrachloride when heated with phenol, *o*-cresol, or anisole appears to undergo Friedel-Crafts type condensation reaction whereby, TeCl<sub>3</sub><sup>+</sup> unit attacks a position *para* to the electron releasing (-OH / -OCH<sub>3</sub>) groups in the aromatic ring, resulting in the formation of diorganyltellurium dichlorides [16,17].

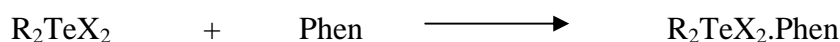


(R = *p*-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, *p*-methoxyphenyl)

These diaryltellurium dichlorides when treated with KBr/KI undergo halogen-exchange processes to yield the corresponding dibromides and diiodides.



These diaryltellurium dihalides when reacted with 1,10-phenanthroline give 1 : 1 type complexes.



All the complexes have been analysed for their tellurium, halogen, C, H, N contents and the analytical data are presented in Table-1.

These complexes are generally coloured crystalline solids which are stable in dry air. These are generally soluble in polar organic solvents.

**Conductance and cryoscopic studies**

The molar conductance and cryoscopic data for 1,10-phenanthroline complexes are presented in Table 2.

**Table 1. Analytical data, physical properties and yields for 1, 10-phenanthroline complexes**

Complex (R)	Empirical formula (Colour)	Analyses Found (Calculated) %					M.P. °C (dec.)	Yield %
		Te	X	C	H	N		
R <sub>2</sub> TeCl <sub>2</sub> .Phen ( <i>p</i> -hydroxyphenyl)	C <sub>24</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Orange brown)	22.34 (22.59)	12.43 (12.55)	50.20 (51.03)	2.84 (3.21)	5.10 (4.96)	186-188	80
R <sub>2</sub> TeBr <sub>2</sub> .Phen ( <i>p</i> -hydroxyphenyl)	C <sub>24</sub> H <sub>18</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Reddish brown)	20.40 (19.52)	23.60 (24.44)	43.70 (44.09)	3.40 (2.77)	4.11 (4.28)	175-177	78
R <sub>2</sub> TeI <sub>2</sub> .Phen ( <i>p</i> -hydroxyphenyl)	C <sub>24</sub> H <sub>18</sub> I <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Grey)	16.37 (17.06)	33.33 (33.94)	37.82 (38.55)	2.37 (2.43)	3.48 (3.75)	150-152	78
R <sub>2</sub> TeCl <sub>2</sub> .Phen (3-methyl-4-hydroxyphenyl)	C <sub>26</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Orange brown)	20.78 (21.52)	10.99 (11.96)	53.20 (52.66)	3.63 (3.74)	4.57 (4.72)	95-97	70
R <sub>2</sub> TeBr <sub>2</sub> .Phen (3-methyl-4-hydroxyphenyl)	C <sub>26</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Orange brown)	19.20 (18.71)	22.93 (23.44)	45.09 (45.80)	3.51 (3.25)	4.13 (4.11)	200-202	68
R <sub>2</sub> TeI <sub>2</sub> .Phen (3-methyl-4-hydroxyphenyl)	C <sub>26</sub> H <sub>22</sub> I <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Shining chocolate brown)	17.10 (16.45)	31.87 (32.71)	39.93 (40.25)	2.76 (2.86)	3.14 (3.61)	140-142	75
R <sub>2</sub> TeCl <sub>2</sub> .Phen ( <i>p</i> -methoxyphenyl)	C <sub>26</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Very light pink)	20.77 (21.52)	11.78 (11.96)	53.31 (52.66)	3.66 (3.74)	4.92 (4.72)	136-138	65
R <sub>2</sub> TeBr <sub>2</sub> .Phen ( <i>p</i> -methoxyphenyl)	C <sub>26</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Light purple)	19.01 (18.71)	22.38 (23.44)	44.92 (45.80)	4.12 (3.25)	3.78 (4.11)	148-150	70
R <sub>2</sub> TeI <sub>2</sub> .Phen ( <i>p</i> -methoxyphenyl)	C <sub>26</sub> H <sub>22</sub> I <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Te (Brown)	16.21 (16.45)	32.15 (32.71)	39.74 (40.25)	2.49 (2.86)	3.23 (3.61)	158-160	72

The  $\Lambda_M$  values for 1,10-phenanthroline complexes of bis(*p*-anisyl)tellurium dihalide complexes in nitrobenzene, acetone and acetonitrile are lower than the values reported [20] for 1 : 1 electrolytes reflecting their partial dissociation or weak electrolyte type behaviour in these solvents. The phenanthroline complexes of bis(hydroxyaryl)tellurium dihalides, where the  $\Lambda_M$  values at *ca.* 10<sup>-3</sup> M in nitrobenzene and acetonitrile are close to the ranges reported for 1 : 1 electrolyte, appear to behave as weak to 1 : 1 electrolyte probably dissociating into (R<sub>2</sub>TeX. Phen)<sup>+</sup> and X<sup>-</sup> ions in these solvents. The  $\Lambda_M$  values of these phenanthroline complexes in acetone reflect the weak electrolyte type nature in acetone.

**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 diaryltellurium dihalide and phenanthroline.

All the bis(hydroxyaryl)tellurium dihalide complexes (Table 3) show a medium broad band at 3450-3200 cm<sup>-1</sup> (O- H stretching) and at 1344-1336 cm<sup>-1</sup> (OH deformation) which reflect the non participation of hydroxyl group of bis(hydroxyaryl)tellurium dihalides toward bonding with phenanthroline. Several workers [1,21-23] 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 [21] in three frequency regions namely between 700 and 900 cm<sup>-1</sup>, between 1125 and 1250 cm<sup>-1</sup> and between 1400 and 1650 cm<sup>-1</sup>. In the spectra of complexes of diaryltellurium dihalides, the satisfactory assignments of bands in earlier two regions are not possible due to the presence of organyl moiety of R<sub>2</sub>TeX<sub>2</sub> group. It is

the third region that characteristic ring frequencies of phenanthroline occur. The intense bands at about  $1500\text{ cm}^{-1}$ ,  $1590\text{ cm}^{-1}$  and  $1423\text{ cm}^{-1}$  are reported [21] to move towards higher frequencies on coordination, the  $1423\text{ cm}^{-1}$  band being least sensitive. This is the  $\nu_{\text{C=N}}$  band, which the most workers have reported [1,15,22,23] to shift towards higher frequency upon complexation. The complexes of diaryltellurium dihalides show medium to strong intensity bands around  $1601\text{--}1655\text{ cm}^{-1}$ , which were not present in the parent  $\text{R}_2\text{TeX}_2$ . This certainly suggests the linkage of 1,10-phenanthroline molecule to the tellurium atom of  $\text{R}_2\text{TeX}_2$  through the two nitrogen atoms, thus enhancing the coordination number of tellurium to six in these complexes.

**Table 2. Molar conductance and cryoscopic data for 1, 10-phenanthroline complexes**

Compound	$\Lambda_M$ at ca. $10^{-3}\text{ M}$ , $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$			Formula weight	Conc. Range, mmol/L	Avg mol wt. found in nitrobenzene
	Nitrobenzene	Acetone	Acetonitrile			
$\text{R}_2\text{TeCl}_2\cdot\text{Phen}$ ( $R=p$ -hydroxyphenyl)	23.98	78.00	116.80	564.9	1.74-3.48	382.5
$\text{R}_2\text{TeBr}_2\cdot\text{Phen}$ ( $R=p$ -hydroxyphenyl)	27.50	62.20	99.96	653.8	1.94-3.76	480.6
$\text{R}_2\text{TeI}_2\cdot\text{Phen}$ ( $R=p$ -hydroxyphenyl)	20.56	96.30	104.57	747.8	1.38-3.83	510.1
$\text{R}_2\text{TeCl}_2\cdot\text{Phen}$ ( $R=3$ -Methyl-4-hydroxyphenyl)	20.75	88.73	121.44	592.9	1.39-3.43	336.8
$\text{R}_2\text{TeBr}_2\cdot\text{Phen}$ ( $R=3$ -Methyl-4-hydroxyphenyl)	21.36	93.14	88.56	681.9	1.88-3.87	451.2
$\text{R}_2\text{TeI}_2\cdot\text{Phen}$ ( $R=3$ -Methyl-4-hydroxyphenyl)	17.32	121.0	124.86	775.9	1.47-3.16	408.9
$\text{R}_2\text{TeCl}_2\cdot\text{Phen}$ ( $R=p$ -methoxyphenyl)	14.57	69.77	120.06	592.9	1.85-4.19	463.2
$\text{R}_2\text{TeBr}_2\cdot\text{Phen}$ ( $R=p$ -methoxyphenyl)	15.23	66.81	82.10	681.9	1.65-4.19	570.4
$\text{R}_2\text{TeI}_2\cdot\text{Phen}$ ( $R=p$ -methoxyphenyl)	12.73	75.42	118.50	775.9	1.48-3.74	588.2

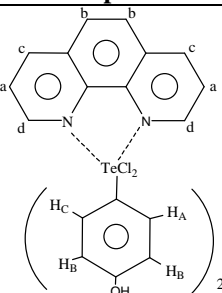
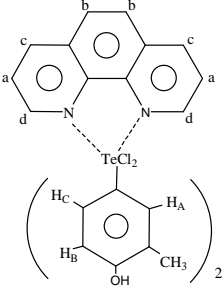
$\Lambda_M$  reported [20] for 1: 1 electrolyte: nitrobenzene = 20 - 30, acetone = 100 - 140 and acetonitrile = 120 - 160.

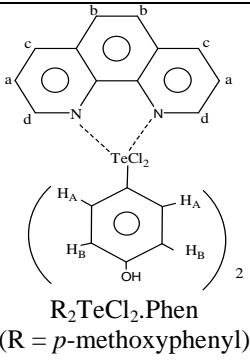
Table 3. IR Data for 1,10-phenanthroline complexes

Complex	$\nu$ (O-H)	$\nu$ (C=N)	$\delta$ (OH)
R <sub>2</sub> TeCl <sub>2</sub> .Phen (R= <i>p</i> -hydroxyphenyl)	3400-3200 mb	1634 s	1342 m
R <sub>2</sub> TeBr <sub>2</sub> .Phen (R= <i>p</i> -hydroxyphenyl)	3429-3220 mb	1637 s 1618 m	1340 m
R <sub>2</sub> TeI <sub>2</sub> .Phen (R= <i>p</i> -hydroxyphenyl)	3461-3200 mb	1640 s 1619 m	1344 m
R <sub>2</sub> TeCl <sub>2</sub> .Phen (R=3-Methyl-4-hydroxyphenyl)	3360-3280 mb	1640 m 1614 m 1601 m	1337 m
R <sub>2</sub> TeBr <sub>2</sub> .Phen (R=3-Methyl-4-hydroxyphenyl)	3335-3240 mb	1645 m 1615 m	1337 m
R <sub>2</sub> TeI <sub>2</sub> .Phen (R=3-Methyl-4-hydroxyphenyl)	3409-3240 mb	1615 m	1336 w
R <sub>2</sub> TeCl <sub>2</sub> .Phen (R= <i>p</i> -methoxyphenyl)	-	1653 m	-
R <sub>2</sub> TeBr <sub>2</sub> .Phen (R= <i>p</i> -methoxyphenyl)	-	1647 m	-
R <sub>2</sub> TeI <sub>2</sub> .Phen (R= <i>p</i> -methoxyphenyl)	-	1655 m	-

*s* = strong, *m* = medium, *w* = broad

Table 4. <sup>1</sup>H NMR data (δ ppm) for 1,10-phenanthroline complexes in DMSO-d<sub>6</sub>.

Compound	Chemical Shift	Assignment
 R <sub>2</sub> TeCl <sub>2</sub> .Phen (R = <i>p</i> -hydroxyphenyl)	6.90 <sup>d</sup> (4H) 7.79 <sup>d</sup> , 7.83 <sup>m</sup> , 8.10 <sup>d</sup> (8H) 8.47 <sup>d</sup> (2H) 9.23 <sup>d</sup> (2H) 9.90 <sup>b</sup> (2H)	H <sub>B</sub> H <sub>a</sub> , H <sub>b</sub> + H <sub>A</sub> H <sub>c</sub> H <sub>d</sub> -OH
 R <sub>2</sub> TeCl <sub>2</sub> .Phen (R = 3-methyl-4-hydroxyphenyl)	2.18 <sup>s</sup> (6H) 6.81, 6.96 <sup>b</sup> (2H) 7.78, 7.91, 8.01 - 8.20 <sup>cm</sup> (8H) 8.74 <sup>d</sup> (2H) 9.23 <sup>d</sup> (2H) 9.69 <sup>b</sup> (2H)	-CH <sub>3</sub> protons H <sub>B</sub> H <sub>a</sub> , H <sub>b</sub> , H <sub>c</sub> + H <sub>A</sub> H <sub>c</sub> H <sub>d</sub> -OH

 <p style="text-align: center;">R<sub>2</sub>TeCl<sub>2</sub>.Phen (R = <i>p</i>-methoxyphenyl)</p>	3.85 <sup>s</sup>	(6H)	-OCH <sub>3</sub>
	7.02 <sup>d</sup>	(4H)	H <sub>B</sub>
	7.81-7.84 <sup>m</sup> , 7.91-8.0 <sup>m</sup>	(8H)	H <sub>a</sub> , H <sub>b</sub> , H <sub>c</sub>
	8.52 <sup>d</sup>	(2H)	H <sub>c</sub>
	9.18 <sup>d</sup>	(2H)	H <sub>d</sub>

*s* = singlet, *b* = broad, *m* = multiplet, *cm* = complex multiplet, *d* = doublet

The cryoscopic data of these complexes in nitrobenzene generally support the predictions of conductance measurements.

### Proton Magnetic Resonance Spectra

<sup>1</sup>H NMR spectral data for 1,10-phenanthroline complexes are presented in Table 4. 1,10-Phenanthroline shows [24] 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 R<sub>2</sub>TeCl<sub>2</sub> these are shifted to downfield side, whereas the aryl protons of diaryltellurium moiety shift to upfield side. The OH protons of hydroxyaryl group in their complexes remains intact, showing its non participation as predicted by IR studies as well. Although a lot of mixing of signals of protons of phenanthroline and diaryl groups takes place, yet independent assignment of downfield proton (H<sub>c</sub> and H<sub>d</sub>) are possible. These results of <sup>1</sup>H 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 a *distorted octahedral* environment.

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