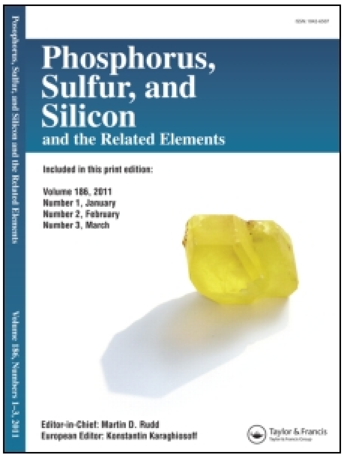

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# STUDIES ON THIOUREA COMPLEXES OF SOME HYDROXYARYLTELLURIUM TRICHLORIDES

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# STUDIES ON THIOUREA COMPLEXES OF SOME HYDROXYARYLTELLURIUM TRICHLORIDES

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The synthesis and structural features of some newly synthesized thiourea complexes of hydroxyaryltellurium trichlorides derived from isomeric cresols and ortho-chlorophenol is reported. The resulting complexes have been subjected to elemental analyses, conductance measurements, molecular weight determination and infra-red spectral studies. Solution studies reveal the weak-electrolyte and non-electrolyte type behavior respectively for 1:1 and 1:2 thiourea complexes, except the 1:2 thiourea complex of hydroxyaryltellurium trichloride derived from ortho-chlorophenol, which behaves as 1:1 electrolyte in solution. Spectral studies indicate the linkage of thiourea to the tellurium atom through the sulfur atom.

*Keywords:* Hydroxyaryltellurium trichlorides-thiourea complexes; synthesis and characterization

## INTRODUCTION

Thiourea is known[1–5] to reduce aryltellurium trichlorides to aryltellurium chlorides and then form the 1:1 adduct, $RTeCl.SC(NH_2)_2$, when the aryltellurium trichloride in methanol is mixed with thiourea in water in a 1:3 molar ratio. Addition of a little concentrated hydrochloric acid to a mixture containing the reagents in a 1:5 molar ratio produces the 1:2 adduct, $RTeCl.2SC(NH_2)_2$[2]. However, similar reactions of thiourea with *p*-methoxy-[6], *p*-phenoxy-[6] and *p*-ethoxyphenyltellurium trichlorides[7] in organic solvents are known to yield the 1:1, $RTeCl_3.Tu$ type complexes. These complexes are also reported to possess considerable antibacterial and antifungal[6,7]activities. Recently we have reported[8] the formation of

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1:1 as well as 1:2 type complexes of thiourea with 4-hydroxyphenyltellurium trichloride. The present paper describes the synthesis and characterization of thiourea complexes of hydroxyaryltellurium trichlorides derived from isomeric cresols and *o*-chlorophenol.

## RESULTS AND DISCUSSION

The formation of 3-methyl-4-hydroxyphenyltellurium trichloride and 3-chloro-4-hydroxyphenyltellurium trichloride by reactions of tellurium tetrachloride with *o*-cresol[9,10] and *o*-chlorophenol[9,11] involves the electrophilic substitution of the aromatic ring, by a $TeCl_3^+$ group at a position *para* to the hydroxyl group

$$\text{R-H} + TeCl_4 \rightarrow RTeCl_3 + HCl$$

Similar reactions of tellurium tetrachloride with *meta* and *para* cresols, however, do not yield the $RTeCl_3$ type compound and higher organyl derivatives are reported[9,10]. Thus, the hydroxyaryltellurium trichlorides derived from *meta* and *para*-cresols are obtained by the mercuration method[1,12].

$$\text{R-HgCl} + TeCl_4 \rightarrow RTeCl_3 + HgCl_2.$$

(R = 2-methyl-4-hydroxyphenyl and 3-methyl-6-hydroxyphenyl)

Reactions of these methyl- and chlorohydroxyphenyltellurium trichlorides with thiourea in different molar ratios yield $RTeCl_3$.Tu and $RTeCl_3$.2Tu type complexes.

$$RTeCl_3 + SC(NH_2)_2 \rightarrow RTeCl_3.SC(NH_2)_2.$$
$$RTeCl_3 + 2\,SC(NH_2)_2 \rightarrow RTeCl_3.2SC(NH_2)_2.$$

These complexes are colored crystalline solids, fairly stable in dry air except those of *meta* cresol *and ortho*-chlorophenol (1:2) which are hygroscopic in nature. These are soluble in polar organic solvents.

### Conductance and Cryoscopic Studies

The molar conductance data (Table I) in nitrobenzene, acetonitrile and acetone reflect the 1:1 electrolyte type behavior of $RTeCl_3$. 2Tu complex derived from *o*-chlorophenol, where the values of $\Lambda_M$ are close or within the range reported[13] for 1 :1 electrolytes. The 1:2 complexes of methylhydroxyphenyltellurium trichlorides, however, are non-electrolytes in these solvents. All the 1:1, $RTeCl_3.Tu$ complexes have values of molar conductance much lower than those reported for 1:1 electrolytes, exhibiting their weak electrolytic behavior in solution. The cryoscopic data for complexes having sufficient solubility in nitrobenzene (Table I) well support the results of conductance measurements.

## Infra-red Spectra

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

All the complexes show a strong band at about 3500–3300 $cm^{-1}$ (O-H stretching) and a medium to strong intensity band at about 1350 $cm^{-1}$ (OH deformation), which reflects the non participation of the hydroxyl group of hydroxyaryltellurium trichlorides towards bonding with thiourea.

The N-H stretching (3365–3090 $cm^{-1}$, mixed with O-H stretching) and $NH_2$ bending (1612 $cm^{-1}$) bands in thiourea do not suffer a shift towards lower frequencies upon complexation. This rules out the linkage of thiourea through nitrogen atoms[14–17], and thus the bonding should be through the sulfur atom. This is expected since sulfur is a relatively better donor than nitrogen, as the lone pair on nitrogen is not readily available for donation as indicated by crystal structure[18], dipole moment[19] and NMR studies[20].

The important IR frequencies of thourea and its complexes are given in Table II.The 1468 $cm^{-1}$ band of thiourea (N-C-N stretching) suffers a positive shift in the complexes. This shift can be explained due to greater double bond character of the C to N bond on complexation due to linkage through the sulfur atom[15,16]. The 1420 $cm^{-1}$ band of thiourea appears at 1402–1412 $cm^{-1}$ in the complexes. A conspicuous difference in the spectra of thiourea and its complexes is that thiourea shows a strong band at 1083 $cm^{-1}$ and this band weakens in the complexes due to a change in the nature of the N-C bond as well as of the C=S bond on coordination through the sulfur. In these complexes, the N-C-N stretching frequency is increased and the C=S stretching frequency is decreased. Therefore, contribution of C=S to this band is decreased and the intensity of the band is reduced. The symmetrical N-C-N stretching vibration cannot contribute much to this intensity. Another composite band of thiourea, which is shifted to a lower frequency due to decreased C=S character, is the 730 $cm^{-1}$ band. All these shifts in IR bands of thiourea upon complexation, confirms[6,7,21,22] the linkage of thiourea to the tellurium atom of hydroxyaryltellurium trichlorides through the sulfur atom.

TABLE I Molar conductance and molecular weight data of thiourea complexes of hydroxyaryltellurium trichlorides

| *Parent Hydroxybenzene* | *Complex* | *Molar conductance $\Lambda_M$ at ca. $10^{-3}M$* | | | *Conc. range m moles/L* | *Formula weight* | *Average Mol. Wt. found* |
|---|---|---|---|---|---|---|---|
| | | *$Ohm^{-1}\ cm^2\ mol^{-1}$* | | | | | |
| | | *Nitrobenzene* | *Acetonitrile* | *Acetone* | | | |
| *o*-Cresol | $RTeCl_3$.Tu | 16.8 | 69.9 | 56.9 | 3.19–3.99 | 417.2 | 202.9 |
| | $RTeCl_3$.2Tu | 2.8 | 30.1 | 26.6 | 3.33–8.78 | 493.3 | 484.7 |
| *m*-Cresol | $RTeCl_3$.Tu | 7.7 | 60.1 | 60.1 | * | 417.2 | -- |
| | $RTeCl_3$.2Tu | 2.4 | 33.1 | 22.0 | 3.33–8.78 | 493.3 | 478.9 |
| *p*-Cresol | $RTeCl_3$.Tu | 9.7 | 60.1 | 50.1 | * | 417.2 | -- |
| | $RTeCl_3$.2Tu | 0.75 | 14.5 | 15.0 | 3.33–8.78 | 493.3 | 491.8 |
| *o*-Chlorophenol | $RTeCl_3$.Tu | 6.06 | 49.60 | 38.57 | * | 437.7 | -- |
| | $RTeCl_3$.2Tu | 33.06 | 120.24 | 70.14 | 3.24–8.43 | 513.8 | 265.8 |

Values of $\Lambda_M$ reported[13] for 1:1 electrolyte, nitrobenzene = 20–30, acetonitrile = 120–160 and acetone = 100–140.

*Insufficient solubility

TABLE II IR data of thiourea complexes of hydroxyaryltellurium trichlorides

| *Compound (parent hydroxy benzene)* | *N-C-N stretch. (cm$^{-1}$)* | *$NH_2$ rocking + N-C-N and C=S stretch (cm$^{-1}$)* | *Composite band (cm$^{-1}$)* | *Composite band (cm$^{-1}$)* |
|---|---|---|---|---|
| Thiourea | 1468 vs | 1420 s | 1083 s | 730 w |
| $RTeCl_3.Tu$ (*o*-cresol) | 1500 m | 1404 s | 1080 w | 706 w<br>690 w |
| $RTeCl_3.2Tu$ (*o*-cresol) | 1500 s | 1412 m | 1070 vw | 700 w |
| $RTeCl_3.Tu$ (*m*-cresol) | 1516 m<br>1484 vs | 1404 m | 1080 vw | 698 w |
| $RTeCl_3.2Tu$ (*m*-cresol) | 1484 m | 1404 s | 1075 vw | 696 m |
| $RTeCl_3.Tu$ (*p*-cresol) | 1500 m | 1402 m | - | 700 m |
| $RTeCl_3.2Tu$ (*p*-cresol) | 1500 w<br>1484 m | 1404 m | 1075 vw | 710 w<br>690 vw |
| $RTeCl_3.Tu$ (*o*-chlorophenol) | 1500 m<br>1484 s | 1404 m | 1080 w | 714 vw<br>690 vw |
| $RTeCl_3.2Tu$ (*o*-chlorophenol) | 1500 s<br>1484 s | 1408 m | 1080 w | 702 w |

w = weak, m = medium, s = strong, vs = very strong.

On the basis of above spectral evidence tellurium appears to be pentacoordinated in $RTeCl_3.Tu$ complexes, whereas, it acquires a coordination number of six in $RTeCl_3.2Tu$ complexes. 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. The $RTeCl_3.Tu$ complexes most likely display a square pyramidal structure with the organo-group occupying the apical position as observed in other complexes of this nature[6–8,23–26]. The $RTeCl_3.2Tu$ complexes, are even more difficult to predict in the absence of more definitive structural data due to the presence of a lone pair of electrons in the valence shell and the possibilities of geometrical isomerism.

## EXPERIMENTAL

All preparations were carried out under an atmosphere of dry nitrogen and the solvents used were dried and distilled before use.

## Preparation of Hydroxyaryltellurium Trichlorides

The 3-methyl-4-hydroxyphenyltellurium trichloride and 3-chloro-4-hydroxyphenyltellurium trichloride were prepared by reactions of tellurium tetrachloride with *ortho*-cresol and *ortho*-chlorophenol respectively[9–11]. The corresponding hydroxyaryltellurium trichlorides of *meta* and *para* cresols were prepared by the mercuration method[1,12].

## Synthesis of Thiourea Complexes

### $RTeCl_3.Tu$ *(R = 3-methyl-4-hydroxyphenyl and 3-chloro-4-hydroxyphenyl)*

A saturated solution of 5 mmol of thiourea in methanol was added to a saturated solution of 5 mmol of hydroxyaryltellurium trichloride in the same solvent. The contents were refluxed for 3–4 hours and then concentrated under reduced pressure to about one third of the original volume and kept overnight in a vacuum desiccator to yield the crystals of the complex. They were then filtered, washed with chloroform and dried in vacuo.

### $RTeCl_3.Tu$ *(R = 2-methyl-4-hydroxyphenyl and 3-methyl-6-hydroxyphenyl)*

A saturated solution of 5 mmol of thiourea in methanol was added to a saturated solution of 5 mmol of hydroxyaryltellurium trichloride in the same solvent. The contents upon stirring for about 3–4 hours yielded the solid complex, which was filtered, washed and dried as above.

### $RTeCl_3.2Tu$ *(R = methylhydroxyphenyl and chlorohydroxyphenyl)*

A saturated solution of 5 mmol of $RTeCl_3$ in dry methanol was added to a saturated methanolic solution of 10 mmol of thiourea, slowly and with constant stirring. The solid product that separated was filtered, washed with chloroform and dried in vacuo.

The complexes were recrystallized from dry acetone or acetonitrile and the purity was checked by T.L.C. using silica gel-G. The analytical data and physical properties of the complexes are reported in Table III.

TABLE III Physical characteristics and elemental analyses of thiourea complexes of hydroxyaryltellurium trichlorides

| *Parent hydroxybenzene* | *Complex (Empirical formula)* | *Color* | *M.P.°C (dec.)* | *Yield (%)* | *Elemental analysis (%)* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *C Found (Calcd.)* | *H Found Calcd.)* | *N Found (Calcd.)* | *S Found (Calcd.)* | *Te Found Calcd.)* | *Cl Found (Calcd.)* |
| *o*-Cresol | $RTeCl_3$.Tu<br>($C_8H_{11}ON_2STeCl_3$) | Black | 62–65 | 80 | 21.82<br>(22.99) | 2.58<br>(2.65) | 5.88<br>(6.70) | 8.32<br>(7.68) | 29.92<br>(30.56) | 25.68<br>(25.50) |
| | $RTeCl_3$.2Tu<br>($C_9H_{15}ON_4S_2TeCl_3$) | Dark brown | 102–105 | 85 | | | | 1 3.44<br>(13.00) | 24.68<br>(25.84) | 20.98<br>(21.57) |
| *m*-Cresol | $RTeCl_3$.Tu<br>($C_8H_{11}ON_2STeCl_3$) | Dark brown | Hygroscopic | 75 | 22.94<br>(22.99) | 2.58<br>(2.65) | 5.90<br>(6.70) | 7.28<br>(7.68) | 30.42<br>(30.56) | 24.98<br>(25.50) |
| | $RTeCl_3$.2Tu<br>($C_9H_{15}ON_4S_2TeCl_3$) | Yellow Green | Hygroscopic | 85 | | | | 12.58<br>(13.00) | 24.92<br>(25.84) | 20.86<br>(21.57) |
| *p*-Cresol | $RTeCl_3$.Tu<br>($C_8H_{11}ON_2STeCl_3$) | Dark violet | 77–80 | 70 | 22.40<br>(22.99) | 2.38<br>(2.65) | 5.90<br>(6.70) | 7.34<br>(7.68) | 30.52<br>(30.56) | 24.60<br>(25.50) |
| | $RTeCl_3$.2Tu<br>($C_9H_{15}ON_4S_2TeCl_3$) | Dark Yellow | 168–170 | 80 | | | | 12.57<br>(13.00) | 25.62<br>(25.84) | 20.62<br>(21.57) |
| *o*-Chlorophenol | $RTeCl_3$.Tu<br>($C_7H_8ON_2STeCl_4$) | Black | 125–132 | 65 | 19.12<br>(19.21) | 1.92<br>(1.84) | 6.28<br>(6.40) | 7.08<br>(7.32) | 29.20<br>(29.15) | 31.98<br>(32.44) |
| | $RTeCl_3$.2Tu<br>($C_9H_{15}ON_4S_2TeCl_4$) | Dark brown | Hygroscopic | 70 | 18.19<br>(18.69) | 2.30<br>(2.35) | 10.38<br>(10.90) | 12.08<br>(12.48) | 24.36<br>(24.83) | 27.20<br>(27.64) |

## Analytical Methods and Physical Measurements

Carbon, hydrogen and nitrogen analyses were obtained microanalytically from the Chemistry Department, Indian Institute of Technology , New Delhi. Conductivity was measured at 35 ± 1°C with a conductivity bridge type 305 Systronics model and the molecular weights were determined by the cryoscopic method in nitrobenzene. IR spectra were recorded at Indian institute of Technology, New Delhi on a NICOLET-DX IR spectrophotometer using KBr pellets.

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