Studies on Some Schiff Bases Complexes of Diaryltellurium(IV)

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ABSTRACT

Salicyldehyde-2-hydroxyanil (H₂SAP) and salicyldehyde-2-mercaptoanil (H₂SSP) have been prepared by the condensation of salicyldehyde with 2-aminophenol and 2-aminothiophenol, respectively. Reactions of disodium salt of these Schiff bases i.e. Na₂SAP and Na₂SSP, with diaryltellurium(IV) dichlorides (R₂TeCl₂; R = p-hydroxyphenyl, 4-hydroxy-3-methyl-phenyl and p-methoxyphenyl) yield the complexes R₂TeSAP and R₂TeSSP. These new complexes have been characterized by various physiochemical techniques such as elemental analyses, conductance, cryoscopy, infrared and proton magnetic resonance spectral studies. On the basis of these studies, their behaviour in solution as well as in the solid state has been predicted and the possible structures proposed. The molar conductance data in acetone, acetonitrile and nitrobenzene reveal their molecular nature, which is well supported by cryoscopic data in nitrobenzene. The IR and ¹H NMR studies predict the binegative tridentate (ONO or ONS) nature of these ligands, thus making the tellurium atom pentacoordinated probably in a square pyramidal or pseudooctahedral environment.

Keywords: Diaryltellurium dichlorides, salicyldehyde, Schiff bases, 2-aminophenol, 2-aminothiophenol.

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 number¹⁻¹³. It has been reported that Lewis acidity of tellurium atom falls significantly on going from RTeX₃ to R₂TeX₂.¹⁴ A few such compounds are known¹⁻¹² to posses antimicrobial activity as well. In continuation of our earlier
work on Schiff bases complexes on organotellurium trihalides. We hereby report the synthesis and characterization of some Schiff bases of diaryltellurium dichlorides.

**MATERIALS AND METHODS**

All preparations were carried out under an atmosphere of dry N₂ and the solvents were dried and purified by the standard method before use.

**Preparation of diaryltellurium dichlorides**

The bis(-hydroxyphenyl), bis(4-hydroxy-3-methyl-phenyl) and bis(-methoxyphenyl) tellurium dichlorides were prepared by the reaction of tellurium tetrachloride with phenol, o-cresol and anisole, respectively.

**Synthesis of Schiff bases**

Two dibasic tridentate Schiff bases namely salicyldehyde-2-hydroxyanil(H₂SAP) and salicyldehyde-2-mercaptoanil(H₂SSP) have been prepared by the condensation of salicyldehe with 2-aminophenol/2-aminothiophenol respectively as reported.

**Synthesis of Schiff bases complexes of diaryltellurium, R₂TeSAP and R₂TeSSP**

The disodium salt of the ligand (Na₂SAP/Na₂SSP) was prepared from sodium metal (0.46g, 20 mmol) and the Schiff base (2.13g H₂SAP/2.29g H₂SSP, 10 mmol) in absolute methanol. The excess methanol was removed by distillation and the disodium salt was suspended in benzene (30-40 mL). To this, a warm saturated solution of 10 mmol of diaryltellurium dichloride in CHCl₃/CH₃OH was added dropwise under reflux. The reaction mixture was further refluxed for 3-4 h, cooled to room temperature and precipitated sodium chloride filtered off. The filtrate was concentrated to about one third of the original volume under reduced pressure and cooled in an ice bath to yield crystals of colored product. A further crop of the product was obtained by the addition of petroleum ether to the filtrate. This was filtered, washed with chloroform and dried in vacuum desiccators over P₂O₅. The purity of these compounds was controlled by the TLC using silica gel-G.

**Analytical methods and physical measurements**

Carbon, hydrogen and nitrogen analyses were obtained micro-analytically from Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The tellurium and chlorine contents were determined volumetrically. IR spectra of the complexes have been recorded in the region 4000-400 cm⁻¹ at the SAIF on a Perkin Elmer Model 2000 FTIR spectrometer using the KBr pellet technique and the ¹H NMR spectra were recorded on a BRUKER AC-300F at 299.9486 MHz and BRUKER AVANCE II 400 NMR spectrometer operating at 400.13 MHz at SAIF, Punjab University, Chandigarh in DMSO-d₆.
RESULTS AND DISCUSSION

The formation of diaryltellurium(IV) dichlorides by the reactions of TeCl$_4$ with phenol$^{17}$, o-cresol$^{18}$ and anisole$^{19}$ involves two step reactions. In first step, there is an electrophilic substitution of the phenyl ring by a trichlorotellurium moiety at a position para to the hydroxy or the methoxy groups. This can be represented by the following equation:

$$R-H + TeCl_4 \rightarrow RTeCl_3 + HCl$$  \hspace{1cm} (1)

(R = p-hydroxy, p-methoxy or 4-hydroxy-3-methyl-phenyl)

These aryltellurium trichlorides, further react with phenol/o-cresol or anisole to give the diaryltellurium(IV) dichlorids as per equation:

$$RTeCl_3 + R-H \rightarrow R_2TeCl_2 + HCl$$  \hspace{1cm} (2)

Two Schiff bases were prepared by the usual condensation reaction$^{20-23,26}$ as shown in Scheme-1.

These Schiff bases when reacted with 2 mole of sodium metal in methanol give the corresponding disodium salt and these disodium salt upon reaction with diaryltellurium dichlorides yield the complexes as shown.

$$R_2TeCl_2 + Na_2SAP \rightarrow R_2Te.SAP + 2NaCl$$  \hspace{1cm} (3)

$$R_2TeCl_2 + Na_2SSP \rightarrow R_2Te.SSP + 2NaCl$$  \hspace{1cm} (4)

These complexes are colored, crystalline solids, fairly stable in dry air, and are soluble only in polar donor organic solvents. The analytical data and physical properties of the complexes are presented in the Table 1.
Table 1. Physical Characteristics and analytical results of the Schiff base complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M. Pt. (°C)</th>
<th>Analyses % Found (Calculated)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_2TeCl_2 ) (p-hydroxyphenyl)</td>
<td>Dark Brown</td>
<td>195-197</td>
<td>Te 57.31 (57.09) H 3.39 (3.61) N 2.31 (2.66)</td>
<td>72</td>
</tr>
<tr>
<td>( R_2TeCl_2 ) (4-hydroxy-3-methyl-phenyl)</td>
<td>Greyish Brown (554.0)</td>
<td>210-212</td>
<td>Te 58.82 (58.53) H 4.30 (4.15) N 2.17 (2.53)</td>
<td>70</td>
</tr>
<tr>
<td>( R_2TeCl_2 ) (p-methoxyphenyl)</td>
<td>Brown</td>
<td>164-166</td>
<td>Te 58.82 (58.53) H 4.30 (4.15) N 2.17 (2.53)</td>
<td>75</td>
</tr>
<tr>
<td>( R_2TeCl_2 ) (p-hydroxyphenyl)</td>
<td>Greenish Brown (541.9)</td>
<td>158-160</td>
<td>Te 55.68 (55.41) H 3.36 (3.51) N 2.27 (2.59)</td>
<td>70</td>
</tr>
<tr>
<td>( R_2TeCl_2 ) (4-hydroxy-3-methyl-phenyl)</td>
<td>Yellow Brown (569.9)</td>
<td>116-118</td>
<td>Te 56.71 (56.90) H 3.87 (4.04) N 2.68 (2.46)</td>
<td>65</td>
</tr>
<tr>
<td>( R_2TeCl_2 ) (p-methoxyphenyl)</td>
<td>Dark Brown</td>
<td>108-110</td>
<td>Te 56.71 (56.90) H 3.87 (4.04) N 2.68 (2.46)</td>
<td>68</td>
</tr>
</tbody>
</table>

*melts with decomposition

Table 2. Important IR Data (cm\(^{-1}\)) for Schiff bases and their Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu ) OH</th>
<th>( \nu ) C=N</th>
<th>( \nu ) C=C</th>
<th>( \nu ) C=O</th>
<th>( \nu ) S-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2SAP )</td>
<td>3050 w</td>
<td>1636 m</td>
<td>1600 m</td>
<td>1532 s</td>
<td>-</td>
</tr>
<tr>
<td>( R_2TeSAP ) (p-hydroxyphenyl)</td>
<td>3396' mb</td>
<td>1634 s</td>
<td>1610 m</td>
<td>1574 m</td>
<td>1514 m</td>
</tr>
<tr>
<td>( R_2TeSAP ) (4-hydroxy-3-methyl-phenyl)</td>
<td>3420' mb</td>
<td>1630 s</td>
<td>1612 m</td>
<td>1591 m</td>
<td>1512 w</td>
</tr>
<tr>
<td>( R_2TeSAP ) (p-methoxyphenyl)</td>
<td>-</td>
<td>1650 m</td>
<td>1600 m</td>
<td>1584 vs</td>
<td>1530 m</td>
</tr>
<tr>
<td>( H_2SSP )</td>
<td>3280 b</td>
<td>1615 m</td>
<td>1590 s</td>
<td>-</td>
<td>2810 w</td>
</tr>
<tr>
<td>( R_2TeSSP ) (p-hydroxyphenyl)</td>
<td>3424' mb</td>
<td>1616 vs</td>
<td>1583 s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( R_2TeSSP ) (4-hydroxy-3-methyl-phenyl)</td>
<td>3431' mb</td>
<td>1616 vs</td>
<td>1586 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( R_2TeSSP ) (p-methoxyphenyl)</td>
<td>-</td>
<td>1615 m</td>
<td>1585 vs</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

s = strong, m = medium, vs = very strong, w = weak, b = broad

Thus, in \( R_2TeSAP \) and \( R_2TeSSP \), the Schiff bases function as tridentate ligands, enhancing the coordination number of central tellurium atom to five.

Infra-Red Spectra

The important IR frequencies for these Schiff bases and their complexes are presented in Table 2. The \( \nu_{C=N} \) in the complex may be utilized to study the involvement of azomethine.
N in complexation. This frequency (~1630 cm\(^{-1}\)) shifts to lower side upon complexation indicating coordination through the azomethine nitrogen\(^{27-34}\). Actually chelate ring formation with metal ion allows stabilization of Schiff bases -C=N- bonds\(^{20}\). Also \(\nu_{C=O}\) (phenolic) appearing at about 1525 cm\(^{-1}\) shifts to higher frequency (5-15 cm\(^{-1}\)) due to coordination. This band shift to higher energy expected due to maintenance of ring current arising from electron delocalization in the chelate ring\(^{32-34}\). The \(\nu_{S-H}\) (~2810 cm\(^{-1}\)) in \(\text{H}_2\text{SSP}\)\(^{23}\) disappears on complexation indicating the linkage of S to Te atom. The absence of \(\nu_{O-H}\) in \(\text{R}_2\text{Te.SAP}\) and \(\text{R}_2\text{Te.SSP}\) (R= p-anisyl) suggest the binding through oxygen atom as well, but in the complexes of hydroxyaryl tellurium derivatives, it could not be ascertained due to the presence of OH group in the aryltellurium moiety.

**Proton Magnetic Resonance Spectra**

\(^1\)H NMR spectrum of \(\text{H}_2\text{SAP}[35,36]\) in DMSO-d\(_6\) shows the two hydroxyl protons at 13.75 and 9.64 \(\delta\) ppm (hydrogen bonded) which disappear with the addition of D\(_2\)O. The single proton singlet at 8.95 \(\delta\) ppm is due to azomethine proton\(^{37}\). Broad multiplets assignable to phenyl protons appear in the range 6.4-7.9 \(\delta\) ppm.

Spectra of \(\text{H}_2\text{SAP}\) complex (Table 3), \(\text{R}_2\text{Te.SAP}\) are very complex and a lot of mixing of aryl protons signals of Schiff bases and diaryltellurium moiety takes place, thus making the independent assignment almost impossible. The peaks at \(\delta\) 13.75 ppm and 9.64 ppm of \(\text{H}_2\text{SAP}\) disappear in the complex due to deprotonation of both hydroxyl protons of Schiff bases. The azomethine proton resonate as a singlet at 8.65-8.80 \(\delta\) ppm (comparable to \(\text{Me}_2\text{PbSAP}\) and \(\text{Ph}_2\text{PbSAP}\), at 8.20-8.25 formimidoyl signal\(^{27}\)). This reveals the tridentate nature (ONO) of this ligand and a pentacoordinated tellurium atom in the \(\text{R}_2\text{Te.SAP}\) complexes.

\(^1\)H NMR spectrum\(^{23}\) of \(\text{H}_2\text{SSP}\) exhibits two multiplet signals of integration corresponding to 9 protons observed at \(\delta\) 6.5-8.4 ppm due to aromatic protons. The presence of two multiplet signals may be due to the fact that protons of two aromatic rings are not shielded. The protons of N-phenyl ring are more shielded due to conjugation of the lone pair of electron of nitrogen atom with the \(\pi\)-system of phenyl ring shifting the signal upfield. The other downfield multiplet is attributed to the less shielded benzyl ring protons. The singlet at \(\delta\) 3.4 ppm with an integration corresponding to 1H is assigned to the SH proton. Signal at \(\delta\) 10.90 ppm is assigned to the OH proton. The thio Schiff base exhibit a heterocyclic benzothiazoline form\(^{22,23}\) where the N-H proton (identified by ready exchange with D\(_2\)O) appear at \(\delta\) 4.97 ppm.

**Table 3.** \(^1\)H NMR Spectral Data \(\delta\) ppm for salicyldehyde-2-hydroxyanil complexes in DMSO-d\(_6\)

<table>
<thead>
<tr>
<th>(\text{R}_2\text{Te.SAP}) (p-hydroxyphenyl)</th>
<th>(\text{R}_2\text{Te.SAP}) (4-hydroxy-3-methyl-phenyl)</th>
<th>(\text{R}_2\text{Te.SAP}) (p-methoxyphenyl)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>2.14(^{s}) (6H)</td>
<td>-</td>
<td>-CH(_3)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3.87</td>
<td>-OCH(_3)</td>
</tr>
<tr>
<td>6.67-7.11(^{cm}) (16H)</td>
<td>*</td>
<td>6.42-7.96(^{cm}) (16H)</td>
<td>Aryl of SAP + Phenyl of (\text{R}_2\text{Te})</td>
</tr>
<tr>
<td>7.35-7.92(^{cm}) (16H)</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.80(^{s}) (1H)</td>
<td>*</td>
<td>8.65(^{s}) (1H)</td>
<td>Azomethine</td>
</tr>
<tr>
<td>9.90(^{s}) (2H)</td>
<td>*</td>
<td>-</td>
<td>-OH of (\text{R}_2\text{Te})</td>
</tr>
</tbody>
</table>

\(s = \) singlet, \(cm = \) complex multiplet, \(b = \) broad, Spectra not well resolved
The H$_2$SSP Schiff base in these complexes functions as a binegative tridentate ligand through $ONS$, thus making the tellurium atom pentacoordinated.

All the Schiff bases complexes (Table 3) show the disappearance of signal at $\delta$ 3.4, 10.90 ppm due to deprotonation of SH and OH protons. The signal at $\delta$ 4.97 ppm in parent Schiff base could not be ascertained, but a one proton signal at 8.46-9.47 may be due to azomethine proton after coordination through nitrogen atom. The aryl proton could not be assigned independently for Schiff base and diaryltellurium moiety due to very complex nature of spectra in this region.

**CONCLUSIONS**

Schiff bases complexes have been prepared by reaction of diaryltellurium dichlorides with disodium salts of salicyldehyde-2-hydroxyanil and salicyldehyde-2-mercaptoanil. These complexes have been characterized using elemental analyses conductance, cryoscopy, infrared and proton magnetic resonance spectral techniques. Tellurium atom in these Schiff bases complexes acquires a coordination number of five.

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**REFERENCES**