The Phthalhydroxamate Ligand and its Organotellurium(IV) Chloride Complexes: Preparation and Spectral Studies

Sonu Chauhan

Department of Chemistry,
Maharshi Dayanand University, Rohtak-124001, Haryana, INDIA.
email: chauhansonu7777@gmail.com.

(Received on: January 17, 2018)

ABSTRACT

The potassium phthalhydroxamate ligand (o-carboxybenzohydroxamate) was prepared and its donor behaviour with organo- and diorganotellurium(IV) chloride compounds was studied. The hydroxamate ligand with organotellurium compounds to form complexes which is coordinated to the tellurium centre through the deprotonated $O$ and carbonyl $O$ of the hydroxamate group, and the carboxylate group, behaving as dibasic tetradeutate ligand. The metal complexes were characterized by elemental analyses, IR and NMR spectroscopy. On the basis of the experimental data, structures of the complexes are proposed.

Keywords: Potassium phthalhydroxamate, organotellurium trichloride, diorganotellurium dichloride.

INTRODUCTION

The chemistry of hydroxamic acids began in 1869 when H. Lossen isolated oxalohydroxamic acid from the reaction products of ethyl oxalate and hydroxylamine$^1$. Hydroxamic acids, a class of compounds having the presence of a terminal $-\text{C(O)NHOH}$ functional group was derived from inserting $-\text{NHOH}$ moiety into carboxylic acid which replace $-\text{OH}$ group by $-\text{NHOH}$ moeity. Due to its chelating property with metal ion$^{2-4}$ and affinity for ‘hard’ cation, having wide variety of application in pharmacological, biological$^5$ and in analytical chemistry. Chattergee$^6$ reviewed the donor properties of the hydroxamate metal complexes. The ligands behave as monobasic bidentate $O, O'$ donor. However, if the ligands contain other donor sites like acetyl moiety adjacent to the hydroxamate group, a range of coordination possibilities exists as in the phthalohydroxamate ligand.

Also, organotellurium(IV) trichlorides are known to behave as lewis acids and form complexes with N-, O- and S- donor bases. Diorganotellurium(IV) dichlorides also form such complexes but only with strong chelating ligands$^{7-9}$. 
MATERIALS AND METHODS

All preparations were carried out under an atmosphere of dry nitrogen and the solvents used were purified by standard method\textsuperscript{10,11} before use. The purity of compounds was checked by TLC using Silica gel-G (Merck). Melting points were determined in open capillary tube and are uncorrected.

Carbon, hydrogen and nitrogen analyses were obtained microanalytically from SAIF, Panjab University Chandigarh on a ThermoFinnigan CHNS analyser. Conductivity was measured in DMSO at 25±2 °C with a dip type conductivity cell on microprocessor based conductivity bridge type MICROSOIL.

Infrared spectra were recorded in KBr pellets at Department of Pharmaceutical Sciences, M. D. University, Rohtak on Bruker FT-IR spectrometer. Proton Magnetic Resonance spectra were recorded in DMSO-d\textsubscript{6} using TMS as an internal reference on BRUKER AVANCE II 400 NMR spectrometer at Sophisticated Analytical Instrumentation Facility, Panjab University Chandigarh.

Preparation of Aryltellurium(IV) Trichlorides and Diaryltellurium(IV) Dichlorides

4-Methoxyphenyltellurium(IV) trichloride\textsuperscript{12,13}, bis(4-methoxyphenyl)tellurium(IV) dichloride\textsuperscript{13,14}, 4-hydroxyphenyltellurium(IV) trichloride\textsuperscript{15}, bis(4-hydroxyphenyl)tellurium(IV) dichloride\textsuperscript{15}, 3-methyl-4-hydroxyphenyltellurium(IV) trichloride\textsuperscript{16} and bis(3-methyl-4-hydroxyphenyl)tellurium(IV) dichloride\textsuperscript{16} were prepared by the reactions of TeCl\textsubscript{4} with anisole/ phenol/ o-cresol as reported in the literature\textsuperscript{12-16}.

Preparation of Potassium phthalhydroxamate(K\textsubscript{2}L)\textsuperscript{17}

Diethyl phthalate

Phthalic acid (49.8 g, 300 mmol) was dissolved in 150 mL of ethanol. The solution was acidified with H\textsubscript{2}SO\textsubscript{4} (6.50 mL) and refluxes with stirring for 6 hours. The excess ethanol was removed on a rotary evaporator and H\textsubscript{2}SO\textsubscript{4} was neutralized with 5 % of aqueous NaHCO\textsubscript{3} solution until formation of CO\textsubscript{2} ceased. The formed diethyl phthalate was washed with H\textsubscript{2}O and separated in a separatory funnel. Yield- 68%.

Potassium phthalhydroxamate(K\textsubscript{2}L)

Hydroxylamine hydrochloride (1.74 g, 25 mmol) dissolved in methanol(20 mL) was mixed with a methanolic solution (20mL) containing 1.40g (25 mmol) of KOH. KCl was precipitated from the solution was removed by suction filtration and then, methanol solution (20 mL) with 1.40 g (25 mmol) KOH was added to the filtrate. Subsequently, diethyl phthalate (4.90 g, 25 mmol) dissolved in 20 mL methanol was added to the NH\textsubscript{2}OH solution and stirred for 1 h at room temperature. A colour change to yellow occurred during the reaction. The volume of the resulting solution was reduced to 15 mL by evaporating at 50°C and adding 25 mL acetone to the solution precipitated the potassium salt of PHA. This was filtered and dried in air. Yield- 70%. M. Pt. 134-136°C.
Preparation of phthalhydroxamate complexes of organotellurium(IV)

Organotellurium(IV) chlorides, RTeCl$_3$ and R$_2$TeCl$_2$ (R = 4-methoxyphenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl), when reacted with potassium phthalhydroxamate in 2:1 molar ratios, yield (RTeCl$_2$)$_2$.L and (R$_2$TeCl)$_2$.L type complexes.

(RTeCl$_2$)$_2$.L

A warm saturated methanolic solution of potassium phthalhydroxamate (2 mmol) was added dropwise to a solution of organotellurium(IV) trichloride (4 mmol) in about 20 mL chloroform/methanol. An immediate precipitation of KCl resulted which was removed by filtration. The filterate was refluxed for 3-4 hours to precipitate out any KCl and clear solution was then concentrated to about one third of the original volume and kept overnight to yield crystalline product. This was filtered, washed with chloroform and dried in a vacuum desiccator over P$_2$O$_5$.

(R$_2$TeCl)$_2$.L

The saturated solution of organotellurium(IV) dichloride (4 mmol) in chloroform/methanol was added dropwise with constant stirring to a saturated methanolic solution of potassium phthalhydroxamate (2 mmol). An immediate change in colour with precipitation of KCl took place, which was removed by filtration. The contents were then refluxed for about 3-4 hours. The clear solution thus obtained was concentrated to about one third of original volume and left overnight to obtain coloured crystalline product, which was filtered, washed with chloroform and dried in a vacuum desiccator over P$_2$O$_5$.

RESULT AND DISCUSSION

Preparation of potassium phthalhydroxamate can be represented as below:

Organotellurium(IV) trichlorides and diorganotellurium(IV) dichlorides when reacted with ligand in 2:1 molar ratios give the corresponding organotellurium(IV) hydroxamates.
2 RTeCl$_3$ + K$_2$L $\rightarrow$ (RTeCl$_2$)$_2$(L) + 2 KCl
2 R$_2$TeCl$_2$ + K$_2$L $\rightarrow$ (R$_2$TeCl)$_2$(L) + 2 KCl

The analytical data, physical properties and yields for these complexes are compiled in Table 1.

**Table 1: Analytical data and physical properties of organotellurium(IV) phthalhydroxamate complexes.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical Formula (Formula Wt.)</th>
<th>Colour (Yield, %)</th>
<th>Analyses % Found (Calculated)</th>
<th>M. P., (°C) dec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(RTeCl$_2$)$_2$.L (4-methoxyphenyl)</td>
<td>C$_2$H$_9$ClNO$_2$Te$_2$ (790.40)</td>
<td>Light brown(65)</td>
<td>Te 32.40 (32.29) Cl 17.90 (17.94) C 33.37 (33.43) H 2.33 (2.42) N 1.60 (1.77)</td>
<td>102-104</td>
</tr>
<tr>
<td>(RTeCl$_2$)$_2$.L (4-hydroxyphenyl)</td>
<td>C$_2$H$_9$ClNO$_2$Te$_2$ (762.35)</td>
<td>Light cream(70)</td>
<td>Te 33.37 (33.48) Cl 18.48 (18.60) C 31.48 (31.51) H 1.59 (1.98) N 1.74 (1.84)</td>
<td>72-74</td>
</tr>
<tr>
<td>(RTeCl$_2$)$_2$.L (3-methy-4-hydroxyphenyl)</td>
<td>C$_2$H$_9$ClNO$_2$Te$_2$ (790.40)</td>
<td>Cream (50)</td>
<td>Te 32.37 (32.29) Cl 17.88 (17.94) C 33.32 (33.43) H 2.20 (2.42) N 1.58 (1.77)</td>
<td>88-90</td>
</tr>
<tr>
<td>(R$_2$TeCl)$_2$.L (4-methoxyphenyl)</td>
<td>C$_6$H$_5$ClNO$_2$Te$_2$ (933.76)</td>
<td>Dull white(60)</td>
<td>Te 27.19 (27.33) Cl 7.50 (7.59) C 46.21 (46.31) H 3.42 (3.56) N 1.41 (1.50)</td>
<td>84-86</td>
</tr>
<tr>
<td>(R$_2$TeCl)$_2$.L (4-hydroxyphenyl)</td>
<td>C$_6$H$_5$ClNO$_2$Te$_2$ (877.65)</td>
<td>Light pink (70)</td>
<td>Te 26.88 (27.08) Cl 7.98 (8.08) C 43.50 (43.79) H 2.73 (2.87) N 1.52 (1.60)</td>
<td>120-124</td>
</tr>
<tr>
<td>(R$_2$TeCl)$_2$.L (3-methy-4-hydroxyphenyl)</td>
<td>C$_6$H$_5$ClNO$_2$Te$_2$ (933.76)</td>
<td>Light cream(75)</td>
<td>Te 27.21 (27.33) Cl 7.40 (7.59) C 46.19 (46.31) H 3.47 (3.56) N 1.39 (1.50)</td>
<td>118-120</td>
</tr>
</tbody>
</table>

**Infrared Spectral studies**

The infrared spectra of the organotellurium(IV) phthalhydroxamates are quite complexes and an attempt has therefore been made to identify the donor sites of phthalhydroxamates ligand by comparing with those of parent organotellurium(IV) chlorides and potassium phthalhydroxamates, which indicated clear differences. The spectrum of ligand (K$_2$L) has strong absorption band at 1645 cm$^{-1}$ due to C=O vibration of the hydroxamate carboxyl group shifted to lower frequency in the spectra of complexes, such behavior clearly provides evidences for coordination through the carbonyl oxygen$^{18}$. The typically N-H stretching band at 3190 cm$^{-1}$ in the free ligand is somewhat lower than those of complexes indicates coordination of the O$^-$ site to tellurium centre of complexes$^{19}$. The strong band at 3190 cm$^{-1}$ in the free ligand is somewhat lower than those of complexes indicates coordination of the O$^-$ site to tellurium centre of complexes$^{19}$. The strong band at 1550 cm$^{-1}$ and 1380 cm$^{-1}$ are attributed to the asymmetric and symmetric vibration of the carboxylate group of ligand. The asymmetric vibration frequencies shifted to lower wavenumber and symmetric vibration frequencies shifted to higher wavenumber in complexes indicate bidentate coordination of the carboxylate group of ligand$^{20}$. The appearance of new weak band around at 280-295 cm$^{-1}$ is due to the Te-O confirm the bonding of ligand to tellurium through oxygen atom. IR studies reveal that ligand behaves as tetradeutate via oxygen donor atom with trigonal bipyramidal geometry around tellurium centre in complexes.
Table 2: IR Data of organotellurium(IV) phthalhydroxamate complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>v(NH) (Hydroxamic)</th>
<th>v(C=O) (carboxyl)</th>
<th>v asymm.(COO) (carboxyl)</th>
<th>v symm.(COO) (carboxyl)</th>
<th>v(C-N)</th>
<th>v(Te-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2L</td>
<td>3190 m</td>
<td>1645 s</td>
<td>1550 s</td>
<td>1380 s</td>
<td>1325 m</td>
<td>-</td>
</tr>
<tr>
<td>(RTeCl2)2.L (4-methoxyphenyl)</td>
<td>3350 m</td>
<td>1575 s</td>
<td>1535 s</td>
<td>1405</td>
<td>1305 m</td>
<td>285 w</td>
</tr>
<tr>
<td>(RTeCl2)2.L (4-hydroxyphenyl)</td>
<td>3336 m</td>
<td>1580 s</td>
<td>1542 s</td>
<td>1400</td>
<td>1320 m</td>
<td>295 w</td>
</tr>
<tr>
<td>(RTeCl2)2.L (3-methy-4-hydroxyphenyl)</td>
<td>3320 m</td>
<td>1585 s</td>
<td>1540 s</td>
<td>1410</td>
<td>1295 m</td>
<td>290 w</td>
</tr>
<tr>
<td>(R2TeCl)2.L (4-methoxyphenyl)</td>
<td>3332 m</td>
<td>1578 s</td>
<td>1535 s</td>
<td>1401</td>
<td>1290 m</td>
<td>280 w</td>
</tr>
<tr>
<td>(R2TeCl)2.L (4-hydroxyphenyl)</td>
<td>3260 m</td>
<td>1589 s</td>
<td>1545 s</td>
<td>1405</td>
<td>1315 m</td>
<td>288 w</td>
</tr>
<tr>
<td>(R2TeCl)2.L (3-methy-4-hydroxyphenyl)</td>
<td>3315 m</td>
<td>1595 s</td>
<td>1542 s</td>
<td>1415</td>
<td>1398 m</td>
<td>290 w</td>
</tr>
</tbody>
</table>

NMR Spectral studies

Proton magnetic resonance spectra of organotellurium(IV) phthalhydroxamates are very complex and a lot of overlapping of aryl proton singals of the ligand and organotellurium(IV) moiety takes place, thus making the independent assignment almost impossible. The chemical shift data for the complexes are presented in the Table 3. The complex shows downfield singlet at around 12.4 δ ppm, which The complexes show downfield singlets at around 12.5 δ ppm, which may be assigned to –NH of benzohydroxamate group, which rules out the linkage of phthalhydroxamate through nitrogen atom. Absence of -NOH proton signals around 9.0 δ ppm confirms the deprotonation of this proton and subsequently linkage to the tellurium atom\textsuperscript{21}. These signals are not well resolved in some cases due to poor solubility of the complexes.

Further, the aryl protons of organotellurium(IV), diorganotellurium(IV) and phthalhydroxamate groups exhibit a lot of mixing of signals and are observed as complex multiplets in the region 6.721 - 8.347 δ ppm, as observed in \textsuperscript{1}H NMR Spectra of organotellurium(IV) complexes of phthalohydroxamte\textsuperscript{22}. Also, a careful examination of \textsuperscript{1}H NMR Spectra of complexes reveal the shielding of aryl protons of RTe/R2Te compared to RTeCl2/R2TeCl2 due to flow of electron density from the ligand to the aryltellurium moiety as a result of complexation. Thus, on the basis of infrared and proton magnetic resonance spectral studies it may be concluded that phthalhydroxamate acts as a tetradentate ligand involving the carbonyl group of hydroxamate, hydroxamic hydroxyl oxygen and oxygen of carboxylate of phthalhydroxamte giving rise to penta coordinated tellurium complexes in (RTeCl2)2.(L) and (R2TeCl)2.(L). These study show the ligand in complexes is a dianion resulting from carboxylate and hydroxamate group ionization. The suggested structures are as shown in figure 1.
Table 3: NMR Data of organotellurium(IV) phthal hydroxamate complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift in DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>((R_{2}TeCl)_{2}L)</td>
<td>((R_{2}TeCl)_{2}L)</td>
</tr>
<tr>
<td>(4-methoxyphenyl)</td>
<td>3.362, 3.826(s, 6H, OCH(_{3})), 6.940-8.272(cm, 12H, aromatic proton of L and RTe), 12.390(bs, 1H, NH)</td>
</tr>
<tr>
<td>(4-hydroxyphenyl)</td>
<td>2.169(s, 3H, CH(_{3})), 6.721-8.216(cm, 10H, aromatic proton of L and RTe), 9.17(bs, 1H, phenolic OH of RTe)</td>
</tr>
</tbody>
</table>

ACKNOWLEDGMENT

The author are grateful to M. D. University, Rohtak for providing the necessary facilities. One of the author (Sonu Chauhan) is thankful to SAIF, Panjab University Chandigarh for providing the CHN analyses and NMR spectral data.

REFERENCES