Synthesis and characterization of 2-[2-aryltelluroethyl] -3-methyl pyridines (Te,N) and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (N,Te,N)

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ABSTRACT

The potentially bidentate hard and soft acid containing (Te,N) compounds, 2-[2-aryltelluroethyl]-3-methyl pyridines (L) [C₁₄H₁₅NTe] and tridentate (N,Te,N) 2-[2-(3-methyl pyridoethyltelluro)ethyl]-3-methyl pyridine (L') [C₁₆H₂₀N₂Te] have been synthesized in good yield (> 75%) and characterized by physical, analytical and spectroscopic [¹H, ¹³C{¹H} and ¹²⁵Te{¹H}] NMR and IR ] methods. The reaction of methyl iodide with L [C₁₄H₁₅NTe] results in the formation of the salt of the type ArTe (CH₂)₂-2-(CH₃)₂CH3I with affecting the tellurium moiety.

Key words: Ligands (Te, N) and (N, Te, N); IR spectra, NMR spectra.

INTRODUCTION

There has been a recent interest in the ligand chemistry of tellurium¹,² but despite this growth of activity the literature contains few reports of bi-or multidentate ligands containing tellurium. Incorporation of the ditelluride group into a cyclic system may be expressed to enhance the reactivity at the Te-Te bond as a result of strain involving both entropic and enthalpic effect³. Here we report synthesis and characterization of 2-(2-aryltelluroethyl)-3-methyl pyridines (L) [C₁₄H₁₅NTe], where Ar = Phenyl (La) [C₁₄H₁₅NTe], 4-methylphenyl (Lb) [C₁₅H₁₇N₂Te], 4-methoxyphenyl (Lc) [C₁₅H₁₇ONTe], 4-ethoxyphenyl (Ld) [C₁₅H₁₇ONTe], and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (L') [C₁₆H₂₀N₂Te].

MATERIAL AND METHODS

Tellurium tetrachloride, aryl tellurium trichlorides, diarylditellurides, diphenyldiselenides, 2-(2-chloroethyl) pyridine are the main starting materials used in this work. The methods of conductance and magnetic moment measurement are given. The instruments and techniques used to record IR and NMR [¹H, ¹³C{¹H}] were obtained from BDH, Aldrich, Strem and Sigma are used without purification. Organic solvents (BDH, Merck and Glaxo) were used after purification and drying (whenever required) by standard methods⁴⁵.

EXPERIMENTAL

2-(2-chloroethyl) pyridine and
diarylditellurides (aryl = phenyl, 4-methylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl) prepared by the literature methods\(^6\). The detailed procedure for the synthesis of \(L\) and \(L'\) are given below.

**Synthesis of 2-[2-aryltelluroethyl]-3-methyl pyridines (La-d)**

To the hot ethanolic (25 cm\(^3\)) solution of appropriate ditelluride (3 mmol), solution of sodium boro hydride (1.0 gm, 10 cm\(^3\) of 10% NaOH), added slowly in nitrogen atmosphere, till colourless solution of sodium aryl telluride formed. To this 2-(2-chloroethyl)-3-methyl pyridine (6 mmol dissolved in 5 cm\(^3\) ethanol) was added drop wise with vigorous stirring and the resulting solution further refluxed for one hour. The ligand (La-Ld) thus formed were extracted into chloroform (250 cm\(^3\)). After removing the excess of chloroform, liquid form of the compound separated out, which was purified by column chromatography, using silica column and chloroform: hexane (5: 95; 10: 90) as elutent.

**Synthesis of 2-[2-(3-methyl pyridoethyltelluro)ethyl]-3-methyl pyridine (L')**

In a round bottom (100 ml) flask Tellurium powder (2 gm, 16 mmol) and sodium borohydride (5 gm dissolved in 10 cm\(^3\) of 10% NaOH) were refluxed in water (50 cm\(^3\)) until the colourless solution of Na\(_2\)Te was obtained. To this 2-(2-chloroethyl)-3-methyl pyridine (4.9 gm, 32 mmol) in 5 cm\(^3\) of ethanol was added drop wise and the content further refluxed for two hours with vigorous stirring. The compound extracted into chloroform (250 cm\(^3\)), after removal of excess of chloroform, red colour liquid was obtained, washed with water and dried over anhydrous calcium chloride under vacuum.

**RESULTS AND DISCUSSION**

Synthesis of 2-(2-Aryltelluroethyl)-3-methyl pyridines (L) and 2-[2-(3-methyl pyridoethyltelluro)ethyl]-3-methyl pyridine (L') in schematic reaction shown as:

\[
\text{2ArTeNa} \\
(C_6H_5NCH_3)_2-2-CH_2CH_2Cl \xrightarrow{\text{EtOH-H}_2\text{O}} \text{ArTeCH}_2\text{CH}_2-2-(C_6H_5\text{NCH}_3) \\
(L) \\
(C_6H_5NCH_3)_2-2-CH_2CH_2Cl \xrightarrow{\text{EtOH-H}_2\text{O}} ([C_6H_5NCH_3]_2-2-\text{CH}_2\text{CH}_2)\text{Te} \\
(L') \\
Ar = C_6H_5 (La), 4-CH_3C_6H_4 (Lb), 4-CH_3OC_6H_4 (Lc), 4-C_2H_5OC_6H_4 (Ld),
\]

The high boiling liquids L and L' are pale yellow to red in colour, soluble in nonpolar and polar organic solvents. On exposure to air they change their colour from yellow to dark red. The various physical and spectroscopic properties of L and L' are discussed below:

**Conductance and molecular weight measurements**

The molar conductance (\(\Lambda_m\)) values of ligand L and L' (Table 1) determined in acetonitrile and nitro methane (1mM), reveals their nonelectrolytic behaviour. Molecular weights (Table 1) of L and L' determined in chloroform have been found close to the molecular formulations arrived at by analytical data.

**IR spectra**

The important IR bands along with their assignments and are presented in table 2. The assignments of the bands have been made on the
Table 1: Physical properties of ligands La-Ld and L' 

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color (Liquid)</th>
<th>Yield</th>
<th>Bpt. (°C)</th>
<th>Solubility</th>
<th>Mol.wt. (Calcd.)</th>
<th>Te % (Calcd.)</th>
<th>( \lambda_m ) (in CH(_3)CN/CH(_2)NO(_2))</th>
<th>( \lambda_m ) (in CHCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>La [C(<em>{14})H(</em>{15})N(_{5})Te]</td>
<td>Pale yellow</td>
<td>85</td>
<td>172</td>
<td>Hexane, CHCl(_3), CH(_3)CN</td>
<td>310</td>
<td>38.20</td>
<td>16.30/2.6</td>
<td></td>
</tr>
<tr>
<td>Lb [C(<em>{15})H(</em>{17})N(_{5})Te]</td>
<td>Yellow</td>
<td>82</td>
<td>180</td>
<td>Hexane, CHCl(_3), CH(_3)CN</td>
<td>303</td>
<td>37.50</td>
<td>14.2/3.4</td>
<td></td>
</tr>
<tr>
<td>Lc [C(<em>{15})H(</em>{17})ON(_{5})Te]</td>
<td>Orange yellow</td>
<td>85</td>
<td>178</td>
<td>CHCl(_3), CH(_3)CN, Hexane</td>
<td>325</td>
<td>35.93</td>
<td>15.2/2.9</td>
<td></td>
</tr>
<tr>
<td>Ld [C(<em>{16})H(</em>{19})ON(_{5})Te]</td>
<td>Pale yellow</td>
<td>90</td>
<td>184</td>
<td>CHCl(_3), CH(_3)CN, Hexane</td>
<td>375</td>
<td>34.0</td>
<td>15.6/2.8</td>
<td></td>
</tr>
<tr>
<td>L' [C(<em>{16})H(</em>{20})N(_{5})Te]</td>
<td>Red</td>
<td>90</td>
<td>136</td>
<td>Hexane, CHCl(_3), CH(_3)CN</td>
<td>325</td>
<td>33.60</td>
<td>14.0/2.6</td>
<td></td>
</tr>
</tbody>
</table>

For 1:1 electrolyte \( \lambda_m \) in acetonitrile = 100-160 and in nitrobenzene = 20-30 ohm\(^{-1}\)cm\(^2\)mol\(^{-1}\)

La = C\(_{6}\)H\(_{5}\)TeCH\(_2\)CH\(_2\)-2-(C\(_{5}\)H\(_3\)NCH\(_3\))
Ld = 4-C\(_{2}\)H\(_5\)OC\(_6\)H\(_4\)TeCH\(_2\)CH\(_2\)-2-(C\(_{5}\)H\(_3\)NCH\(_3\))
Lb = 4-CH\(_3\)C\(_6\)H\(_4\)TeCH\(_2\)CH\(_2\)-2-(C\(_{5}\)H\(_3\)NCH\(_3\))
Lc = 4-CH\(_3\)OC\(_6\)H\(_4\)TeCH\(_2\)CH\(_2\)-2-(C\(_{5}\)H\(_3\)NCH\(_3\))
L' = [(C\(_{5}\)H\(_3\)NCH\(_3\))-2-CH\(_2\)CH\(_2\)]\(_2\)Te

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Table 2: Important ir bands (cm⁻¹) of L and L'<sup>1</sup>

<table>
<thead>
<tr>
<th>Ligands</th>
<th>υ(Te-C(aliphatic))</th>
<th>υ(Te-C(aromatic))</th>
<th>δ (C-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La [C₁₄H₁₅NTe]</td>
<td>480</td>
<td>262,292</td>
<td>410</td>
</tr>
<tr>
<td>Lb [C₁₅H₁₇NTe]</td>
<td>482</td>
<td>248,288</td>
<td>408</td>
</tr>
<tr>
<td>Lc [C₁₅H₁₇ONTe]</td>
<td>480</td>
<td>250,290</td>
<td>410</td>
</tr>
<tr>
<td>Ld [C₁₆H₁₉ONTe]</td>
<td>484</td>
<td>256,298</td>
<td>408</td>
</tr>
<tr>
<td>L' [C₁₆H₂₀N₂Te]</td>
<td>497</td>
<td>-</td>
<td>410</td>
</tr>
</tbody>
</table>

Table 3: <sup>1</sup>H and <sup>125</sup>Te (<sup>1</sup>H) NMR data for 2-(2-chloroethyl) pyridine, La-Ld, and L' in CdCl₃ at 25°C (δ, ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>H₆ (d)</th>
<th>Aryl and pyridyl protons (m)</th>
<th>H₆ &amp; H₈ (m)</th>
<th>H (R) &lt;sup&gt;1&lt;/sup&gt;H</th>
<th>&lt;sup&gt;125&lt;/sup&gt;Te(&lt;sup&gt;1&lt;/sup&gt;H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₅H₄N)-2-(CH₂)₂Cl</td>
<td>8.45</td>
<td>7.20(H₃,H₅); 7.58(H₄)</td>
<td>3.9t,3.2t</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La [C₁₄H₁₅NTe]</td>
<td>8.56</td>
<td>7.00-7.60</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lb [C₁₅H₁₇NTe]</td>
<td>8.51</td>
<td>6.95-7.70</td>
<td>3.2</td>
<td>2.38s</td>
<td>-</td>
</tr>
<tr>
<td>Lc [C₁₅H₁₇ONTe]</td>
<td>8.50</td>
<td>6.70-7.70</td>
<td>3.2</td>
<td>2.75s</td>
<td>481</td>
</tr>
<tr>
<td>Ld [C₁₆H₁₹ONTe]</td>
<td>8.55</td>
<td>6.70-7.70</td>
<td>3.2</td>
<td>3.97q, 1.40t</td>
<td>-</td>
</tr>
<tr>
<td>L' [C₁₆H₂₀N₂Te]</td>
<td>8.55</td>
<td>7.39(H₃,H₅); 7.58(H₄)</td>
<td>3.3</td>
<td>-</td>
<td>167</td>
</tr>
</tbody>
</table>

(s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet)

La = 2-(2-Aryltelluroethyl)-3-methyl pyridine
Lb = 2-[2-(4-methylaryl) Telluroethyl]-3-methyl pyridine
Lc = 2-[2-(4-methoxyaryl) Telluroethyl]-3-methyl pyridine
Ld = 2-[2-(4-ethoxyaryl) Telluroethyl]-3-methyl pyridine
L' = 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine

Table 4: <sup>13</sup>C (<sup>1</sup>H) NMR chemical shifts for ligands La-Ld and L' IN CDCl₃ (δ, ppm)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>C₇</th>
<th>C₈</th>
<th>Aryl and Pyridyl</th>
<th>C(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La'</td>
<td>40.0</td>
<td>6.5</td>
<td>137.8(C₂), 121.4(C₃), 136.2(C₄), 122.7(C₅), 149.5(C₆), 112.6(C₇), 138.3(C₈), 129.0(C₉), 127.3(C₁₀)</td>
<td>-</td>
</tr>
<tr>
<td>Lb</td>
<td>40.1</td>
<td>3.2</td>
<td>134.0(C₂), 117.7(C₃), 135.0(C₄), 119.0(C₅), 149.5(C₆), 105.6(C₇), 132.5(C₈), 126.5(C₉), 121.3(C₁₀)</td>
<td>17.6</td>
</tr>
<tr>
<td>Lc</td>
<td>40.3</td>
<td>6.8</td>
<td>140.0(C₂), 121.3(C₃), 136.3(C₄), 122.7(C₅), 149.5(C₆), 101.2(C₇), 141.0(C₈), 115.1(C₉), 160.1(C₁₀)</td>
<td>55.1</td>
</tr>
<tr>
<td>Ld</td>
<td>40.2</td>
<td>6.8</td>
<td>140.0(C₂), 121.4(C₃), 136.4(C₄), 122.2(C₅), 149.5(C₆), 101.2(C₇), 141.1(C₈), 115.8(C₉), 159.3(C₁₀)</td>
<td>63.5,14.9</td>
</tr>
<tr>
<td>L'</td>
<td>40.2</td>
<td>2.2</td>
<td>136.5(C₂), 120.2(C₃), 135.6(C₄), 122.3(C₅), 148.2(C₆)</td>
<td>-</td>
</tr>
</tbody>
</table>

* = Not Observed.
La = 2-(2-Aryltelluroethyl)-3-methyl pyridine [C₁₄H₁₅NTe]
Lb = 2-[2-(4-methylaryl) Telluroethyl]-3-methyl pyridine [C₁₅H₁₇NTe]
Lc = 2-[2-(4-methoxyaryl) Telluroethyl]-3-methyl pyridine [C₁₅H₁₇ONTe]
Ld = 2-[2-(4-ethoxyaryl) Telluroethyl]-3-methyl pyridine [C₁₆H₁₹ONTe]
L' = 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine [C₁₆H₂₀N₂Te]
basis of earlier reports\textsuperscript{8,10}. The IR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] show characteristic bands at 410 cm\textsuperscript{-1} due to δ(C-N) vibration (out of plane ring deformation) \textsuperscript{(8)}. Two medium to low intensity υ [Te-C (aromatic)] bands appear between 240-260 and 280-295 in the IR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] concurring with earlier observations\textsuperscript{8}. A band of medium to strong intensity at around 480 cm\textsuperscript{-1} in the IR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] attributed to υ[Te-C(aliphatic)] vibration\textsuperscript{(9)}.

\textbf{1H and \textsuperscript{125}Te(\textsuperscript{1}H) NMR spectra}

The \textsuperscript{1}H NMR spectra of Ligands 2-(2-aryl telluroethyl)-3-methyl pyridines (L) and 2-[2-(3-methyl pyridinoethyltelluro)ethyl]-3-methyl pyridine (L) were recorded in CDCl\textsubscript{3} \textsuperscript{(11-13)}. The various chemical shifts along with their assignments are given in table 3.

The \textsuperscript{1}H NMR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] show multiplet at ~δ,3.2 for H\textsubscript{7} and H\textsubscript{8} rather than two triplets (centered at δ, 3.9 and 3.2 ppm respectively) as observed in the precursor, 2-(2-chloroethyl)-3-methyl pyridine. The up field shift (0.7ppm) of H\textsubscript{8} in the ligand with respect to their precursor may be attributed to replacement of chlorine atom by tellurium, an atom of much lower electronegativity. This shielding of H\textsubscript{8} protons result in their merger with H\textsubscript{7} signals\textsuperscript{14-16}.

The atomic ring protons in L [C\textsubscript{14}H\textsubscript{15}NTe] appear as multiplet and merged with the pyridine ring protons between δ 7.00-7.60 ppm. The aromatic ring protons of Lb-Ld [C\textsubscript{15}H\textsubscript{17}NTe], [C\textsubscript{15}H\textsubscript{17}ONTe], [C\textsubscript{16}H\textsubscript{19}ONTe] do not appear as two doublets as expected for a 1, 4-disubstituted benzene ring having substituents of different electro negativities\textsuperscript{19} but merge with the pyridine ring protons and appear as a multiplet between δ 6.70-7.70 ppm.

In L [C\textsubscript{14}H\textsubscript{15}NTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] the proton linked to the carbon ortho to nitrogen (H\textsubscript{6}) appears most downfield as compare to other ring protons and appears at δ, 8.5ppm as a doublet. The nitrogen being electronegative in nature deshields the adjacent carbon most, and consequently the proton linked to it, is deshielded most\textsuperscript{17,18}.

In L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] H\textsubscript{6} appear at δ, 7.25ppm, and H\textsubscript{7} and H\textsubscript{8} appear at δ, 7.08 ppm as multiplet as expected for ortho substituted alkyl pyridine\textsuperscript{20}.

The \textsuperscript{125}Te (\textsuperscript{1}H) NMR spectra of Lc [C\textsubscript{15}H\textsubscript{17}ONTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] show a sharp singlet at Δ, 481 and 167 ppm respectively which are in concordance with the values reported for asymmetric alkyl aryltellurides and symmetric dialkyttelluride\textsuperscript{(21-23)}.

\textbf{13C (\textsuperscript{1}H) NMR spectra}

The assignment of the signals (Table 4) in the \textsuperscript{13}C (\textsuperscript{1}H) NMR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] and L\textsuperscript{'} [C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}Te] recorded in CDCl\textsubscript{3} have been made on the basis of literature reports on the related compounds and additivity principle \textsuperscript{24-26}. The C\textsubscript{8} appears between δ, 2.2 and 6.8 ppm and C\textsubscript{7} around δ, 40.0 ppm. The C\textsubscript{8} have been found to be shielded because of the presence of a lone pair of electrons on the less electronegative tellurium atom in the ligand concurring with the earlier reports\textsuperscript{27} on such compounds.

This observation supports the shielding of CH\textsubscript{2}Te protons and consequently their merger with the C\textsubscript{8} protons in \textsuperscript{1}H NMR spectra. The phenyl ring carbon linked to tellurium (i.e. C\textsubscript{3}) appears around δ, 100 ppm in the \textsuperscript{13}C (\textsuperscript{1}H) NMR spectra of L [C\textsubscript{14}H\textsubscript{15}NTe] because it experiences greatest shielding among the phenyl carbons due to lone pair of electrons of the tellurium\textsuperscript{28}. The carbons of the pyridine ring appear as expected for the ortho substituted alkyl pyridine. The carbon ortho to nitrogen (C\textsubscript{6}) appears at δ, 149.5 ppm, most downfield as compared to the other carbons of the ring. This is because of the greater electron negativity of the nitrogen which deshields C\textsubscript{6} most; consequently it appears at most downfield\textsuperscript{29-31}.

\textbf{REFERENCES}


Selenium and Tellurium Univ. Aston.


