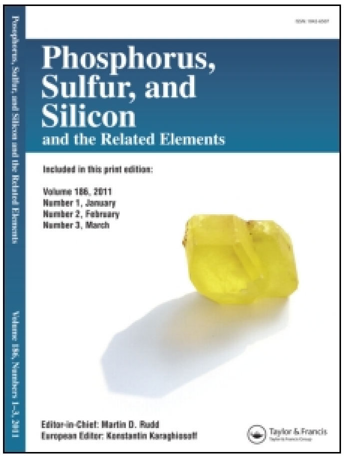

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SYNTHESIS OF NOVEL BIDENTATE (Te, N) LIGANDS—2-ARYLTELLUROETHYLAMINES AND THEIR COMPLEXATION WITH MERCURY(II)

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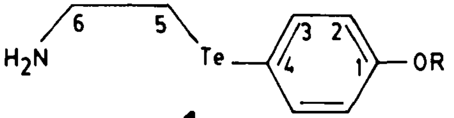
Sodium aryltellurolate ($ArTe^-Na^+$, where Ar = 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) reacts with 2-bromoethylamine resulting in the (Te, N) ligands 2-aryltelluroethylamine ($ArTeCH_2CH_2NH_2$, **1**) which have been characterized by elemental analyses, molecular weight, IR, ^1H and ^{13}C NMR spectra. With $HgCl_2$, they form $HgCl_2$·**1** type of complexes. IR, ^1H and ^{13}C NMR spectra of the complexes suggest that **1** ligates as a bidentate ligand with respect to Hg(II). Osmometric molecular weight measurements suggest that on heating the mercury complex $HgCl_2$.**1b** (Ar = 4-$EtOC_6H_4$) in solution, relatively less soluble species result. It seems to have two Hg atoms bridged by two (Te, N) ligands. The $HgCl_2$·**1a** (Ar = 4-$MeOC_6H_4$) has very low solubility in organic solvents and, therefore, seems to be dimerized or polymerized during the synthesis. Analysis of CH_2 rocking bands in IR spectra suggests that two CH_2 groups of the ligands are most probably in a *gauche* conformation in the mercury complexes.

Key words: (Te, N) donor; 2-aryltelluroethylamine; mercury(II)-Te-donor complexes

INTRODUCTION

The coordination chemistry of organotellurium ligands is mainly limited to complexes of RTe^-, R_2Te or R_2Te_2[1-2] (R = alkyl or aryl group). Very few bidentate or polydentate ligands containing the tellurium are known.[3-8] We are interested in synthesizing potentially multidentate ligands containing donor atoms such as N or O along with tellurium and to investigate their ligand chemistry. Therefore, 2-aryltelluroethylamines (**1**) have been synthesized as a part of our programme on the ligand chemistry of tellurium by reacting $ArTe^-$ with $BrCH_2CH_2NH_2$. Synthesis, spectra (IR and NMR) and complex formation of these ligands with mercury(II) are the subject of the present paper.



1

	R
(a)	CH_3
(b)	C_2H_5

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RESULTS AND DISCUSSION

2-Aryltelluroethylamines are formed in the reactions given in Equations 1 to 3. They are more soluble in organic solvents like

$$Ar_2Te_2 \xrightarrow[N_2\,atm]{NaBH_4/NaOH} 2ArTe^-Na^+ \tag{1}$$

$$2ArTe^-Na^+ + Br(CH_2)_2NH_2 \cdot HBr \rightarrow ArTe(CH_2)_2NH_2 \cdot HBr + NaBr \tag{2}$$

$$ArTe(CH_2)_2NH_2 \cdot HBr \xrightarrow{NaOH\,(10\%)} ArTe(CH_2)_2NH_2 \tag{3}$$

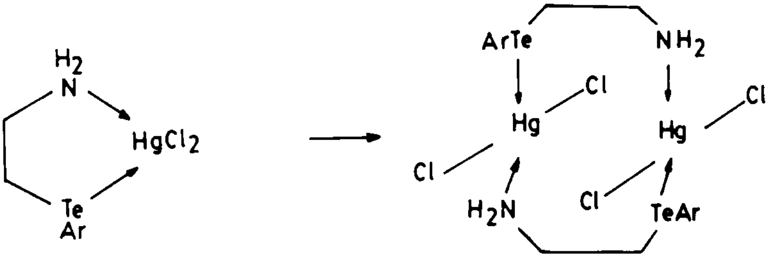
chloroform and are found to be monomeric by molecular weight measurements on their 10–15 millimolal solutions in chloroform. ^1H NMR spectra of **1a** and **1b** are as expected, except the occurrence of a broad singlet for the $CH_2(Te/N)$ protons. In the ^1H NMR spectrum of ethanolamine, triplets of NCH_2 and OCH_2 appear at 2.78 and 3.56 ppm respectively. Probably the replacement of the OH group with the much less electronegative and large TeAr group causes the corresponding CH_2 protons to shift upfield and merge with NCH_2, resulting in a broader singlet. However, on recording their ^1H NMR spectra in CF_3COOD it has been observed that protons of the NCH_2 and $TeCH_2$ groups of **1a** give two triplets around δ 3.49 and 3.07 ppm respectively, as expected. A similar observation has been made for **1b**. The ^{13}C NMR spectra of **1a** and **1b** were as expected, having separate signals for CH_2Te and CH_2NH_2 each. This was confirmed further by off-resonance experiments. In the IR spectra of **1a** and **1b** N—H stretching, N—H bending and ν(C—N) bands occur around 3240, 1570 and 1180 cm^{-1} respectively. The band around 370 cm^{-1} seems to arise from Te—C(alkyl) stretching.[9] The Te—C(aryl) vibrations contribute to bands appearing around 250 and 315 cm^{-1}. The regions in the IR spectrum generally assigned to the CH_2 rocking mode[10] have bands around 930, 820 and 720 cm^{-1} which suggest that **1a** and **1b** probably exist in both *trans* and *gauche* forms, at least in the solid state.

Mercury(II) chloride reacts with **1a** and **1b** according equation 4. Of the resulting complexes $HgCl_2 \cdot$**1a** has poor solubility in organic solvents like $CDCl_3$, inadequate for recording an NMR spectrum. ^1H and ^{13}C NMR spectra of $HgCl_2 \cdot$**1b** are as expected. The NH_2 signal in the ^1H NMR spectrum of this complex appears downfield (~1.9 ppm) with respect to a similar signal of **1b**, indicating the involvement of NH_2 in coordination with Hg(II). The CH_2 protons give two triplets (partially resolved and may be considered very close to broad singlets), which suggest that in **1** shielding of carbon linked to Te and of protons

$$HgCl_2 + \mathbf{1} \rightarrow HgCl_2 \cdot \mathbf{1} \tag{4}$$

on it is due to the lone pair of tellurium. In the ^{13}C NMR spectrum of this complex the signals arising from C_4, C_5 and C_6 carbons have been found deshielded (2.5, 10.5 and 19 ppm respectively) in comparison to ligand **1b**, suggesting that mercury is coordinated through both tellurium and the NH_2 group. Red shift (~25 cm^{-1}) in N—H stretching and a blue shift (~15 cm^{-1}) in

N—H bending frequency support the coordination of Hg via NH_2. The bands having contribution from Te—C vibrations also undergo a red shift (20–30 cm^{-1}) which is consistent with the inference drawn from ^{13}C NMR data about the formation of a Hg—Te bond. The CH_2 rocking bands in the IR spectra of Hg-complexes appear in the ranges 925–890 and 825–815 cm^{-1}, suggesting that probably the two CH_2 groups of **1a** or **1b** adopt a *gauche* conformation.[10] The ν(Hg—Cl) was observed around 320–330 cm^{-1}. The molecular weight of $HgCl_2$·**1b** has been found almost double of its formula weight by the vapour pressure osmometric method.



SCHEME 1

The heating of a chloroform solution of $HgCl_2$·**1b** results in a less soluble complex which gives an IR spectrum identical to that of its precursor and has similar elemental composition. Probably due to instantaneous dimerization on heating, represented in Scheme 1, higher molecular weight has been observed. The attempts to characterize $HgCl_2$·**1a** by mass spectrum did not succeed due to its insignificant vaporization during the spectrum recording. Similarly our inability to obtain its suitable crystals restricted us from determining its crystal structure. The $HgCl_2$·**1b** also defied further characterization by mass spectrum or X-ray due to similar reasons.

CONCLUSION

Novel bidentate (Te, N) ligands $ArTe(CH_2)_2NH_2$ have been synthesized by reacting $ArTe^-$ with $BrCH_2CH_2NH_2$. They ligate with Hg(II) resulting in $(Te,N)HgCl_2$ type of complexes. The complex $HgCl_2$·**1b** seems to dimerize on heating. The $HgCl_2$·**1a** having poor solubility in organic solvents, appears to be dimerized or polymerized during the synthesis. Most probably the two CH_2 groups in the coordinated ligands are in *gauche* conformation and mercury is tetrahedrally surrounded by tellurium, nitrogen and chlorine atoms.

EXPERIMENTAL

The carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer elemental analyzer 240C. The tellurium content was estimated volumetrically.[11] Molecular weights were estimated with a Knauer vapour pressure osmometer. The IR spectra (of Nujol mulls or KBr/CsI disc) in the range 4000–200 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer at 99.55 and 25 MHz respectively.

Bis(4-ethoxyphenyl) and bis(4-methoxyphenyl) ditelluride were prepared by published methods.[12]

Synthesis of 2-aryltelluroethylamine (**1**). Bis(4-ethoxyphenyl) or bis(4-methoxyphenyl) ditelluride (~0.5 mmol) was dissolved and refluxed in ethanol (25 cm^3) under oxygen free N_2 atmosphere. Sodium borohydride (~0.2 g) dissolved in 1M NaOH was added to this solution dropwise till it became colourless. 2-Bromoethylamine hydrobromide (Fluka, 1 mmol) dissolved in a minimum amount of water was added dropwise to the colourless solution and the resulting mixture refluxed for 1 h. On neutralizing the reaction mixture with 10% NaOH an oil separated out, which was extracted into $CHCl_3$. The chloroform extract was dried on Na_2SO_4 and concentrated to small volume. Pale yellow plates of **1a** or **1b** appeared after keeping aside the concentrate for 24 h. The crystals of **1a** or **1b** thus obtained were filtered, washed with methanol and recrystallized from a chloroform-benzene mixture (4:1). The physical properties, results of elemental analyses and spectral data of the (Te,N) ligands are recorded below.

1a: Yield 70%; m.p. 90°C. Analysis: Found: C, 39.08; H, 4.75; N, 4.69; Te, 44.23. $C_9H_{13}NOTe$ calc.: C, 38.76; H, 4.66; N, 5.00; Te, 45.80%. Mol. wt.: Found: 287.0; calc.: 278.6. NMR (^1H, $CDCl_3$, 25°C): δ 1.59 (s, NH_2), 2.93 (bs, 4H, CH_2N/Te), 3.79 (s, 3H, OCH_3), 6.70–6.79 (d, 2H, phenyl protons *m* to Te), 7.64–7.73 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C)[13]: δ 14.9 (s, CH_2Te), 43.9 (s, CH_2N), 55.1 (s, OCH_3), 99.8 (s, C_4), 115.1 (s, C_2), 141.1 (s, C_3)), 159.7 (s, C_1).

1b: Yield 80%; m.p. 95°C. Analysis: Found: C, 41.95; H, 5.26; N, 4.47; Te, 42.75. $C_{10}H_{15}NOTe$ calc.: C, 41.30; H, 5.12; N, 4.78; Te, 43.61%. Mol. wt.: Found: 305; calc.: 292.6. NMR (^1H, $CDCl_3$, 25°C): δ 1.30–1.40 (t, 5H, $CH_3 + NH_2$), 2.92 (bs, 4H, CH_2N/Te), 3.91–4.11 (q, 2H, OCH_2), 6.69–6.77 (d, 2H, phenyl protons *m* to Te), 7.63–7.71 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C)[13]: δ, 14.1 (s, CH_2Te), 14.8 (s, CH_3), 43.0 (s, NCH_2), 63.3 (s, OCH_2), 99.7 (s, C_4), 115.7 (s, C_2), 141.0 (s, C_3), 159.1 (s, C_1).

Synthesis of mercury(II)-complexes of **1a** *and* **1b**. Mercuric chloride (1 mmol) dissolved in acetone (5 cm^3) was mixed with a solution of **1a** or **1b** (1 mmol) in 5 cm^3 chloroform. The mixture was stirred for 30 min. The off-white precipitate of $HgCl_2$·**1a** separated immediately whereas the complex of **1b** was precipitated by adding hexane (10 cm^3). The precipitates were washed with methanol and hexane successively. The elemental analyses, molecular weights, ^1H and ^{13}C NMR spectral data of the complexes are given below.

$HgCl_2$·**1a**: Yield 90%; m.p. 115°C. Analysis: Found: C, 18.92; H, 2.56; N, 2.34. $C_9H_{13}NOTeHgCl_2$ calc.: C, 19.63; H, 2.36; N, 2.54%. NMR could not be recorded due to poor solubility in most of the common organic solvents.

$HgCl_2$·**1b**: Yield 92%; m.p. 80°C. Analysis: Found: C, 22.05; H, 2.80; N, 2.57. $C_{10}H_{15}NOTeHgCl_2$ calc.: C, 21.27; H, 2.65; N, 2.48%. Mol. wt.: Found 1090; calc.: 564.2 NMR (^1H, $CDCl_3$, 25°C): δ 1.29–1.43 (t, 3H, CH_3), 3.35 (bs, 2H, NCH_2), 3.58 (bs, 2H, CH_2Te), 3.85–4.89 (q, 2H, OCH_2), 6.76–6.84 (d, 2H, phenyl protons *m* to Te), 7.72–7.80 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 14.7 (s, CH_3), 25.0 (s, $TeCH_2$), 62.1 (s, NCH_2), 63.8 (s, OCH_2), 102.2 (s, C_4), 116.7 (s, C_2), 139.9 (s, C_3), 160.6 (s, C_1).

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