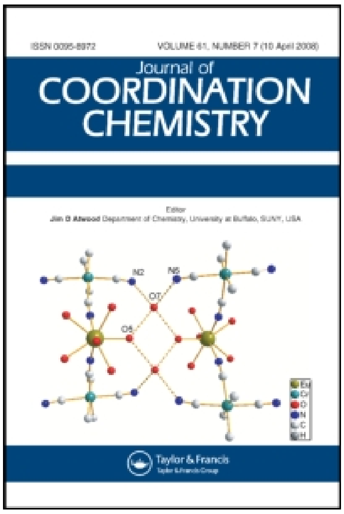

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Synthesis of Potential Tripodal Tellurium Ligands and Their Complexation with Mercury(II)

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SYNTHESIS OF POTENTIAL TRIPODAL TELLURIUM LIGANDS AND THEIR COMPLEXATION WITH MERCURY(II)

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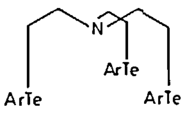
Sodium aryltellurolate ($ArTe^-Na^+$, where Ar = $4\text{-}MeOC_6H_4$ or $4\text{-}EtOC_6H_4$) reacts with tris(2-chloroethyl)amine resulting in the potentially tripodal tellurium ligand tris(2-aryltelluroethyl)amine [$N(CH_2CH_2TeAr)_3$, **1**]. These newly synthesized (N, Te_3) ligands form HgX_2.**1** (X = Cl or Br) complexes. IR, ^1H and ^{13}C NMR spectra in conjunction with molecular weight measurements suggest that **1** coordinates with mercury(II) through its two tellurium atoms and there is fast exchange between free and coordinated tellurium in solution.

Keywords: Telluro ligands, terdentates, mercury(II) complexes, synthesis

INTRODUCTION

Despite the recently developing interest in the ligand chemistry of tellurium,[1–3] few bidentate or polydentate ligands[4–6] containing the element are known. So far, no tripodal tellurium ligand is reported; such ligands having other donors are well documented.[7–8] One reason for interest in tripodal ligands is the fact that they can stabilize metal ions in the relatively rare trigonal bipyramidal geometry[8]. It would be of interest if such a possibility were to be explored when three of the four donor atoms of the ligand are relatively large. Therefore, the ligands **1a** and **1b** have been synthesized by reacting $ArTe^-$ with $N(CH_2CH_2Cl)_3$. In the present paper the synthesis, IR and NMR spectra and complexation with mercury(II) of these ligands is reported.



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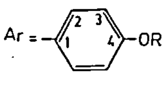

(a) R = CH_3
(b) R = C_2H_5

EXPERIMENTAL

The carbon, hydrogen and nitrogen analysis were carried out on a Perkin-Elmer 240C elemental analyzer. The tellurium content was estimated volumetrically.[9]

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Molecular weights were determined with a Knauer vapour pressure osmometer at 5–20 millimolal concentration levels. The IR spectra (Nujol mull or KBr/CsI disc) in the 4000–200 cm^{-1} range 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)ditelluride and bis(4-methoxyphenyl)ditelluride were synthesized by published methods.[10]

Tris(2-aryltelluroethyl)amine (1)

Bis(4-methoxyphenyl) or bis(4-ethoxyphenyl)ditelluride (~2.5 mmol) was refluxed in ethanol (40 cm^3) under an oxygen-free nitrogen atmosphere. Sodium borohydride (~1g) dissolved in 1 M NaOH was added dropwise to this refluxing solution until it became colourless. Tris(2-chloroethyl)amine[11] liberated from its hydrochloride by treating the salt with a stoichiometric amount of 10% NaOH, was dissolved in ethanol (1.66 mmol in 20 cm^3) and added dropwise to the solution of aryltellurolate generated earlier. The mixture was refluxed for 1 h. The resulting pale yellow oil was separated from the solution and stirred with 5–7 cm^3 ethanol for 30–60 min. The off-white solid thus separated was filtered off. It was washed with petroleum ether (60–80), recrystallized from a 1 : 1 chloroform-hexane mixture and dried *in vacuo*.

1a: Yield ~75%; m.p. 57°C. Analysis: Found: C, 40.05; H, 4.30; N, 1.54; Te, 46.53%. $C_{27}H_{33}O_3Te_3N$ calc.: C, 40.40; H, 4.11; N, 1.74; Te, 47.74%. Mol. wt.: Found: 730–860; Calc.: 801.8. NMR (^1H, $CDCl_3$, 25°C): δ, 2.83 (s, 4H, CH_2Te/N), 3.76 (s, 3H, OCH_3), 6.68–6.77 (d, 2H, phenyl protons *m* to Te), 7.58–7.67 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 7.9 (s, CH_2Te), 53.9 (s, CH_2N), 54.9 (s, OCH_3), 101.0 (C_1), 114.8(C_3), 140.3 (C_2), 159.2 (C_4).

1b: Yield ~80%; m.p. 65°C. Analysis: Found: C, 43.05; H, 4.82; N, 1.71; Te, 44.62%. $C_{30}H_{39}O_3Te_3N$ calc.: C, 42.66; H, 4.62; N, 1.65; Te, 45.36%. Mol. wt.: Found: 720–930; calc.: 843.8. NMR(^1H, $CDCl_3$, 25°C): δ, 1.3–1.4 (t, 3H, CH_3), 2.92 (s, 4H, CH_2Te/N), 3.89–4.11 (q, 2H, OCH_2), 6.68–6.77 (d, 2H, phenyl protons *m* to Te), 7.61–7.70 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 7.9 (s, CH_2Te), 14.7 (s, CH_3) 54.0 (s, CH_2N), 63.1 (s, OCH_2), 100.9 (C_1), 115.5 (C_3), 140.4 (C_2), 158.7 (C_4).

Mercury(II) complexes of 1a and 1b

Mercuric chloride dissolved in 5 cm^3 acetone was added to a soluton of **1a** or **1b** (0.5 mmol) in chloroform and the mixture stirred for 30 min. $HgCl_2$.**1a** separated as a white solid, immediately. The white coloured $HgCl_2$.**1b** complex was precipitated by adding 10 cm^3 of hexane to the mixture. The precipitates were thoroughly washed with methanol and hexane, successively.

$HgCl_2$.1a: Yield ~87%; m.p. 110°C. Analysis: Found: C, 29.81; H, 3.53; N, 1.20%. $C_{27}H_{33}O_3Te_3NHgCl_2$ calc.: C, 30.18; H, 3.07; N, 1.30%. NMR could not be recorded due to poor solubility.

$HgCl_2$.1b: Yield 80%; m.p. 100°C. Analysis: Found: C, 31.87; H, 3.20; N, 1.37%. $C_{30}H_{39}O_3Te_3NHgCl_2$ calc.: C, 32.27; H, 3.50; N, 1.25%. Mol. wt.: Found: 1060–1280; calc.: 1115.3. NMR (^1H, $CDCl_3$, 25°C): δ, 1.32–1.46 (t, 3H, CH_3), 2.98 (bs, 2H, NCH_2), 3.28 (bs, 2H, $TeCH_2$), 3.87–4.08 (q, 2H, OCH_2), 6.75–6.83 (d, 2H, phenyl

protons *m* to Te), 7.76–7.84 (d, 2H, phenyl protons *o* to Te); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 14.8 (s, CH_3), 19.3 (s, CH_2Te), 51.9 (s, CH_2N), 63.5 (s, OCH_2), 102.8 (C_1), 116.4 (C_3), 139.6 (C_2), 160.3 (C_4)

RESULTS AND DISCUSSION

Tris(2-aryltelluroethyl)amines (**1a** and **1b**) have been found to be soluble in organic solvents like chloroform, benzene and acetone, and monomeric by molecular weight measurements. ^1H NMR spectra of **1a** and **1b** are as expected, except for the occurrence of a singlet for two CH_2 groups. The NCH_2 and OCH_2 protons in the ^1H NMR spectrum of $N(CH_2CH_2OH)_3$ appear as triplet at 2.59 and 3.60 ppm respectively. Probably on replacement of the OH group by TeAr, the CH_2 protons linked to Te are shielded and merged with the NCH_2 protons, resulting in a somewhat broader singlet for the two CH_2 groups. On recording the ^1H NMR of **1a** in CF_3COOD, the NCH_2 and $TeCH_2$ groups appear as two partially resolved triplets at 3.47 and 2.83 ppm, respectively. **1b** also exhibits a similar ^1H NMR spectrum in CF_3COOD. The $^{13}C\{H\}$ NMR spectra of **1a** and **1b** are as expected.[12] The carbons of the two CH_2 groups in the ^{13}C NMR spectra give the expected two signals which have been confirmed by off-resonance experiments as methylene carbons. The shielding of the carbons of CH_2Te in the ^{13}C NMR spectrum further supports the inference drawn above concerning the broad singlet for CH_2 in the ^1H NMR. When tellurium is engaged in complexation with a metal ion (e.g. Hg(II)), its shielding influence on carbons linked to it diminishes and CH_2 protons give two broad singlets or partially resolved triplets. This suggests that the shielding of carbon linked to tellurium and of protons on it is due to the lone pair of Te. IR spectra of **1a** and **1b** have bands at 1180 and 380 cm^{-1} which may be assigned to C–N and Te–CH_2 vibrations, respectively. The bands around 250 and 315 cm^{-1} seem to have a contribution from Te–C(aryl) vibrations.[13]

Mercury(II) chloride forms adducts, $HgCl_2$.**1**, with **1a** and **1b**. Mercury(II) bromide gives complexes of a similar type with **1a** and **1b**, and detailed investigations of such adducts have been restricted to those of $HgCl_2$. The complex $HgCl_2$.**1a** was found to be poorly soluble in common organic solvents and therefore its NMR spectrum could not be recorded. $HgCl_2$.**1b** was found to be monomeric by osmometric molecular weight measurements. Its ^1H NMR spectrum is as expected. The CH_2Te and CH_2N signals appear separately as broad singlets which have features indicating that they may be considered as partially resolved triplets. In the ^{13}C NMR the C_1 and H_2C–Te carbon signals of **1b** were observed respectively ~2 and 12 ppm downfield (on the formation of Hg-complex). This indicates clearly the formation of the Hg–Te bond. The CH_2N signal group does not appear downfield on complexation, suggesting that nitrogen is not involved in coordination with mercury. In the IR spectra of $HgCl_2$.1a and $HgCl_2$.**1b**, weak bands have been observed in the regions ($\pm 5\,cm^{-1}$) where Te–C (alkyl/aryl) vibrations occur. New bands 15–50 cm^{-1} lower than these also seem to arise from Te–C (alkyl/aryl) vibrations. This probably indicates that all the available tellurium atoms of **1a**/**1b** do not coordinate with mercury in these complexes. Presuming the stereochemistry of the present mercury adducts to be tetrahedral and on considering their stoichiometries, it seems reasonable to infer that in the solid state one of the three tellurium atoms remains uncoordinated. The remaining two corners of the tetrahedron around mercury are occupied by chlorine atoms. ^1H and ^{13}C NMR spectra of the Hg-complex suggest that all three atoms (tellurium) are involved in coordination with mercury, at least in solution. The equivalence of the three tellurium atoms inferred from the NMR spectra is, however, contrary to the IR data. Probably the equivalence is due to exchange between free and coordinated tellurium atoms in solution (faster than the NMR time scale at room temperature). Due to the presence of two lone pairs on tellurium, such fluxionality is not unexpected.

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