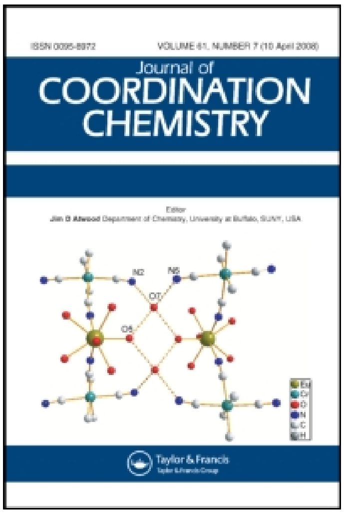

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Aryltelluroacetic Acids-Synthesis and Ligation with Mercury(II)

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ARYLTELLUROACETIC ACIDS-SYNTHESIS AND LIGATION WITH MERCURY(II)

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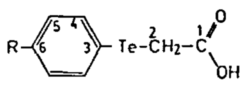
Sodium aryltellurolates ($ArTe^-Na^+$, where Ar = C_6H_5, 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) react with chloroacetic acid resulting in aryltelluroacetic acids or aryl carboxymethyl tellurides ($ArTeCH_2COOOH$, **1**) which have been characterized by molecular weight measurements, elemental analyses, IR, ^1H and ^{13}C NMR spectra. Mercury(II) chloride forms with **1** a complex $HgCl(OOCCH_2TeAr)$, in which the (Te,O) ligand has been demonstrated to behave as an uninegative bidentate donor by IR, ^1H and ^{13}C NMR spectra. Presuming tetrahedral stereochemistry for mercury(II), a dimeric formulation having two bridging chloro groups seems to be most plausible. The bridges, however appear to be weak in DMSO.

Keywords: Aryltelluroacetic acids, Hg(II), complexes, synthesis

INTRODUCTION

There is a considerable growth in current interest in the ligand chemistry of tellurium,[1–3], yet relatively very few papers have been published describing the coordination behaviour of bidentate or polydentate[4–7] tellurium ligands. Examples of multidentate tellurium ligands containing hard[8] donor atoms like O or N along with tellurium are scarce.[9–10]. Tellurium ligands favourably coordinate with class B metals and therefore (Te,O) or (Te,N) ligands are expected to be interesting on two accounts. First, they may ligate with 'hards' metals *via* N/O affording an opportunity to study the possibility of forced interaction of tellurium with such metals. Secondly, they may be used to synthesize bimetallic complexes in which a (Te,N)/(Te,O) ligand acts as a bridge between 'hard' and 'soft' metals. In view of these facts we have been researching the synthesis and ligation of new (Te,N) and (Te,O) ligands.[11] In the present paper, the syntheses of the ligands, (**1a–1c**) and their complexation with Hg(II), are described.



	R
(a)	H
(b)	OMe
(c)	OEt

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EXPERIMENTAL

Published methods[12] were used for the synthesis of $(4\text{-}MeOC_6H_4)_2Te$ and $(4\text{-}EtOC_6H_4)_2Te_2$. The carbon, hydrogen and nitrogen analysis were carried out on a Perkin-Elmer 240C elemental analyzer. Tellurium contents were estimated volumetrically.[13] Molecular weights were determined with a Knauer vapour pressure osmometer. IR spectra (KBr disc or Nujol mull sandwiched between CsI plates) in the range 200–4000 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer at 99.55 and 25 MHz respectively.

Synthesis of aryltelluroacetic acid (1a–1c)

Diarylditelluride (5 mmol) was dissolved in ethanol (50 cm^3) and solution of sodium borohydride (~1 g) in 10% NaOH (10 cm^3) was slowly added until the solution became almost colourless. Chloroacetic acid (10 mmol) dissolved in ethanol (20 cm^3) was slowly added to the colourless solution and the mixture was stirred for 2–3 h. It was poured into 250 cm^3 water and the resulting aqueous mixture was filtered. The filtrate was acidified with dilute acetic acid and shaken with 50–60 cm^3 chloroform. The organic extract was separated and concentrated to 10–15 cm^3. 40–60 petroleum ether (40–50 cm^3) was added to the concentrate. The resulting yellow crystals of aryltelluroacetic acid (**1a**–**1c**) were filtered, washed with petroleum ether (15–20 cm^3), recrystallized from chloroform and dried *in vacuo*. Elemental analyses, physical properties ^1H and ^{13}C NMR spectral data for **1a** and **1b** are given below.

1a: Yield 65%; m.p. 80–81°C. Analysis: Found: C, 36.40; H, 3.12; Te, 49.20%. $C_8H_8O_2Te$ Calc.: C, 36.42; H, 3.03; Te, 48.41%. NMR (^1H, $CDCl_3$, 25°C): δ, 3.51(s, 2H, CH_2), 7.1–7.9(m, 5H, phenyl), 10.68(bs, OH); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 9.2 (C_2), 128.7 (C_5), 139.1 (C_4), 141.3 (C_6), 180.2 (C_1). Mol. wt.: Found: 249; Calc.: 263.6.

1b: Yield 70%; m.p. 102–104°C. Analysis: Found: C, 36.74; H, 3.31; Te, 44.20%. $C_9H_{10}O_3Te$ Calc: C, 36.78; H, 3.41; Te, 43.46%, NMR (^1H, $CDCl_3$, 25°C): δ, 3.43(s, 2H, CH_2), 3.78(s, 3H, OCH_3), 6.73–7.83(m, 4H, phenyl), 9.94(bs, OH), ($^{13}C\{H\}$, $CDCl_3$, 25°C) δ, 5.6 (C_2), 55.1 (OCH_3), 101.1 (C_3), 115.3 (C_5), 141.8 (C_4), 160.4 (C_6), 180.5 (C_1). Mol. wt.: Found: 280; Calc.: 293.6.

1c: Yield 70%; m.p. 110–111°C. Analysis: Found: C, 39.20; H, 3.84; Te, 40.96%. $C_{10}H_{12}O_3Te$ Calc.: C, 39.01; H, 3.90; Te, 41.48%, NMR (^1H, $CDCl_3$, 25°C): δ, 1.33–1.47(t, 3H, CH_3), 3.42(s, 2H, CH_2), 3.91–4.12(q, 2H, OCH_2), 6.73–7.82(m, 4H, phenyl), 9.0(bs, OH); ($^{13}C\{H\}$, $CDCl_3$, 25°C): δ, 5.7 (C_2), 14.7 (CH_3), 63.4 (OCH_2), 100.1 (C_3), 115.9 (C_5), 141.8 (C_4), 159.8 (C_6), 180.2 (C_1). Mol. wt.: Found, 320; Calc.: 307.6.

Synthesis of mercury(II) complexes of aryltelluroacetic acids (1a–1c)

Mercuric chloride (1 mmol) dissolved in ethanol (20 cm^3) was added to a solution of 1 mmol ligand (**1a**–**1c**) in ethanol (20 cm^3). The mixture was refluxed for 2–3 h. The resulting light yellow precipitate was filtered, washed 2–3 times with 10 cm^3 ethanol, recrystallized from dimethylsulphoxide and dried *in vacuo*. Elemental analyses, physical properties, ^1H and ^{13}C NMR spectral data are given below.

HgCl(**1a**–H): Yield 75%; m.p. 145–146°C Analysis: Found: C, 20.40; H, 1.74; Te, 26.10; Hg 41.20; Cl, 7.53%, $C_8H_7O_2Te$ HgCl Calc.: C, 19.4; H, 1.40; Te, 25.62; Hg, 40.16; Cl, 7.12%. NMR(^{1}H, DMSO-d$_6$, 25°C): δ, 7.32–7.88(m, phenyl); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 20.8 (C_2), 116.2 (C_3), 130.1 (C_4), 137.8 (C_5), 156.3 (C_6), 172.2 (C_1).

HgCl(1b–H): Yield 78%; m.p. 138–139°C, Analysis: Found: C, 20.26; H, 1.92; Te, 25.20, Hg, 36.24, Cl, 6.81%. $C_9H_9O_3TeHgCl$ Calc.: C, 20.45; H, 1.70, Te, 24.10; Hg, 37.80; Cl, 6.71%. NMR(^{1}H, DMSO-d$_6$, 25°C); δ, 6.80–7.17(d, 2H, phenyl), 7.60–7.78(d, 2H, phenyl); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 20.9 (C_2), 55.8 (OCH_3), 116.0 (C_3), 139.8 (C_4), 140.6 (C_5), 156.2 (C_6), 171.9 (C_1).

HgCl(1c–H): Yield 80%; m.p. 154–156°C, Analysis: Found: C, 22.14; H, 2.16; Te, 24.30; Hg, 36.40; Cl, 6.52%. $C_{10}H_{11}O_3TeHgCl$ Calc.: C, 22.10; H, 2.02; Te, 23.50; Hg, 36.80; Cl, 6.54%. NMR(^{1}H, DMSO-d$_6$, 25°C): δ, 1.30–1.47(t, 3H, CH_3), 6.72–7.06(d, 2H, phenyl), 7.59–7.70(d, 2H, phenyl); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 14.5 (CH_3), 63.4 (OCH_2), 116.2 (C_6), 139.8 (C_4), 140.2 (C_5), 155.7 (C_6), 172.4 (C_1).

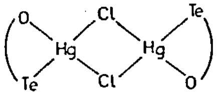
In the ^{1}H NMR spectra of all of the mercury complexes, CH_2, OCH_2 and OCH_3 signals were obscured by the solvent (DMSO) signal.

RESULTS AND DISCUSSION

The aryltelluroacetic acids (**1a**–**1c**) synthesized have good solubility in chloroform, acetonitrile, ethanol/methanol, DMSO and DMF and do not exhibit any association at the millimolal concentration levels used in the course of their molecular weight determinations. The ^{1}H NMR spectra of **1a** to **1c** are characteristic. The broad signal in the spectrum of **1a** due to the hydroxyl group appears around 10.68 ppm, significantly deshielded in comparison to that of acetic acid (OH signal at 8.63 ppm). This indicates that hydrogen bonding is greater in phenyltelluroacetic acid than in acetic acid. Apparently, the TeAr fragment acts as the electron withdrawing group. This is consistent with the polarity of the Te–C bond, where tellurium becomes positively charged. The ^{13}C NMR spectra of **1a**–**1c** have signals in agreement with the literature.[14] The occurrence of the C_2 carbon signal at 9.2 ppm further supports the positive charge distribution on tellurium. The ^{1}H NMR spectra of **1b** and **1c** indicate that the strength of hydrogen bonding decreases when an RO group is present at a position *para* to tellurium. When R is ethyl, the strength of hydrogen bonding decreases almost to the level of acetic acid. IR spectra of **1a**–**1c** have ν(OH), ν(C=O), δ(CH_2), ν(C–O) and δ(CH_2) bands around 2700, 1685, 1470, 1400 and 1290 cm^{-1}, respectively. The position of ν(OH) is consistent with the hydrogen bonding inferred from ^{1}H NMR data. The bands at 450 and 250 cm^{-1} have contribution from Te–CH_2 and Te–C(aryl) vibrations,[15] respectively.

Complexation of 1a–1c with mercury(II)

Mercury(II) chloride forms complexes, of stoichiometry ($ArTeCH_2COO$)HgCl, with **1a**–**1c**, and which have been found sparingly soluble in chloroform and acetonitrile but fairly soluble in DMSO and hot ethanol. Their IR spectra do not show a ν(OH) band, indicating that the aryltelluroacetic acids behave as an uninegative ligand in the complexes. The value of Δ [ν(C=O) – ν(C–O)] for these mercury complexes has been found to be approximately 320 cm^{-1}, suggesting the monodentate mode[16] of bonding for the carboxylate group. The red shift in ν(C–O) (~45 cm^{-1}) and a blue shift in ν(C=O) (~15 cm^{-1}) further support the monodentate nature of the COO^- group. The red shift (~10 cm^{-1}) in Te–CH_2 and TeC(Ar) vibrations suggests the involvement of tellurium in coordination. The ^1H NMR spectra of the mercury complexes could not be recorded in any solvent except DMSO-d_6, due to solubility problems. This restricted us from using CH_2 signal for any diagnostic purpose. The absence of an OH signal in the ^1H NMR spectra of the Hg-complexes supports the formulation inferred from IR data. The ^{13}C NMR spectra of Hg-complexes were found to be characteristic.[14] The deshielding of the C_2 ($\sim$ 11 ppm) and C_3($\sim$ 15 ppm) signals clearly indicates that **1a** to **1c** ligate with mercury(II) *via* tellurium. The shielding of the C_1 signal ($\sim$8 ppm) supports the unidentate bonding mode for COO^- group, as deduced from IR data. Presuming a tetrahedral stereochemistry for mercury(II) in the present complexes and on considering the bonding mode of $ArTeCH_2COOH$ (inferred on the basis of IR and NMR data) in conjunction, the dimeric structural formulation A seems to be plausible at least in solid stae. The molecular weights in DMSO have been found to be nearly half of the value expected for A. This is probably due to cleavage of the chloro bridges by DMSO, resulting in species of the type $HgCl.(OOClH_2TeAr).DMSO$.



(A)

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