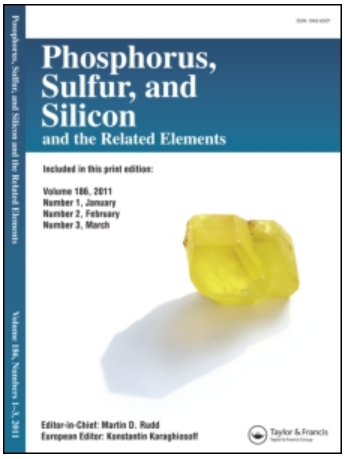

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FUNCTIONALIZED DIORGANOTELLURIDE AND DIORGANODITELLURIDE: COMPLEXATION BEHAVIOUR AS A HYBRID (Te, O) LIGAND

S. Thomas[a]; B. L. Khandelwal[a]; Ajai K. Singh[a]
[a] Department of Chemistry, Indian Institute of Technology, New Delhi, India

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FUNCTIONALIZED DIORGANOTELLURIDE AND DIORGANODITELLURIDE: COMPLEXATION BEHAVIOUR AS A HYBRID (Te, O) LIGAND

S. THOMAS, B.L. KHANDELWAL and AJAI K SINGH*

Department of Chemistry, Indian Institute of Technology, New Delhi - 110016, India

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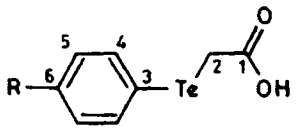
The ligation of asymmetric diorganotelluride aryltelluroacetic acid (**1**) with Pd(II) and Pt(II) and bis(5-methyl–2-hydroxyphenyl)ditelluride (**2**) with Hg(II) and Cu(II) have been studied. In square planar complexes of stoichiometry $[MCl(\mathbf{1}\text{-}H)]_2$(M = Pd or Pt) the bidentate uninegative behaviour of **1** has been inferred on the basis of IR ^1H and $^{13}C\{^1H\}$ NMR, data in conjunction with elemental analysis. The presence of an M-Cl(bridging) vibration band in the IR spectra around 260–270 cm^{-1} supports the dimeric formulation of these complexes. In DMSO these chloro bridges are broken which result in lower values for molecular weights in comparison to those calculated on the basis of dimeric stoichiometry. The reaction of **2** with $CuCl_2$ results in an unusually stable aryltellurenyl chloride. The Te ← O secondary interaction seems to be responsible for its stability. The reaction of $HgCl_2$ with **2** gives an intricate material of composition $ArTeHgCl_2$. It seems to be aryltellurenyl chloride which is mercurated at a position *ortho* to the OH group.

Keywords: Aryltelluroacetic acid, bis(5-methyl–2-hydroxyphenyl)ditelluride, palladium, platinum, copper, mercury, complexation, ligand, diorganotelluride, diorganoditelluride

INTRODUCTION

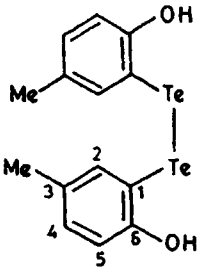
There is a current interest in the chemistry of telluroether ligands[1-6]. It partly stems from the possibility of using telluoether ligands in the designing of precursors for MOCVD of semiconducting metal-tellurides[7]. The hybrid tellurium ligands[5-6]containing besides tellurium other donors like O, N, P and S have also got attention in the recent past. The chemistry of such ligands is important in connection with the donor characteristics of tellurium vis-a-vis other donors. Only few hybrid ligands studied so far are of the (Te, O) type[1,2]. In all such ligands one of the organic groups of telluride or ditelluride is functionalized

* Corresponding author.



1

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



2

Alkyl groups may be functionalized with COOH and aryl groups with OH or COOH to obtain such ligands. In the present paper, ligand chemistry of two functionalized diorganoltellurides and ditellurides (**1-2**) is reported. Very few functionalized diorgano ditellurides[1,2,8] have been explored for the ligation properties so far.

EXPERIMENTAL

Published methods were used to synthesize aryltelluroacetic acids (**1**)[9] and 1-(chloro mercury)-2-hydroxy–5-methylbenzene[10]. The carbon and hydrogen analyses were carried out on a Perkin-Elmer elemental analyzer 240C. Tellurium contents were estimated volumetrically[11]. Molecular weights were determined with the Knauer vapour pressure osmometer. IR spectra (of KBr disc or Nujol mulls sandwiched between CsI plates) in the range 200-4000 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrometer. Far-IR spectra (up to 50 cm^{-1}) were recorded on a Perkin-Elmer Far-IR spectrometer model 1700 X. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer at 99.55 and 25 MHz respectively.

Synthesis of palladium(II) - aryltelluroacetic acid complexes

The complex $(PhCN)_2PdCl_2$ (0.5 mmol) was dissolved in 20 cm^3 chloroform and added to a solution of 0.5 mmol ligand (**1a-1c**) in 20 cm^3 chloroform. The mixture was stirred for 2 h at room temperature and 20-25 cm^3 petroleum ether (40-60°C) was added. The resulting reddish brown precipitate was filtered, washed with chloroform and recrystallized from acetonirile. The physical characteristics, results of elemental analyses and spectral data are given below.

[PdCl(1a-H)]$_2$: Yield ~78%; m.p. 142-144°C. Analysis: Found: C, 24.48; H, 2.11. Calc. for $C_8H_7O_2TePdCl$: C, 23.74; H, 1.73%. NMR (^{1}H, DMSO-d_6, 25°C): δ, 6.8-7.6 (m, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 22.9 (C_2), 118.0 (C_3), 130.6 (C_5), 138.3 (C_4), 126.3 (C_6), 171.0 (C_1).

[PdCl(1b-H)]$_2$: Yield ~ 85%; m.p. 130–132°C. Analysis: Found: C, 24.39; H, 2.28. Calc. for $C_9H_9O_3TePdCl$: C, 24.86; H, 2.07%. NMR (^{1}H, DMSO-d_6, 25°C): δ, 6.7-7.8 (m, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 23.8 (C_2), 55.9 (OCH_3), 116.1 (C_3), 138.3 (C_5), 138.7 (C_4), 161.4 (C_6), 171.0 (C_1).

[PdCl(1c-H)]$_2$: Yield ~ 85%; m.p. 146–147°C. Analysis: Found: C, 25.81; H, 2.47. Calc. for $C_{10}H_{11}O_3TePdCl$: C, 26.70; H, 2.68%. NMR (^{1}H, DMSO-d_6, 25°C):δ, 1.3-1.4 (q, 3H, CH_3); 6.7 - 7.8 (m, 4H, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 15.1 (CH_3), 63.9 (OCH_2), 116.5 (C_3), 138.3 (C_5), 138.7 (C_4), 160.7 (C_6), 170.9 (C_1).

Synthesis of platinum(II) - aryltelluroacetic acid complexes

The complex salt K_2PtCl_4 (0.5 mmol) dissolved in 10 cm^3 of water was mixed with a solution of 0.5 mmol ligand in acetone (10 cm^3). The mixture was stirred for 2 h at room temperature, concentrated under vacuum to 10 cm^3 and set aside for overnight at 5°C. The orange-yellow precipitate formed, was filtered, washed with acetone-water mixture and recrystallized from acetonitrile. The physical characteristics, results of elemental analyses and spectral data are given below.

[PtCl(1a-H)]$_2$: Yield ~ 75%; m.p. 146-148 °C. Analysis: Found: C, 20.11; H, 1.89%; Calc. for $C_8H_7O_2TePtCl$: C, 19.42, H, 1.41%. NMR (^{1}H, DMSO-d_6, 25°C): δ, 6.7-7.8 (m, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 22.8 (C_2), 116.5 (C_3), 130.2 (C_5), 138.2 (C_4), 127.2 (C_6), 172.3 (C_1).

[PtCl(1b-H)]$_2$: Yield ~ 70%; m.p. 130–132 °C. Analysis: Found: C, 21.21; H, 2.00%; Calc. for $C_9H_9O_3TePtCl$: C, 20.59, H, 1.72%; NMR (^{1}H, DMSO-d_6, 25°C): δ, 6.6-7.7 (m, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 22.9 (C_2), 55.5 (OCH_3), 116.3 (C_3), 138.5 (C_5), 140.6 (C_4), 158.9 (C_6), 171.0 (C_1).

[PtCl(1c-H)]$_2$: Yield ~78%; m.p. 146 °C. Analysis: Found: C, 22.42; H, 2.16%; Calc. for $C_{10}H_{11}O_3TePtCl$: C, 22.42, H, 2.16%; NMR (^{1}H, DMSO-d_6, 25°C): δ, 1.3-1.4 (t, 3H, CH_3); 6.7–7.8(m, 4H, phenyl); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 14.8 (CH_3), 63.5 (OCH_2), 116.3 (C_3), 138.7 (C_5), 140.2 (C_4), 158.9 (C_6), 171.2 (C_1).

The signals of CH_2-Te, OCH_3 and OCH_2 in the ^{1}H NMR spectra were found to be merged with the DMSO signal.

Synthesis of 5-methyl–2-hydroxyphenyltellurium(IV) Chloride

1-(Chloromercury)-2-hydroxy-5-methylbenezene[1] (3.4 g, 10 mmol) and $TeCl_4$ (2.7 g, 10 mmol) were refluxed in dry dioxane (50 cm^3) for 5-6 h under N_2 atmosphere. After cooling the reaction mixture to 40°C the precipitated $HgCl_2$ dioxane adduct was filtered off. The filtrate was concentrated to 5-7 cm^3 and 10-15 cm^3 hexane added to it. The resulting yellow precipitate was washed with benzene/hexane and recrystallized from chloroform. Yield 78%; m.p. 195°C. Analysis: Found: C, 25.20; H, 2.16; Te, 38.20: Cl, 30.12%. Calc. for $C_7H_7OTeCl_3$: C, 24.60; H, 2.06; Te, 38.40, Cl, 30.26%. NMR (^1H, $CDCl_3$, 25°C): δ, 2.34 (s, 3H, CH_3), 6.91 - 7.70 (m, 3H, phenyl), 10.08 (bs, OH).

Synthesis of 2

A suspension of 5-methyl–2-hydroxyphenyltellurium (IV) chloride (3.4 g, 10 mmol) in cold water was slowly mixed with sodium metabisulphite (50 mmol) dissolved in water. The mixture was stirred for 2 h at 0-5 °C and filtered the resulting solid was washed several times with water and recrystallized from ethanol. Yield ~ 65%; m.p. 100 °C. Analysis: Found: C, 34.64; H, 3.02; Te, 55.36%. Calc. for $C_{14}H_{14}O_2Te_2$: C, 34.80: H 2.98; Te, 55.60%. NMR (^1H, $CDCl_3$, 25°C) δ, 2.30 (s, 6H, CH_3), 6.80 (bs, OH), 6.90-7.70 (m, 6H, phenyl); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 20.15 (CH_3), 106.1 (C_1), 114.0 (C_5), 131.4 (C_3), 131.9 (C_2), 140.0 (C_4), 154.9 (C_6).

Reaction of $CuCl_2$ with 2

The solution of **2** (1 mmol) in benzene (10 cm^3) was added to $CuCl_2$ (2 mmol) dissolved in ethanol (10 cm^3) with stirring. The reaction mixture was stirred further for 1 h; the deep red colour disappeared. The while precipitate formed during the reaction was filtered off and the filtrate was concentrated to 5-7 cm^3. The resulting off-white solid was filtered, washed with benzene and recrystallized from ethanol. Yield ~ 75%. Analysis: Found: C, 30.86: H, 2.60; Te, 46.60; Cl, 13.12%. Calc for C_7H_7OTeCl: C, 31.10; H, 2.59; Te, 47.30; Cl, 13.14%. NMR (^1H, DMSO-d_6, 25 °C): δ, 2.50 (s, 3H, CH_3), 6.80-7.60 (m, 3H, phenyl) 11.27 (bs, OH); ($^{13}C\{^1H\}$, DMSO-d_6, 25 °C): δ, 20.7 (CH_3), 116.3 (C_1), 131.4 (C_3), 133.2 (C_5), 134.3 (C_2), 135.7 (C_4) 156.8 (C_6).

Reaction of $HgCl_2$ with 2

A solution of **2** (1 mmol) in benzene (10 cm^3) was stirred with $HgCl_2$ (2 mmol) dissolved in ethanol (10 cm^3) for 1h. The deep red colour of the mixture disappeared and a yellow precipitate formed. This was filtered and washed thoroughly with benzene and cold ethanol successively and dried *in vacuo*. Yield, 80%, m.p. 100 °C. Analysis: Found: C, 16.90; H, 1.44; Te, 26.01; Hg, 39.52; Cl, 14.90%. Calc. for $C_{14}H_{14}O_2Te_2Hg_2Cl_4$: C, 16.60; H, 1.38; Te, 25.24; Hg; 39.56; Cl, 14.04. NMR (^1H, DMSO-d_6, 25 °C): δ, 2.12 (S, 3H, CH_3), 6.88–7.70 (bs, 2H, phenyl), 10.40 (bs, OH).

RESULTS AND DISCUSSION

The palladium (II) and platinum (II) complexes of **1a-1c** are probably result of the following reactions

$$2(PhCN)_2PdCl_2 + 2\mathbf{1} \rightarrow [PdCl(\mathbf{1} - H)]_2 + 4PhCN + 2HCl \quad (1)$$

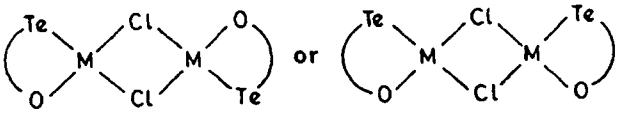
$$2K_2PtCl_4 + 2\mathbf{1} \rightarrow [PtCl(\mathbf{1}\text{-}H)]_2 + KCl + 2HCl \quad (2)$$

The complexes are diamagnetic and fairly soluble in DMSO, acetonitrile, acetone and ethanol and sparingly in solvents like chloroform and benzene. The IR spectra of these complexes exhibits bands around 1700, 1468, 1380 and 1286-1246 cm^{-1} which may be assigned to ν(C = 0), ν(CH_2), ν(C - 0) and ν(CH_2) respectively. On comparing these bands with those of the ligands[9] a red shift in ν(C = 0) (~15 cm^{-1}) was noticed. The value of Δ[ν(C = 0) -ν(C - 0)] for these complexes was found to be of the order of 320 cm^{-1}, Both these observations[12a] suggest that the COO^- group coordinates in a uninegative, monodentate mode in these complexes, consequently ν(OH) has been found to be absent in IR spectra of all the complexes. The ν(Te-CH_2) band[16] appears around 440 cm^{-1} in the spectra of these complexes, nearly 10 cm^{-1} red shifted with respect to that of the free ligand. This suggests that Te is probably involved in the formation of a chelate ring.

The ^1H NMR spectra of these complexes could not be recorded in any solvent except DMSO-d_6 due to solubility problems. This restricted us from quantifying deshielding of the CH_2-Te signal (which is of good diagnostic value) because it was always found merged with the signal of DMSO. It is undoubtedly signficantly deshielded (δ(CH_2-Te)[9] in **1** ~ 3.4-3.5 ppm), which is compatible with the ligation of **1** through tellurium. The absence of an OH signal in the ^1H NMR spectra of these complexes supports the uninegative nature of **1a-1c**. The comparison of ^{13}C NMR spectra[13] of these complexes, which have been found to be

characteristic, with those of the ligands[9], reveals that deshielding of C_2 and C_3 by ~ 13-17 and ~ 15-17 ppm respectively occurs on complexation of **1a-1c** with Pd(II) or Pt(II). This observation even after considering the solvent effect corrborates that the aryltelluroacetic acids ligate via tellurium in the present Pd/Pt complexes. The C_1 signal undergoes shielding of the order of ~8 ppm supporting the monodentate nature of the COO^- group as inferred from IR spectra.

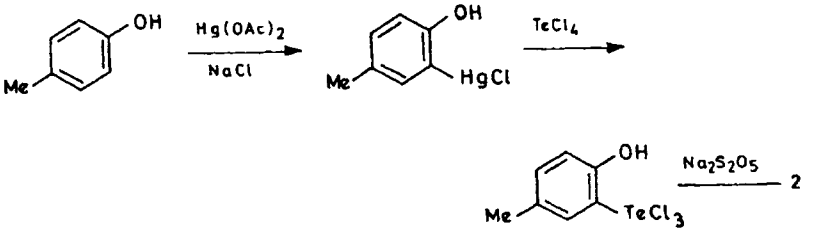
The electronic spectra of all these complexes in DMSO exhibit a band around 27 kK which may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition characteristic of square planar geometry[14]. Keeping in view all these observations, the structure **A**



A

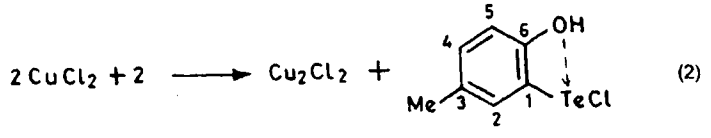
appears to be the most plausible for these complexes. It is supported by the appearance of ν(Pd/Pt - Cl (bridging)) vibrations[12] in the far IR spectra of the complexes around 270/260 cm^{-1}. However, attempts to support the dimeric formulation on the basis of molecular weight measurements in DMSO did not succeed because observed molecular weights were found to be nearly half of the calculated ones (presuming dimeric nature). Most probably in DMSO solution solvolysis of **2** results in [MCl(1-H)(DMSO)], resulting in lower molecular weights than expected. However these Pd/Pt complexes do not give single crystals suitable for X-ray diffraction, which has restricted us to rely on spectral evidences only.

To synthesize an $ArTeCl_3$ type of derivative of p-cresol, mercuration followed by transmetallation (Scheme 1) has been found successful. The OH signal in ^1H NMR spectrum of **2** appears 3.2 ppm shielded



SCHEME 1

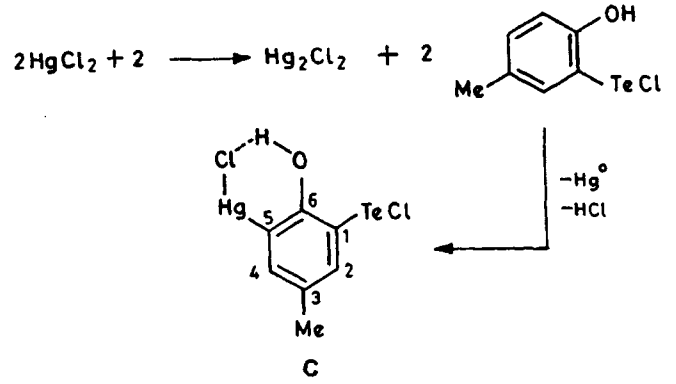
with respect to the similar signal of its precursor chloride. This may be partly due to decrease in the Te ← O secondary interaction[17], when the chloride is reduced to ditelluride. Copper(II)chloride reacts with **2** according to equation (3)



B

Organotellurenyl halides are generally unstable[17]. The present aryltellurenyl chloride (B) seems to be stabilized by Te ← 0 secondary interaction. This is supported by the presence of a highly deshielded OH signal (δ, 11.27 ppm) in its NMR spectrum. The attempt to verify the secondary interaction by single crystal structure determination could not be made because of our failure to grow crystals of tellurenyl compound suitable for X-ray diffraction work.

The ligand **2** reacts with $HgCl_2$ forming a compound of stoichiometry $[(HgCl_2)_2.\mathbf{2}]$. This new compound does not exhibit ν(Te-Te) in its IR spectrum. In its ^1H NMR spectrum, the ratio of the integrated methyl and phenyl protons is nearly 3:2 and the OH signal is ~ 0.87 ppm shielded with respect to that of tellurenyl compound (equation 3). These observations coupled with the fact that the mercury derivative behaves as a non electrolyte in DMSO, suggest that it has structure **C** . Elemental mercury is observed as a product in the reaction of **2** with $HgCl_2$. Therefore, most probably the following sequence of reactions is responsible for the formation of the mercury derivative. The ν(Te-Cl) and



C

ν(Te-C)[14] appear in the spectrum of this mercury compound at 278 and 250 cm^{-1}, respectively. The IR band at 288 cm^{-1} appears to be assignable to the ν(Hg-Cl) vibration[12b]. However, its frequency is somewhat lower than that of a terminal one but does not correspond to ν(Hg-Cl (bridging)). It is thus compatible with structure **C**.

Acknowledgement

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