

Novel synthesis of bis(4-methoxyphenyltelluro)methane and its complexation with Pd(II) and Pt(II): crystal structure of $[\text{Pd}(\{4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te}\}_2\text{CH}_2)\text{Cl}_2]^-$ a chelate with short interdonor linkage

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Abstract

A novel and convenient route for the synthesis of bis(4-methoxyphenyltelluro)methane using one pot reaction of ditelluride, sodium borohydride and chloroform is described. The palladium(II) and platinum(II) complexes of this ditelluroether ligand were also synthesized. The structure of the palladium(II) complex was confirmed by X-ray diffraction studies. The red complex $[\text{Pd}(\{4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te}\}_2\text{CH}_2)\text{Cl}_2]$ crystallizes in monoclinic space group $P2_1/n$ with four formulae in the unit cell. The cell dimensions are $a = 7.872(3)$ Å, $b = 20.372(2)$ Å, $c = 11.421(3)$ Å, $\beta = 100.90(2)^\circ$, $D_c = 2.445(5)$ g cm⁻³. In the complex, the Pd has distorted square planar geometry around it, the two Cl atoms are *cis* to each other and the ditelluroether ligand behaves in a bidentate mode. This is the first example in which the ligand molecule, through two tellurium atoms linked with a single carbon atom, is chelated to a single metal centre; the interdonor distance between the tellurium atoms is $3.2939(2)$ Å. The two parallel aryl rings are almost perpendicular to the square planar geometry on the same side of the chelate ring. The complex is monomeric with weak association between tellurium and a neighbouring chlorine.

Keywords: Palladium(II); Platinum(II); Bis(aryltelluro) methane; Tellurium; Chelation; Crystal structure

1. Introduction

In recent years selenium acetals and mixed acetals containing selenium and other main group elements have shown prominence in the field of organic chemistry [1–3]. A group of compounds closely related to these are bis(aryltelluro)methanes. The synthesis of bis(organyltelluro)methane was first reported in 1970 by the reaction of CH_2N_2 and R_2Te_2 (R is alkyl or aryl group) [4]. Some new examples were added later using a similar route [5,6]. Seebach and Beck synthesized it from lithium aryltelluroolate and diiodomethane in low yield (6%) [7]. Engman and Cava used lithium aryltelluroolate and dichloromethane, obtaining acceptable yield (68%) [8]. Hope et al. used frozen mixtures of lithium alkyl or aryltelluroolate and dichloromethane or diiodomethane in liquid nitrogen bath to obtain good yield of bis(alkyl or aryltelluro)methane [9]. De Silva et al.

used sodium aryltelluroolate and diiodomethane or dibromomethane, obtaining bis(aryltelluro)methane containing 1 mol dihalogenomethane [10]. Nearly two dozen bis(aryltelluro)methanes have been synthesized by using either of these strategies but there is no report on their coordination behaviour except recent reports in which a dimeric platinum(IV) complex and polymeric platinum(II) and palladium(II) complexes of bis(aryltelluro)methane have been synthesized [11,12]. In this paper we report a novel and convenient route for the synthesis of bis(aryltelluro)methanes in good yield (greater than 80%). The palladium(II) and platinum(II) complexes of this ditelluroether have also been synthesized. The structure of the palladium(II) complex has been solved by X-ray diffraction.

2. Experimental section

Published methods were used to synthesize (MeO-4-C₆H₄)₂Te₂ [13]. Far-IR spectra in the range 30–700

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cm^{-1} were recorded in polyethylene on a Perkin-Elmer 1700 X FT IR instrument. ^1H , ^{13}C and ^{125}Te NMR spectra were recorded on a Bruker AMX 400 FT NMR spectrometer. The molecular weight was determined in chloroform using a Knauer vapour pressure osmometer. Elemental analyses were performed on a Perkin-Elmer 240C analyser. Solvents were dried and distilled before use.

2.1. Synthesis of bis(4-methoxyphenyltelluro)methane (L)

To an ethanolic solution of bis(4-methoxyphenyl)ditelluride (1.88 g, 4 mmol in 50 cm^3 ethanol), a solution of sodium borohydride (0.45 g in 5 cm^3 of 10% NaOH) was added dropwise with vigorous stirring in oxygen-free dry nitrogen atmosphere until it became colourless. To this, chloroform (5 cm^3 , 10 mmol) was added in one lot and the mixture was further refluxed for 30 min. On cooling at ice cold temperature, crystal of bis(4-methoxyphenyltelluro)methane separated out. It was washed successively with water, ethanol and hexane and dried in vacuo. Yield, 1.55 g, 80%; mol. wt., 474(484); C, 37.0 (37.25); H, 3.29 (3.31)%; m.p. 98°C (lit. value, $99\text{--}102^\circ\text{C}$); ^1H NMR (25°C); 3.76, 2H, (CH_2Te), (lit. value, 3.78 [4]); ^{13}C NMR -35.8 , (CH_2Te) (lit. value, -35.6 ppm [4]); ^{125}Te NMR 552 (in dms) and 572 (in chloroform).

2.2. Synthesis of palladium(II), $[\text{PdCl}_2\text{L}]$ and platinum(II), $[\text{PtCl}_2\text{L}]$ complexes

To the solution of K_2PdCl_4 (0.294 g, 1.0 mmol) or K_2PtCl_4 (0.416 g, 1.0 mmol) in 7 cm^3 of water, ligand solution (0.48 g, 1.0 mmol dissolved in 5 cm^3 ethanol) was added dropwise with vigorous stirring at room temperature for 1 h. It was filtered, washed with water, ethanol and chloroform and dried under reduced pressure. The product was recrystallized from hot dms. $[\text{PdCl}_2\text{L}]$: C, 27.50 (27.25); H, 2.47 (2.45)%; m.p. 185°C (dec.). IR bands $\nu(\text{Pd}-\text{Cl})$, 290, 323 cm^{-1} . $[\text{PtCl}_2\text{L}]$: C, 24.71 (24.02); H, 2.15 (2.13)%; m.p. 198°C (dec.). IR bands $\nu(\text{Pt}-\text{Cl})$, 310, 337 cm^{-1} .

3. Determination of the crystal structure

The single crystals of $[\text{Pd}((4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\text{CH}_2)\text{Cl}_2]$ were grown from dimethyl sulphoxide solution of the complex. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Cu K α radiation (1.5418 \AA , nickel monochromator). Intensities were measured at the azimuth position corresponding to minimum absorption using an imaginary crystal with infinite but small thickness having an infinitely large surface area (flat psi mode). The ω -scan technique was used to maximum 2θ value of 99.9° and variable scan

Table 1
Crystallographic parameters of $[\text{Pd}((4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\text{CH}_2)\text{Cl}_2]$

Formula	$\text{C}_{15}\text{H}_{16}\text{Te}_2\text{O}_2\text{PdCl}_2$
Formula weight	660.8
Crystal size (mm)	$0.7 \times 0.1 \times 0.12$
Crystal system	Monoclinic
Space group	$P2_1/n$ (non-standard no. 14)
a (\AA)	7.872(3)
b (\AA)	20.372(8)
c (\AA)	11.421(3)
β (deg)	100.90(2)
V (\AA^3)	1799(1)
D_c (g cm^{-3})	2.44
Z	4
Temperature ($^\circ\text{C}$)	20
μ (cm^{-1})	370.94
$F(000)$	1224
Mode of data collection	$\omega-2\theta$
Range of θ (deg)	1–50
Attenuation factor	12.10
Number of reflections collected	2099
Number of unique reflections	1749
Number of unique reflections used with ($I \geq 4\sigma$)	1408
$R(\sigma F_o - F_c / \sigma F_o)$	0.054
$R_w[\{\sigma_w(F_o - F_c)^2 / \sigma_w F_o^2\}]^{1/2}$	0.066
Weighing scheme	Constant weights

rate ($16.48/3\text{ deg min}^{-1}$) (h , $0 \rightarrow 7$; k , $0 \rightarrow 20$; l , $-11 \rightarrow 11$). The crystal data and relevant information about the data collection are summarized in Table 1. The data were corrected for Lorentz and polarization effects and empirical absorption correction was applied (the maximum and minimum correction factors were 0.9998 and 0.8577).

Initial coordinates of the heavy atoms were determined using the Patterson method in the program SHELXS 86 [14]. The remaining non-hydrogen atoms were located from a series of difference Fourier maps. Refinement [15] of the structure was done by a full-matrix least-square procedure using an anisotropic temperature factor. The hydrogen atoms were fixed geometrically to the atoms to which they are connected and were included in the structure factor calculations but not refined. The literature value [16,17] of atomic scattering of hydrogen and non-hydrogen atoms were used. All calculations were performed on a Microwax II system. The refinement details, final atomic coordinates and selected bond lengths and bond angles are listed in Tables 1–3. Supplementary material comprising tables of bond lengths and bond angles, thermal parameters and structure factors is available from the authors on request.

4. Results and discussion

We have recently described the synthesis of hybrid (Te,N) ligands, 2-(2'-aryltelluroethyl)pyridines by the

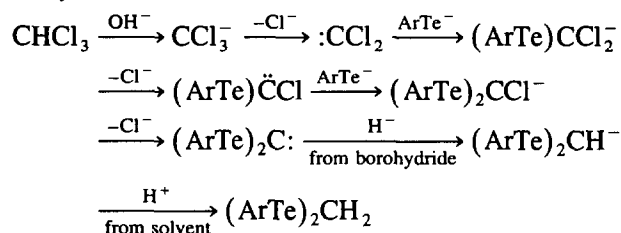
Table 2
Bond angles (deg) and lengths (Å) of $[\text{Pd}((4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\text{CH}_2)\text{Cl}_2]$ with their estimated standard deviations

Bond angles		Bond lengths	
Cl(1)–Pd–Te(2)	172.9(2)	Te(1)–Pd	2.529(2)
Cl(2)–Pd–Te(1)	172.5(2)	Cl(1)–Pd	2.370(7)
Cl(2)–Pd–Cl(1)	93.5(2)	Cl(2)–Pd	2.363(6)
Te(1)–Pd–Te(2)	81.3(1)	Te(2)–Pd	2.527(2)
Te(1)–Pd–Cl(1)	92.8(2)	C(1)–Te(1)	2.160(24)
Te(2)–Pd–Cl(2)	92.2(2)	C(2)–Te(1)	2.078(20)
Te(1)–C(1)–Te(2)	99.6(9)	Te(2)–C(1)	2.150(21)
C(1)–Te(1)–Pd	88.6(6)	Te(2)–C(9)	2.131(19)
C(1)–Te(2)–Pd	88.9(6)		
C(9)–Te(2)–C(1)	98.7(8)		
C(9)–Te(2)–Pd	95.9(5)		
C(2)–Te(1)–Pd	97.5(5)		
C(1)–Te(1)–C(2)	95.5(9)		

nucleophilic substitution of aryltelluroles on 2-(2'-chloroethyl)pyridine [18]. Our attempt to synthesize 2,6-bis(4'-methoxyphenyltelluromethyl)pyridine, a (Te,N,Te) ligand, following the same procedure failed and we recovered the starting material back. However, the addition of chloroform in the reaction mixture resulted in a product, bis(4-methoxyphenyltelluro)methane, in good yield (greater than 80%) unexpectedly. The absence of pyridine nucleus in the product prompted us to carry out the reduction of $(4\text{-MeO-C}_6\text{H}_4)_2\text{Te}_2$ with sodium borohydride in ethanol containing some chloroform, which again resulted in the same product. Thus, this one pot reaction of ditelluride, sodium borohydride and chloroform is a very convenient and high yielding route for the synthesis of bis(aryltelluro)methanes.

The fact that the reaction occurs in the presence of base, chloroform and sodium borohydride suggests that

the reacting entity in this reaction is dichlorocarbene [19] which on reaction with sodium 4-methoxyphenyltelluroate produces the bis(4-methoxyphenyltelluro)methane. The following mechanism can be proposed for its synthesis.



The physical, analytical and spectroscopic (^1H , ^{13}C and ^{125}Te NMR) data of the compound are in excellent agreement with the data reported for bis(aryltelluro)methane synthesized by other routes [4,5].

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent thermal parameters ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses of $[\text{Pd}((4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\text{CH}_2)\text{Cl}_2]$

Atom	X/a	Y/b	Z/c	U(eq)
Te(1)	977(2)	1273(1)	784(1)	331(5)
Te(2)	-2694(2)	564(1)	1040(1)	359(6)
Pd	-1121(2)	601(1)	-693(1)	320(6)
Cl(1)	467(8)	769(3)	-2236(5)	471(21)
Cl(2)	-3368(7)	28(3)	-1946(5)	511(22)
O(1)	-2267(23)	4033(9)	-550(16)	666(76)
O(2)	-6962(19)	3065(7)	-763(12)	417(56)
C(1)	-467(29)	1003(10)	2142(19)	399(87)
C(2)	-185(26)	2182(10)	380(16)	301(76)
C(3)	-39(30)	2679(12)	-1258(21)	522(96)
C(4)	-745(30)	3330(11)	930(19)	418(95)
C(5)	-1521(28)	3423(11)	-175(24)	434(88)
C(6)	-1623(32)	2956(13)	-1028(22)	581(102)
C(7)	-990(29)	2363(11)	-769(19)	431(97)
C(8)	-2076(39)	4552(15)	224(27)	787(137)
C(9)	-4179(22)	1431(10)	566(15)	234(71)
C(10)	-4128(27)	1978(11)	1269(18)	367(78)
C(11)	-5066(27)	2523(11)	895(18)	352(79)
C(12)	-6056(25)	2540(11)	-229(18)	313(88)
C(13)	-6189(24)	1994(11)	-968(17)	352(88)
C(14)	-5244(30)	1409(11)	-591(21)	453(90)
C(15)	-6863(33)	3662(12)	-110(22)	550(102)

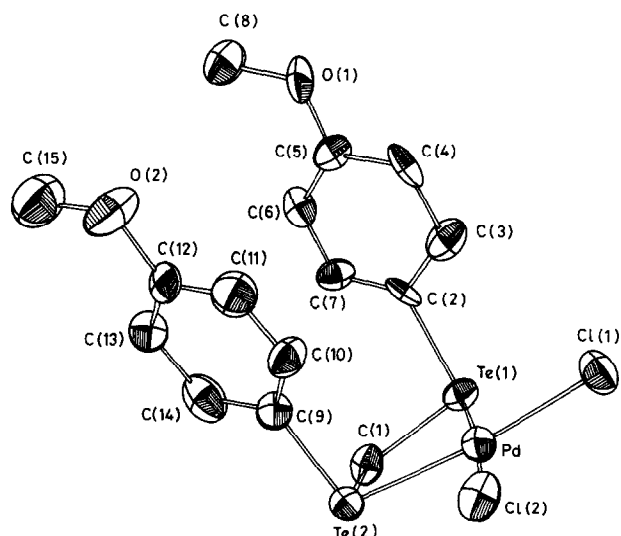


Fig. 1. ORTEP diagram of $[\text{Pd}\{(4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\text{CH}_2\}\text{Cl}_2]$.

The palladium(II) and platinum(II) complexes of the ligand are insoluble in polar and non-polar solvents as reported recently [12] but sparingly soluble in DMSO and DMF. This frustrated the attempts to study them in solution. The presence of two bands in the far-IR spectra around 300 and 330 cm^{-1} assignable to $\nu(\text{M}-\text{Cl})$ vibrations suggests that the two $\text{M}-\text{Cl}$ bonds in these complexes are in cis configuration of a square planar arrangement of the ligands around metal [20].

4.1. Structure of $[\text{Pd}\{(4\text{-CH}_3\text{OC}_6\text{H}_4\text{Te})_2\}\text{Cl}_2]$

The ORTEP diagram of the complex is shown in Fig. 1. The geometry around palladium is found to be distorted square planar and the principle feature of interest is the stereochemistry of the chelating ditelluroether ligand. Only one complex of ditelluroether ligand, i.e. $[\text{Pd}(\text{meso-PhTe}(\text{CH}_2)_3\text{TePh})\text{Br}_2]$ has been characterized by X-ray diffraction [21]. This is the first example of a structurally characterized bis(aryltelluro)methane complex of metal and is most interesting in the sense that, in spite of the short interdonor linkage ($3.293(2)\text{ \AA}$), chelation of the ligand through two tellurium atoms to a single metal atom takes place. The ligand forms a four-membered chelate ring in which $\text{Te}(1)$, $\text{Te}(2)$, and Pd are almost coplanar with $\text{C}(1)$ out of the plane by $-0.31(2)\text{ \AA}$. The two aryl rings are perpendicular to the square plane and almost parallel to each other. The $\text{Pd}-\text{Te}$ bond distance ($2.530(2)\text{ \AA}$) in the present case is comparable with that found in $[\text{Pd}(\text{meso-PhTe}(\text{CH}_2)_3\text{TePh})\text{Br}_2]$ ($2.528(1)\text{ \AA}$) [21] and the $\text{Pd}-\text{Cl}$ bond distance ($2.367(7)\text{ \AA}$) is found to be slightly longer than that reported for $[\text{Pd}\{4\text{-CH}_3\text{OC}_6\text{H}_4\text{TeCH}_2\text{CH}_2\text{-}2\text{-}(\text{C}_5\text{H}_4\text{N})\}\text{Cl}_2]$ ($2.338(1)\text{ \AA}$) [18]. The $\text{Te}-\text{C}(\text{aliphatic})$ bond distance ($2.15(2)\text{ \AA}$) in the present case can be compared with $2.15(2)\text{ \AA}$ in $[\text{PtCl}\{\text{Te}(\text{C}_6\text{H}_4\text{OC}_2\text{H}_5)_2\text{-CH}_2\text{CH}_2\}_2\text{NH}\}\text{Cl}$ [22]. The one $\text{Te}-\text{C}(\text{aromatic})$ bond distance ($\text{Te}(2)-\text{C}(9) = 2.07(2)\text{ \AA}$) is found to be shorter

and the other $\text{Te}-\text{C}$ bond distance ($\text{Te}(1)-\text{C}(2) = 2.15(2)\text{ \AA}$) is comparable with other reported values (approximately $2.15(2)\text{ \AA}$) [18].

The complex is monomeric; however, it is linked to neighbouring molecules by weak $\text{Te}\dots\text{Cl}$ intermolecular interactions. Examination of the intermolecular distances shows that the distance between the Te and Cl atoms is $3.376(6)\text{ \AA}$. This distance, although larger than the sum of covalent radii, 2.36 \AA , is very much shorter than the sum of van der Waals radii, 4.00 \AA . The intermolecular $\text{Pd}\dots\text{Pd}$ contact is $3.249(2)\text{ \AA}$.

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