

# Bis(2-{1,3-dioxan-2-yl}ethyl) telluride (**L**): synthesis and ligation with Pd(II) and Ru(II). Crystal structures of [Ru(*p*-cymene)Cl<sub>2</sub>**L**] and *trans*-[PdCl<sub>2</sub>(**L**)<sub>2</sub>]

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Received 6 July 2000; accepted 3 August 2000

## Abstract

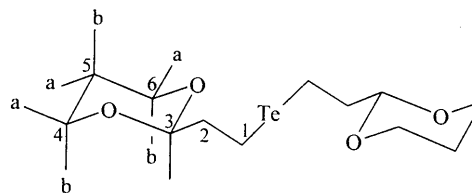
Sodium telluride (Na<sub>2</sub>Te), obtained in situ by borohydride reduction of elemental tellurium, reacts with 2-(2-bromoethyl)-1,3-dioxane resulting in bis(2-{1,3-dioxan-2-yl}ethyl) telluride (**L**), which is isolated as an unstable viscous liquid. The potentially (Te,O<sub>2</sub>) type of ligand **L** is stabilized on the formation of complexes [Ru(*p*-cymene)Cl<sub>2</sub>**L**] (**1**) and *trans*-[PdCl<sub>2</sub>(**L**)<sub>2</sub>] (**2**) which are characterized structurally. The Ru–Te bond length in the half sandwich compound **1** is 2.6559(9) Å. The geometry of Pd in **2** is square planar. The Pd–Te bond length in **2** is 2.5873(2) Å. **1** and **2** are the first examples of structurally characterized complexes in which potentially (Te,O<sub>2</sub>) type ligand molecules are present, of course coordinating through Te only. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Bis(2-{1,3-dioxan-2-yl}ethyl) telluride; Palladium; Ruthenium; Complexation; Crystal structure

## 1. Introduction

The hemilabile (P<sub>*x*</sub>O<sub>*y*</sub>) type ligands are interesting for designing catalytically active species [1] as their oxygen donor atoms can protect the metal by occupying its vacant coordination site until the substrate is reached. Similar tellurium ligands of (Te<sub>*x*</sub>O<sub>*y*</sub>) type [2] are known scantily, in spite of current interest in hybrid organotellurium ligands. We have designed [3] recently four such ligands 2-(phenyltelluromethyl)tetrahydro-2*H*-pyran, 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxane, 2-(phenyltelluromethyl) tetrahydrofuran and 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxolane, which are potentially (Te,O) type donors, but none of their palladium(II) and platinum(II) complexes gives crystals suitable for X-ray diffraction. In continuation of these studies we have now synthesized bis(2-{1,3-dioxan-2-yl}ethyl) telluride (**L**), which is stabilized on

complexation. Its palladium(II) and ruthenium(II) complexes (i.e. *trans*-[PdCl<sub>2</sub>(**L**)<sub>2</sub>] and [Ru(*p*-cymene)Cl<sub>2</sub>**L**]) give stable crystals suitable for X-ray diffraction and therefore both of them were structurally characterized. However, in both the complexes **L** coordinates through Te only. The results of these investigations are reported in the present paper.



**L**

## 2. Experimental

The C and H analyses were carried out with a Perkin–Elmer elemental analyser 240 C. Tellurium was

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estimated volumetrically [4]. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz respectively. IR spectra in the range 4000–250  $\text{cm}^{-1}$  were recorded on a Nicolet Protège 460 FT-IR spectrometer as KBr and CsI pellets. The conductance measurements were made in acetonitrile (concentration ca. 1 mM) using an Orion conductivity meter model 162. The molecular weights (concentration ca. 5 mM) in chloroform were determined with a Knauer vapour pressure osmometer model A0280. The melting points determined in open capillary are reported as such. 2-(2-Bromoethyl)-1,3-dioxane obtained from Aldrich (USA) was used as received. The dimeric complex  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  was synthesized by the reported method [5].

### 2.1. Synthesis of bis(2-(1,3-dioxan-2-yl)ethyl)telluride (**L**)

Tellurium powder (0.65 g, 5 mmol) was added to a solution of sodium borohydride (0.38 g, 10 mmol) made in 10  $\text{cm}^3$  of 2 M NaOH and 50  $\text{cm}^3$  of water. The mixture was refluxed for 2 h under nitrogen atmosphere until a colourless thin slurry of  $\text{Na}_2\text{Te}$  was formed. A solution of 2-(2-bromoethyl)-1,3-dioxane (1.98 g, 10 mmol) made in 5  $\text{cm}^3$  of ethanol was added dropwise to the colourless thin slurry of  $\text{Na}_2\text{Te}$  kept under reflux, with constant stirring under nitrogen atmosphere. The reaction mixture was cooled to 25°C and poured into 100  $\text{cm}^3$  of ice cold water. **L** was extracted into diethyl ether from this aqueous phase. The ether extract was washed with distilled water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . On evaporating off diethyl ether under reduced pressure **L** was obtained as a yellow viscous liquid. Yield 60%.  $A_M$  ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) 12.5.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) 1.28–1.37 (d, 2H,  $\text{H}_{5b}$ ), 1.97–2.12 (m, 6H,  $\text{H}_2 + \text{H}_{5a}$ ), 2.61–2.66 (t, 4H,  $\text{H}_1$ ), 3.71–3.82 (t, 4H,  $\text{H}_{4b} + \text{H}_{6b}$ ), 4.05–4.10 (2d, 4H,  $\text{H}_{4a} + \text{H}_{6a}$ ), 4.54–4.58 (t, 2H,  $\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) –4.8 ( $\text{C}_1$ ), 25.4 ( $\text{C}_5$ ), 37.0 ( $\text{C}_2$ ), 66.4 ( $\text{C}_4$ ,  $\text{C}_6$ ), 102.2 ( $\text{C}_3$ ).

### 2.2. Synthesis of $[\text{RuCl}_2(p\text{-cymene})\text{L}]$ (**1**)

The solution of  $[\text{RuCl}_2(p\text{-cymene})]_2$  (0.61 g, 1 mmol) in 20  $\text{cm}^3$  of dichloromethane was mixed with a solution of **L** (0.72 g, 2 mmol) also made in 10  $\text{cm}^3$  of dichloromethane with vigorous stirring. The reaction mixture was further stirred for 2 h. The solvent was removed under reduced pressure on a rotary evaporator. The residue was dissolved in a 1:1 mixture of dichloromethane and diethylether and kept for 3 days at 0°C. Orange crystals obtained were filtered from solution and dried in vacuo. Yield 80%.  $A_M$  ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) 17. Anal. Calc. for  $\text{C}_{22}\text{H}_{36}\text{O}_4\text{Cl}_2\text{TeRu}$ : C, 39.72;

H, 5.41; Te, 19.26. Found: C, 39.77; H, 5.27; Te, 18.87%. Mol. wt.: 652.7 (calc. 664.5).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) 1.28–1.37 (m, 8H,  $\text{H}_{5b} + \text{CH}_3$  of *i*-Pr), 1.97–2.15 (m, 6H,  $\text{H}_2 + \text{H}_{5a}$ ), 2.16 (s, 3H,  $\text{CH}_3$  of *p*-cymene), 2.67–2.76 (sp, 1H, CH of *p*-cymene), 2.90–2.99 (m, 4H,  $\text{H}_1$ ), 3.72–3.80 (t, 4H,  $\text{H}_{4b} + \text{H}_{6b}$ ), 4.06–4.11 (2d, 4H,  $\text{H}_{4a} + \text{H}_{6a}$ ), 4.56–4.59 (t, 2H,  $\text{H}_3$ ), 5.34–5.36, 5.47–5.49 (2d, 4H, ArH of *p*-cymene).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) 9.1 ( $\text{C}_1$ ), 18.8 ( $\text{CH}_3$  of *i*-Pr), 22.7 ( $\text{CH}_3$ ), 26.1 ( $\text{C}_5$ ), 31.2 (CH of *i*-Pr of *p*-cymene), 34.5 ( $\text{C}_2$ ), 67.1 ( $\text{C}_4$ ,  $\text{C}_6$ ), 82.9, 83.5 (ArC of *p*-cymene *o* and *m* to *i*-Pr), 97.3 (C-*i*-Pr) 102.5 ( $\text{C}_3$ ), 104.5 (C- $\text{CH}_3$ ).

### 2.3. Synthesis of $trans\text{-}[\text{PdCl}_2(\text{L})_2]$ (**2**)

A solution of **L** (0.33 g, 1 mmol) in chloroform (5  $\text{cm}^3$ ) was added dropwise to  $[(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2]$  (0.36 g, 1 mmol) dissolved in chloroform (10  $\text{cm}^3$ ) with stirring. The resulting mixture was further stirred for 2 h and hexane or petroleum ether (40–60°C, 25  $\text{cm}^3$ ) added. The resulting precipitate of **2** was filtered and washed with hexane. It was recrystallized from a 1:1 mixture of chloroform and hexane. Orange coloured crystals were separated, filtered and dried in vacuo. Yield 80%. Anal. Calc. for  $\text{C}_{24}\text{H}_{44}\text{O}_8\text{Te}_2\text{PdCl}_2$ : C, 32.27; H, 4.93; Te, 28.69. Found: C, 32.19; H, 4.83, Te, 28.00%. Mol. wt.: 881.2 (calc. 895).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) 1.28–1.35 (d, 4H,  $\text{H}_{5b}$ ), 2.05–2.21 (m, 6H,  $\text{H}_2 + \text{H}_{5a}$ ), 2.61–2.70, 3.01–3.10 (2m, 4H,  $\text{H}_1$ ), 3.71–3.81 (m, 4H,  $\text{H}_{4b} + \text{H}_{6b}$ ), 4.06–4.10 (m, 4H,  $\text{H}_{4a} + \text{H}_{6a}$ ), 4.63–4.67 (t, 2H,  $\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 25°C) ( $\delta$  versus TMS) 8.5 ( $\text{C}_1$ ), 25.7 ( $\text{C}_5$ ), 34.1 ( $\text{C}_2$ ), 66.8 ( $\text{C}_4$ ,  $\text{C}_6$ ), 102.5 ( $\text{C}_3$ ).

### 2.4. X-ray diffraction analysis

Orange, plate-like crystals of  $[(p\text{-cymene})\text{RuCl}_2(\text{Te}\{\text{CH}_2\text{CH}_2\text{CHO}(\text{CH}_2)_3\text{O}\}_2)]$  (**1**), and  $[\text{PdCl}_2\{\text{Te}\{\text{CH}_2\text{CH}_2\text{CHO}(\text{CH}_2)_3\text{O}\}_2\}]$  (**2**), were mounted on glass fibres. Data were collected on an Enraf Nonius Kappa CCD area detector ( $f$  scans and  $\omega$  scans to fill an Ewald sphere at EPSRC National Crystallography Service, University of Southampton, UK). Data collection and cell refinement [6] gave cell constants corresponding to monoclinic (for **1**) and orthorhombic (for **2**) cells whose dimensions are given in Table 1 along with other experimental parameters. An absorption correction was applied [7]. The structures were solved by direct methods [8]. All of the non-hydrogen atoms were treated anisotropically. The data for **1** were of much better quality than for **2**. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [9] was

based on 5739 for **1** and 3495 for **2**, observed reflections (4762 for **1** and 2681 for **2** for  $F^2 > 2\sigma(F^2)$ ) and 275 for **1** and 167 for **2** variable parameters and converged (largest parameter shift was 0.001 times its e.s.d.). Bond distances and bond angles are given in Tables 2 and 3 and the molecules are displayed as ORTEP diagrams in Figs. 1 and 2.

### 3. Results and discussion

The ligand **L** and complexes **1** and **2** were synthesized by the reaction given below

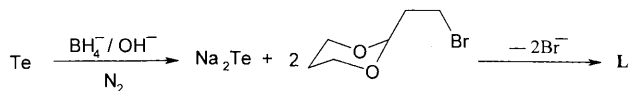
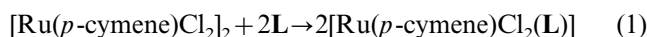


Table 1  
Crystal data and structure refinement for **1** and **2**

|  | <b>1</b>  | <b>2</b>   |
|--|---|--|
| Empirical formula  | C <sub>22</sub> H <sub>36</sub> O <sub>4</sub> Cl <sub>2</sub> RuTe | C <sub>24</sub> H <sub>44</sub> O <sub>8</sub> Cl <sub>2</sub> PdTe <sub>2</sub> |
| Formula weight   | 664.08  | 893.09   |
| Temperature (°C)   | −123(2)   | −150(2)  |
| Wavelength (Å)   | 0.71073   | 0.71073  |
| Crystal system   | Monoclinic  | Orthorhombic   |
| Space group  | C2/c  | Pbca   |
| Unit cell parameters   |   |  |
| <i>a</i> (Å)   | 26.150(5)   | 9.2922(3)  |
| <i>b</i> (Å)   | 9.754(2)  | 16.463(5)  |
| <i>c</i> (Å)   | 20.313(4)   | 20.1027(8)   |
| β (°)  | 103.22(3)   |  |
| Volume (Å <sup>3</sup> )   | 5044(2)   | 3090.8(2)  |
| <i>Z</i>   | 8   | 4  |
| Density (calculated)<br>(g cm <sup>−3</sup> )                                    | 1.749   | 1.919  |
| Absorption<br>coefficient (mm <sup>−1</sup> )                                    | 1.992   | 2.666  |
| <i>F</i> (000)   | 2640  | 1744   |
| Crystal size (mm)  | 0.98 × 0.24 × 0.24  | 0.15 × 0.10 × 0.02   |
| θ range for data<br>collection (°)   | 2.91–27.49  | 2.99–27.48   |
| Limiting indices   | −33 ≤ <i>h</i> ≤ 32,<br>−12 ≤ <i>k</i> ≤ 12,<br>−24 ≤ <i>l</i> ≤ 26 | −12 ≤ <i>h</i> ≤ 12,<br>−21 ≤ <i>k</i> ≤ 21,<br>−23 ≤ <i>l</i> ≤ 25              |
| Reflections collected  | 22670   | 19209  |
| Independent<br>reflections   | 5739 ( <i>R</i> <sub>int</sub> = 0.0542)                            | 3496 ( <i>R</i> <sub>int</sub> = 0.0529)   |
| Refinement method  | Full-matrix<br>least-squares on <i>F</i> <sup>2</sup>               | Full-matrix<br>least-squares on <i>F</i> <sup>2</sup>                            |
| Data/restraints/parameters   | 5739/0/275  | 3495/0/167   |
| Goodness-of-fit on<br><i>F</i> <sup>2</sup>                                      | 1.091   | 1.049  |
| Final <i>R</i> indices<br>[ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] | <i>R</i> <sub>1</sub> = 0.0377,<br><i>wR</i> <sub>2</sub> = 0.0874  | <i>R</i> <sub>1</sub> = 0.0329,<br><i>wR</i> <sub>2</sub> = 0.0789               |
| <i>R</i> indices (all data)  | <i>R</i> <sub>1</sub> = 0.0493,<br><i>wR</i> <sub>2</sub> = 0.0930  | <i>R</i> <sub>1</sub> = 0.0477,<br><i>wR</i> <sub>2</sub> = 0.0882               |
| Extinction coefficient   | 0.00030(4)  | 0.00058(10)  |
| Largest difference<br>peak and hole<br>(e Å <sup>−3</sup> )                      | 51.347 and −1.411   | 1.469 and −1.392   |

Table 2  
Bond lengths (Å) and angles (°) for **1**

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| Te(1)–Ru(1)       | 2.6559(9)  | Ru(1)–Cl(2)       | 2.4122(10) |
| Ru(1)–Cl(1)       | 2.4172(10) | Te(1)–C(17)       | 2.146(3)   |
| Ru(1)–C(6)        | 2.165(3)   | Ru(1)–C(1)        | 2.186(3)   |
| Ru(1)–C(5)        | 2.189(3)   | Ru(1)–C(2)        | 2.192(3)   |
| Ru(1)–C(4)        | 2.211(3)   | Ru(1)–C(3)        | 2.229(3)   |
| Te(1)–C(11)       | 2.157(4)   | C(1)–C(6)         | 1.419(5)   |
| C(1)–C(2)         | 1.428(5)   | C(5)–C(6)         | 1.423(5)   |
| C(2)–C(3)         | 1.396(5)   | C(14)–C(15)       | 1.509(6)   |
| C(3)–C(4)         | 1.434(5)   | C(4)–C(5)         | 1.404(5)   |
| C(1)–C(7)         | 1.514(5)   | C(4)–C(10)        | 1.505(5)   |
| C(7)–C(8)         | 1.525(6)   | C(7)–C(9)         | 1.519(5)   |
| C(11)–C(12)       | 1.518(5)   | C(17)–C(18)       | 1.517(5)   |
| C(12)–C(13)       | 1.493(5)   | C(18)–C(19)       | 1.514(5)   |
| O(1)–C(13)        | 1.403(4)   | O(2)–C(13)        | 1.425(4)   |
| O(2)–C(16)        | 1.441(5)   | O(4)–C(19)        | 1.405(4)   |
| O(1)–C(14)        | 1.432(5)   | C(15)–C(16)       | 1.512(6)   |
| Cl(1)–Ru(1)–Cl(2) | 88.08(3)   | C(11)–Te(1)–C(17) | 91.51(14)  |
| Cl(1)–Ru(1)–Te(1) | 86.70(3)   | Cl(2)–Ru(1)–Te(1) | 87.16(3)   |
| C(11)–Te(1)–Ru(1) | 104.33(11) | C(17)–Te(1)–Ru(1) | 105.60(10) |
| C(6)–C(1)–C(2)    | 116.9(3)   | C(3)–C(2)–C(1)    | 122.6(3)   |
| C(2)–C(3)–C(4)    | 119.5(3)   | C(4)–C(5)–C(6)    | 120.6(3)   |
| C(5)–C(4)–C(3)    | 119.1(3)   | C(1)–C(6)–C(5)    | 121.3(3)   |
| C(2)–C(1)–C(7)    | 119.9(3)   | C(6)–C(1)–C(7)    | 123.2(3)   |
| C(1)–C(7)–C(8)    | 113.9(3)   | C(1)–C(7)–C(9)    | 109.1(3)   |
| C(3)–C(4)–C(10)   | 119.1(3)   | C(5)–C(4)–C(10)   | 121.8(3)   |
| C(9)–C(7)–C(8)    | 110.5(3)   | C(13)–O(2)–C(16)  | 112.4(3)   |
| C(12)–C(11)–Te(1) | 114.7(2)   | C(18)–C(17)–Te(1) | 108.1(2)   |
| C(13)–C(12)–C(11) | 114.3(3)   | C(19)–C(18)–C(17) | 114.7(3)   |
| O(1)–C(13)–C(12)  | 109.0(3)   | C(19)–O(4)–C(22)  | 110.6(3)   |
| C(13)–O(1)–C(14)  | 111.3(3)   | O(4)–C(19)–C(18)  | 109.4(3)   |
| O(1)–C(14)–C(15)  | 109.5(3)   | O(2)–C(16)–C(15)  | 110.0(3)   |
| C(14)–C(15)–C(16) | 109.6(3)   | O(2)–C(13)–C(12)  | 107.0(3)   |



**L**, **1** and **2** are soluble in common organic solvents like dichloromethane, chloroform, acetonitrile, DMF and DMSO. The complexes are stable under ambient conditions but the ligand **L**, after 2–3 days, decomposes to an intricate mixture. The instability of **L** is probably photochemical in origin as observed for several dialkyl tellurides. The stoichiometries of the complexes have been authenticated by their elemental analyses. The molar conductance values ( $\Lambda_M$ ) of **L**, **1** and **2** at ca. 1 mM concentration level in acetonitrile have been found to be much lower than the values expected for a 1:1 electrolyte. Molecular weights of complexes **1** and **2** determined in chloroform by vapour pressure osmometry, are found to be very close to the values calculated from their molecular formulae. This indicates their monomeric nature and authenticates further their stoichiometries.

### 3.1. Spectral data

In IR spectra of **L**, **1** and **2** bands in the region 1110 and 1141  $\text{cm}^{-1}$  may be assigned to C–O–C vibrations. The Te–C(aliphatic) vibrations appear in the spectra of **1** and **2** at 463 and 446  $\text{cm}^{-1}$  respectively. The band at 346  $\text{cm}^{-1}$  in the spectrum of **1** appears to be due to  $\nu(\text{Ru–Cl})$  and at 345  $\text{cm}^{-1}$  in the spectrum of **2** due to vibrations of the *trans* Cl–Pd–Cl system.

Table 3  
Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2**<sup>a</sup>

|                     |            |                    |            |
|---------------------|------------|--------------------|------------|
| Te(1)–C(7)          | 2.144(3)   | Te(1)–C(1)         | 2.146(3)   |
| Te(1)–Pd(1)         | 2.5873(2)  | Pd(1)–Cl(1)'       | 2.2990(8)  |
| Pd(1)–Cl(1)         | 2.2990(8)  | Pd(1)–Te(1)'       | 2.5873(2)  |
| O(1)–C(3)           | 1.411(3)   | C(10)–C(11)        | 1.505(5)   |
| O(2)–C(3)           | 1.400(3)   | C(7)–C(8)          | 1.519(3)   |
| O(3)–C(9)           | 1.408(3)   | C(11)–C(12)        | 1.508(4)   |
| O(4)–C(9)           | 1.413(3)   | C(4)–C(5)          | 1.515(4)   |
| C(1)–C(2)           | 1.518(4)   |                    |            |
| C(7)–Te(1)–C(1)     | 90.08(10)  | C(7)–Te(1)–Pd(1)   | 107.91(8)  |
| C(1)–Te(1)–Pd(1)    | 96.06(7)   | Cl(1)'–Pd(1)–Cl(1) | 180.0      |
| Cl(1)'–Pd(1)–Te(1)  | 92.35(2)   | Cl(1)–Pd(1)–Te(1)  | 87.65(2)   |
| Cl(1)'–Pd(1)–Te(1)' | 87.65(2)   | Cl(1)–Pd(1)–Te(1)' | 92.35(2)   |
| Te(1)–Pd(1)–Te(1)'  | 180.0      | C(3)–O(1)–C(4)     | 110.8(2)   |
| C(3)–O(2)–C(6)      | 110.2(2)   | C(9)–O(3)–C(10)    | 110.8(2)   |
| C(9)–O(4)–C(12)     | 109.9(2)   | C(2)–C(1)–Te(1)    | 112.9(2)   |
| C(3)–C(2)–C(1)      | 111.2(2)   | O(2)–C(3)–O(1)     | 111.7(2)   |
| O(2)–C(3)–C(2)      | 108.8(2)   | O(1)–C(3)–C(2)     | 107.4(2)   |
| O(1)–C(4)–C(5)      | 110.0(2)   | C(6)–C(5)–C(4)     | 108.9(2)   |
| O(2)–C(6)–C(5)      | 110.2(2)   | C(8)–C(7)–Te(1)    | 114.6(2)   |
| C(9)–C(8)–C(7)      | 113.30(13) | O(3)–C(9)–O(4)     | 111.2(2)   |
| O(3)–C(9)–C(8)      | 108.25(12) | O(4)–C(9)–C(8)     | 109.18(11) |
| O(3)–C(10)–C(11)    | 110.7(2)   | C(10)–C(11)–C(12)  | 109.5(3)   |
| O(4)–C(12)–C(11)    | 109.3(2)   |                    |            |

<sup>a</sup> Symmetry equivalent position is given by a prime ( $-x+1, -y, -z+1$ ).

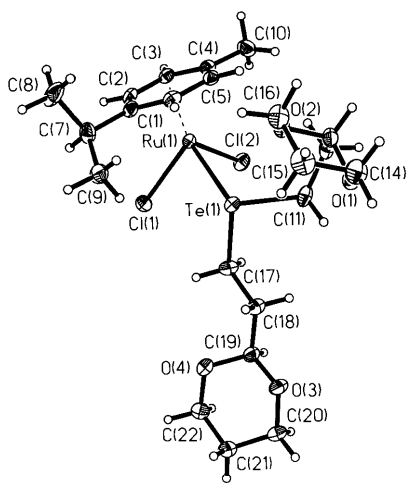


Fig. 1. ORTEP plot of the molecule (*p*-cymene) $\text{RuCl}_2[\text{Te}\{\text{CH}_2\text{CHO}(\text{CH}_2)_3\text{O}\}_2]$  (**1**). The atoms are drawn with 50% probability ellipsoids.

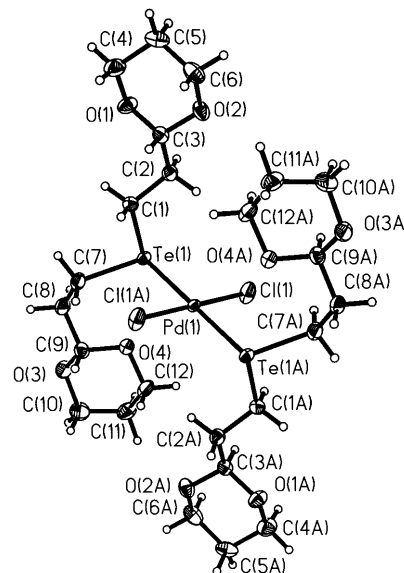


Fig. 2. ORTEP plot of the molecule  $\text{PdCl}_2[\text{Te}\{\text{CH}_2\text{CHO}(\text{CH}_2)_3\text{O}\}_2]$  (**2**). The atoms are drawn with 50% probability ellipsoids.

The  $\text{H}_1$  protons of **L** appear, shielded (ca. 0.6 ppm) in comparison to those of (2-(2-bromoethyl)-1,3-dioxane) due to the heavy atom effect of Te. Two  $\text{CH}_2\text{Te}$  signals of equal intensity appear in  $^1\text{H-NMR}$  spectra of **1** and **2**, each corresponds to one proton and is deshielded (ca. 0.2 to ca. 0.5 ppm) with respect to that of free ligand **L**. The HETCOR spectra of **1** and **2** support the appearance of two signals which most probably originate due to chemical non-equivalence of two  $\text{CH}_2\text{Te}$  protons arising from the bulkiness of the substituent present on the methylene group. The signals due to  $-\text{CH}_2\text{O}-$  protons of the dioxane ring are found virtually unaffected on the formation of **1** and **2** indicating that the ring oxygen does not participate in coordination. HETCOR spectra of **L**, **1** and **2** further support the assignments of various protons.

The DEPT NMR spectra are used to assign signals of various carbon atoms of the dioxane ring, isopropyl and methyl groups of *p*-cymene. The  $\text{C}_1$  signals in  $^{13}\text{C-NMR}$  spectra of **L**, **1** and **2** appear shielded (ca. 25 to 28 ppm) with respect to that of its precursor organic halide, as expected due to the heavy atom effect. In  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of **1** and **2**, the  $\text{C}_1$  signal exhibits a downfield shift of ca. 14 ppm in comparison to that of free ligand. The effect of complexation on the  $\text{CH}_2\text{O}$  signal of **L** has been found to be insignificant, implying that only Te is involved in bonding of **L** with Ru or Pd, as corroborated by crystal structures of **1** and **2**.

### 3.2. Crystal structures of **1** and **2**

The molecular structure of **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. **1**

is a half sandwich compound in which the coordination sphere of metal is composed of two chloride ligands,  $\eta^6$ -bonded *p*-cymene ring and ligand L coordinated through Te. The Ru–Te bond length (2.6559(9) Å) is consistent with the literature value 2.619(4)–2.650(1) Å reported for [Ru{PhTe(CH<sub>2</sub>)<sub>3</sub>TePh}<sub>2</sub>Cl<sub>2</sub>] and [Ru{MeTe(CH<sub>2</sub>)<sub>3</sub>TeMe}<sub>2</sub>Cl PPh<sub>3</sub>]<sub>2</sub>PF<sub>6</sub> [10a]. The average value for the Ru–C bond length is 2.195 Å and concurs with earlier reports [10b]. The ruthenium atom does not appear to be placed at the centre of *p*-cymene ring, but is slightly shifted towards C(3). The average aromatic C–C bond lengths and C–C–C angles are 1.418(0) Å and 120(1)° respectively and are found to be normal. The dioxane ring has a chair conformation as expected. The Ru–Cl bond distances 2.4172(10) and 2.4122(10) Å are normal and consistent with the literature values 2.4173(8) Å [11] reported for [RuCl{ $\eta^2$ -C,N–C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6}{ $\eta^6$ -C<sub>10</sub>H<sub>14</sub>}]. The aromatic ring of the *p*-cymene ligand is almost planar (C–C–C bond angles vary from 116.9(3) to 122.6(3)°) and perpendicular to Ru. The tetrahedral environment of atom C(17) (C–C–Te = 108.1(2)°) is not the same as that of C(11) (C–C–Te = 114.7(2)°). The distortion at C(11) seems to originate due to crystal packing.

The molecular structure of **2** is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. The Pd(II)–Te bond length (2.5873 Å) is consistent with the sum of the respective covalent radii, 2.63 Å [12]. The Te–C bond lengths in **1** and **2** both vary from 2.144(3) to 2.157(4) Å and concur with the earlier reported values (2.00(6)–2.16(4) Å) for Te–C(alkyl) [13]. The C–C and C–O bond lengths of the dioxane ring have normal values in both **1** and **2**. Moreover the dioxane rings in both the complexes have the usual chair conformation. It may also be of interest to compare the Pd(II)–Te bond lengths in **2** with those of other *trans* Te–Pd–Te systems. *Trans*-dichlorobis(tellurapentane-Te)palladium(II) [14], *trans*-bis(thiocyanato)bis[di(3-trimethylsilylpropyl)telluride]palladium(II) [15], bis(tetraphenylphosphonium) and bis(tetratellurido)palladate(II) dimethylformamide solvate [16] and its unsolvated version [17] are four such cases. The Pd–Te bond lengths in these compounds are in the range 2.584–2.606 Å (average 2.593 Å), which is consistent with the present value. The length of the Te–Pd bond *trans* to Pd–Cl is found to be close to 2.52 Å [13,18] whereas *trans* to Pd–P it is nearly 2.63 Å [13,19]. The greater *trans* influence of the P-donor in comparison to that of chloride seems to be responsible for this difference. The present Pd–Te bond length values are close to those of the *trans* P–Pd–Te system, implying that the *trans* influence of Te donors is reasonably strong. The present Pd–Cl bond length may be compared with 2.326(43) Å, the standard statistical value found in four-coordinate Pd complexes containing terminal Cl<sup>–</sup> ligands [20].

#### 4. Conclusion

Bis(2-{1,3-dioxan-2-yl}ethyl)telluride (**L**) is the first ligand of (Te<sub>x</sub>O<sub>y</sub>) type whose complexes with palladium(II) and ruthenium(II) have been structurally characterized; of course **L** coordinates through Te only. The values of Pd–Te bond lengths in **2** are closer to those which are *trans* to Te of the P donor atom. The Ru–Te bond length is normal. In the half sandwich compound of ruthenium, **1**, the *p*-cymene ring is nearly perpendicular to Ru. **L** is also among the few known examples of unstable telluroether ligands stabilized [2] well on coordination with a metal ion.

#### 5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre for compound **1**, no. 151 048 and compound **2**, no. 151 049. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

#### Acknowledgements

One of us (J.E.D.) wishes to thank the Natural Sciences and Engineering Research Council (Canada). A.K.S. and J.S. thank the Department of Science and Technology (India) for financial support.

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