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# *trans* Influence of Telluro- and Thio-ether Donor Sites: First Palladium(II) Complex, [$PdCl_2\{4\text{-}MeOC_6H_4TeCH_2CH_2SEt\}$], showing their Relative Magnitude in the Same Molecule†

**Ajai K. Singh,*[a] C. Valan Amburose,[a] Mridulata Misra[a] and Ray J. Butcher[b]**

[a] *Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India*
[b] *Department of Chemistry, Howard University, Washington, D.C. 20059, USA*

The synthesis of a (Te,S) ligand 4-$MeOC_6H_4TeCH_2CH_2SEt$ (L) and its complex [$PdCl_2L$] is followed by single crystal structure determination of the complex, which indicates that the Pd–Cl bond length *trans* to the ArTe group [2.344(3) Å] is longer than that *trans* to SEt [2.316(4) Å], suggesting a stronger *trans* influence for the former.

The ligand chemistry of polydentate telluroethers, including hybrid ligands, is of some current interest.[1] However, single crystal structures of only a small number of their metal complexes are known at present, despite some development in the recent past.[2] The *trans* influence of telluroether donor sites has been presumed to be somewhat lower or at the most, nearly equal to that of thioether donor sites. We have recently observed[3] that Pt–Cl *trans* to SMe is 2.324(4) Å, whereas in the same molecule of the complex, [$PtCl_2(4\text{-}EtOC_6H_4TeCH_2CH_2SMe)$], Pt–Cl *trans* to ArTe is 2.336(3) Å. This observation prompted us to synthesize a palladium complex of the same (Te, S) ligand and study further the more general status of the relative *trans* influence of telluro- and thio-ethers. As suitable crystals of the palladium(II) complex of 4-$EtOC_6H_4TeCH_2CH_2SMe$ could not be grown, a similar ligand L containing SEt and 4-$MeOC_6H_4$ groups was synthesized. Its palladium complex gave crystals suitable for X-ray diffraction. Ligand L and its palladium complex were prepared by the reactions given in eqns. (1) and (2).

$$(4\text{-}MeOC_6H_4Te)_2 \xrightarrow[\text{EtOH}]{\text{NaBH}_4/\ 1\text{ M NaOH}} 4\text{-}MeOC_6H_4Te^-Na^+ \xrightarrow{EtSCH_2CH_2Cl} \text{L} \qquad (1)$$

$$Pd(PhCN)_2Cl_2 + \text{L} \xrightarrow{CHCl_3} [PdCl_2L] \qquad (2)$$

The detailed procedure used for the synthesis of L was that reported earlier[4] for 4-$EtOC_6H_4TeCH_2CH_2SMe$. The $^1$H NMR spectrum of L, which is a yellow oil that slowly decomposes in air, was as expected.[5] The molecular structure of [$PdCl_2L$] is shown in Fig. 1 while selected bond lengths and angles are given in Table 1. The geometry of the donor atoms around palladium is slightly distorted square planar. Bond length Pd–Cl(2) *trans* to the ArTe group is longer by 0.028 Å than Pd–Cl(1) which is *trans* to SEt. This suggests that the *trans* influence of ArTe is probably greater than that of the thioether donor group SEt. The stronger $\sigma$-donation[5] characteristic of Te in comparison to that of S appears to be responsible for its greater *trans* influence. The Pd–Te bond length of the present complex is slightly shorter than the value of 2.525(1) Å, reported for [$Pd\{meso\text{-}PhTe(CH_2)_3TePh\}Br_2$].[6] The average phenyl ring C–C bond lengths and angles are 1.368(5) Å and 119.9(9)°, respectively, and are normal.

The $^1$H NMR spectrum of [$PdCl_2L$] is characteristic but coordination shifts in $CH_2Te/S$ with respect to that of free L are not unequivocally significant.

**Table 1** Selected bond lengths (Å) and bond angles (°) for [$PdCl_2L$]

| | | | |
|---|---|---|---|
| Pd–S | 2.268(4) | Pd–Te | 2.492(13) |
| Pd–Cl(1) | 2.316(4) | Pd–Cl(2) | 3.344(3) |
| Te–C(1) | 2.124(14) | Te–C(8) | 2.162(15) |
| S–C(9) | 1.78(2) | S–C(10) | 1.80(2) |
| O–C(4) | 1.367(17) | O–C(5) | 1.42(2) |
| S–Pd–Cl(1) | 175.37(13) | S–Pd–Cl(2) | 88.92(13) |
| Cl(1)–Pd–Cl(2) | 94.51(13) | S–Pd–Te | 90.89(10) |
| Cl(1)–Pd–Te | 85.86(10) | Cl(2)–Pd–Te | 176.83(10) |
| C(1)–Te–C(8) | 93.8(6) | C(1)–Te–Pd | 101.7(4) |
| C(8)–Te–Pd | 96.3(4) | C(9)–S–C(10) | 102.7(10) |
| C(9)–S–Pd | 108.0(7) | C(10)–S–Pd | 105.4(7) |

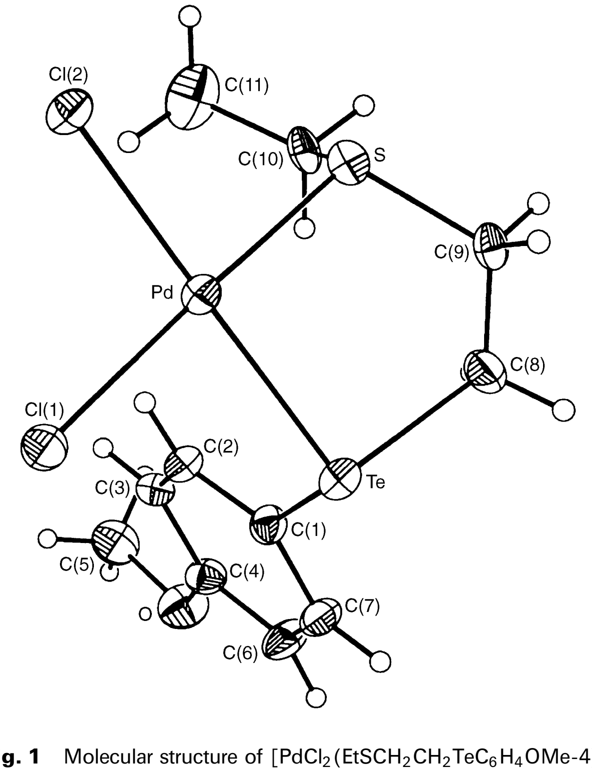

**Fig. 1** Molecular structure of [$PdCl_2(EtSCH_2CH_2TeC_6H_4OMe\text{-}4)$]

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*To receive any correspondence (*e-mail*: aksingh@chemistry.iitd.ernet.in).

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## Experimental

Ligand L was synthesized by using the published method.[4] $^1$H NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.1316507 MHz. C and H analyses were carried out on a Perkin Elmer elemental analyzer 240 C. The palladium complex [PdCl$_2$L] was synthesized by the following procedure.

To [Pd(PhCN)$_2$Cl$_2$] (0.26 g, 0.678 mmol) dissolved in 20 ml of chloroform was mixed a solution of L (0.22 g, 0.678 mmol) in 200 ml of chloroform. The mixture was stirred for 2 h at room temp. and concentrated to 10 ml under reduced pressure. The concentrate was mixed with 10 ml of light petroleum (bp 40–60 °C) and the resulting precipitate filtered off, washed with light petroleum (bp 40–60 °C) and dried *in vacuo*. Single crystals of [PdCl$_2$L] were grown from acetonitrile (yield *ca.* 77%) Mp = 170 °C (decomp.) (Found: C, 26.45; 3.76, C$_{11}$H$_{16}$OSTePdCl$_2$ requires: C, 26.33; H, 3.19%). $\delta_H$ [(CD$_3$)$_2$SO, 25 °C] 1.30 (t, 3H, CH$_3$), 2.55 (m, 2H, CH$_2$S), 3.10 (m, 4H, CH$_2$CH$_2$), 3.90 (s, 3H, OCH$_3$), 7.10–7.20 (d, 2H, ArH *m* to Te), 8.10–8.20 (d, 2H Ar H *o* to Te).

*X-Ray Analysis.*—A Bruker P4S X-ray diffractometer was used for the data collection using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) employing the $\omega$–$2\theta$ technique. The unit cell was determined from 25 randomly selected reflections using automatic search, index and least squares routines. Empirical absorption correction was applied using the SHELXA programme.[7a] The structure was solved by using routine heavy atom/Fourier methods (using SHELXL 93[7b]/SHELX 86[7c]) and refined by full-matrix least squares on $F^2$. The C(9) and C(10) atoms were disordered about S, as commonly noted for saturated carbons attached to S. The occupancies were C(9)/C(10) 0.58882; C(9A)/C(10A) 0.41118. To model the disorder the C(8)–C(9)/C(8)–C(9A), C(11)–C(10)/C(11)–C(10A), S–C(9)/S–C(9A) and S–C(10)/S–C(10A) distances were constrained to be similar. The constrained distances refined to 1.43, 1.44, 1.78 and 1.79 Å, respectively.

*Crystal Data.*—Chemical formula: C$_{11}$H$_{16}$Cl$_2$OPdSTe; $M = 501.20$, $T = 293(2)$ K; triclinic, space group: $P\bar{1}$; $\mu = 3.6$ mm$^{-1}$; unit cell dimensions: $a = 8.315(2)$, $b = 9.674(4)$, $c = 10.552(2)$, $\alpha = 103.02(2)$, $\beta = 105.10(2)$, $\gamma = 104.84(3)°$; $V = 752.4(4)$ Å$^3$, $Z = 2$; reflections collected 3608; independent reflections 3372 ($R_{\text{int}}$ 0.0192); final $R$ indices [$I > 2\sigma(I)$]: $R1 = 0.0659$, $wR2 = 0.2034$. Full crystallographic details excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/29.

See http://www.rsc.org/suppdata/jc/1999/716/ for crystallographic files in .cif format.

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