Organotellurium ligands – designing and complexation reactions

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Abstract. A variety of tellurium ligands has been designed and studied for their complexation reactions in the last decade. Of these hybrid telluroethers, halotellurium ligands and polytellurides are the most notable ones. RTe^- and polytelluride ions have also been used to design clusters. Ligation of ditelluroethers and several hybrid telluroethers is extensively studied in our laboratories. The ditelluroether ligand $RTeCH_2TeR$ (where $R = 4\text{-MeOC}_6H_4$) (**1**), similar to dppm [1,2-*bis*(diphenyl-phosphino)methane], has been synthesized in good yield (~80%) by reacting $CHCl_3$ with RTe^- (generated *in situ* by borohydride reduction of R_2Te_2). Iodine reacts with **1** to give tetra-iodo derivative, which has intermolecular $Te\cdots I$ interactions resulting in a macro structure containing rectangular $Te\text{-}I\cdots Te$ bridges. **1** readily forms four membered rings with Pd(II) and Ru(II). On the formation of this chelate ring, the signal in [125]Te NMR spectra shifts significantly upfield (50–60 ppm). The bridging mode of **1** has been shown in [Ru(*p*-cymene)Cl$_2$](m-**1**)[Ru(*p*-cymene)Cl$_2$]. The hybrid telluroether ligands explored are of the types (Te_x, S_y), (Te_x, N_y) and (Te_x, O_y). The tellurium donor site has strong *trans* influence, which is manifested more strongly in square planar complexes of palladium(II). The morpholine N-donor site has been found to have weaker donor characteristics in (Te_x, N_y) ligands than pyridine and alkylamine donor sites of analogous ligands. The singlet oxygen readily oxidises the coordinated Te. This oxidation follows first order kinetics. The complexation reaction of $RuCl_3.xH_2O$ with N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide (**2**) results in a novel (Te, N, O)-heterocycle, Te-chloro,Te-anisyl-1a-aza-4-oxa-3-tellura-1H, 2H, 4aH-9 fluorenone. The (Te, O) ligands can be used as hemilabile ligands, the oxygen atom temporarily protects the vacant coordination site before the arrival of the substrate. The chelate shifts observed in [125]Te NMR spectra of metal complexes of Te-ligands have a close parallel to those of ^{31}P NMR. For the formation of five-membered rings, the value is positive and of the order of 130 ppm whereas for six-membered rings it is negative and ~30 ppm only.

Keywords. Organotellurium ligands; hybrid telluroether; platinum metal complexes; tellurium-125 NMR.

1. Introduction

Tellurium is the noblest metalloid which may act as a Lewis acid as well as Lewis base. The ligand chemistry of tellurium, which acts as a 'soft' donor, was little explored before 1970, probably due to commercial non-availability of a wide variety of tellurium/organotellurium ligands and some misconception that they are air-sensitive, foul-smelling and toxic. In last three decades, a good number of publications devoted to them has appeared in the literature. This evidences considerable and continuous increase in the interest in tellurium ligands[1,2]. However, even today not many tellurium ligands are available commercially. With modern FT-NMR instruments there is a good possibility of

using ^{125}Te NMR to understand the solution behaviour of the metal–tellurium bond containing systems. This coupled with the fact that metal complexes of organotellurium ligands [3] may be used as single source precursors for MOCVD of II–VI semiconductors, has enhanced interest in ligand chemistry of tellurium. Apart from organotellurium ligands there is also a current interest in inorganic tellurium ligands viz. halogeno-tellurium donors, telluride and polytelluride ligands. Ligand chemistry of polytelluride ions has been reviewed few years ago [4]. The chemistry of inorganic halogenotellurium ligands, e.g. TeX_3^- has been compiled by Beck [5] and of tellurometalates $[M_xTe_y]^{2-}$ by Ansari *et al* [6].

In last one and a half decade, nearly three dozen polydentate telluroether ligands including ditelluroether and hybrid telluroethers) have been synthesized in our laboratory. In this report we briefly discuss our recent work on the ligand chemistry of ditelluroether ligand $RTeCH_2TeR$ (where R = 4-MeOC$_6$H$_4$) (**1**), which is similar to dppm [1,2-*bis*(diphenylphosphino)methane] the (Te_x, N_y) type hybrid organotellurium ligands viz. N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide (**2**) and N-{2-(4-methoxyphenyl-telluro)-ethyl}morpholine (**3**) and *bis*{2-(N-morpholino)ethyl}telluride (**4**), (Te_x, O_y) type ligands viz. 2-(4-ethoxyphenlytelluromethyl)tetrahydro-2H-pyran (**5**), 2-(2-{4-ethoxy-phenyl}-telluroethyl)-1,3-dioxane (**6**), *bis*(2-{1,3-dioxan-2-yl}ethyl) telluride(**7**) and (Te, S) type ligand 1-(4-methoxyphenylelluro)ethyl ethyl sulphide (**8**).

2. Results and discussion

2.1 *Ditelluroethers*

For the tellurium analogue of dppm, $RTeCH_2TeR$ (**1**), where R = C_6H_5, 4-MeOC$_6$H$_4$ a very clean and high yield (~80%) synthesis based on the reaction of $CHCl_3$ with $ArTe^-$ (generated *in situ* in ethanol by $NaBH_4$ reduction of Ar_2Te_2) has been reported recently [7]. The first structurally characterized complexes [8] of a chelating C_1 linked ditelluroether **1** are [{*meso*(4-MeOC$_6$H$_4$Te)$_2$CH$_2$}(dppe)Pd(II)](ClO$_4$)$_2$.4H$_2$O (**9**) and [*meso*(4-MeOC$_6$H$_4$Te)$_2$CH$_2$}Pd(II)Cl$_2$] (**10**) (dppe = [1,2-*bis*(diphenylphosphino)ethane]). The synthesis of **9** and **10** is contrary to the claim of Chiffey *et al* [9], that **1** always make polymeric complexes with Pd(II). The solubility of **9** in common organic solvents is of course very poor. The ^{125}Te{^{1}H} NMR spectrum of **9** has only one prominent signal at *δ* 509 (signal of free **1**; *δ* 571 ppm) favouring the presence of *meso* invertomer.


9
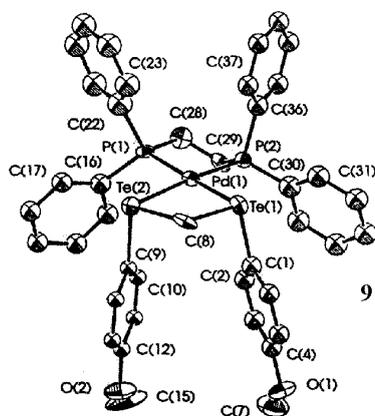
The oxidative addition of iodine with **1** results in {4-MeO-C$_6$H$_4$Te(I$_2$)}$_2$CH$_2$. The crystal structure of **1** and {4-MeO-C$_6$H$_4$Te(I$_2$)}$_2$CH$_2$ (**1a**) have been reported[10]. The Te(1)–C(1)–Te(2) bond angle (117·0(2)°) in **1** is larger than the expected value of about 109°, probably due to the steric influence of the two ArTe groups. However it is consistent with there being little or no Te–C *p*-bonding in the aliphatic link. The bite of **1** is greater than that of dppm [1,2-*bis*(diphenylphosphino)methane] due to the larger size of tellurium. The environment of both tellurium atoms in **1a** is that of the typical saw-horse structure associated with Te(IV) compounds. The two iodine atoms occupy axial positions with angles close to 180°. Two of the Te–I bonds, Te(1)–I(2) and Te(2)–I(4), are longer (average 3·063(3) Å) than the other two, Te(1)–I(1) and Te(2)–I(3) (average 2·815(8) Å). I(2) and I(4) have intermolecular contacts with their neighbouring Te atoms at distances (3·735(1) and 3·879(1) Å) considerably less than the sum of their van der Waal's radii of 4·35 Å. These interactions apparently lead to polymeric links of essentially Te–I–Te′–I′ rectangular bridges (angles 89·07(3) to 94·68(3)°). The carbon atom of the methoxyphenyl group attached to tellurium and that of methylene occupy two of the equatorial positions, with the supposed lone pair occupying the third. Despite the presence of the four iodine atoms, the Te(1)–C(8)–Te(2) bond angle 115·5(6)° is very close to that of the corresponding angle of **1**, i.e. 117·0(2)°.
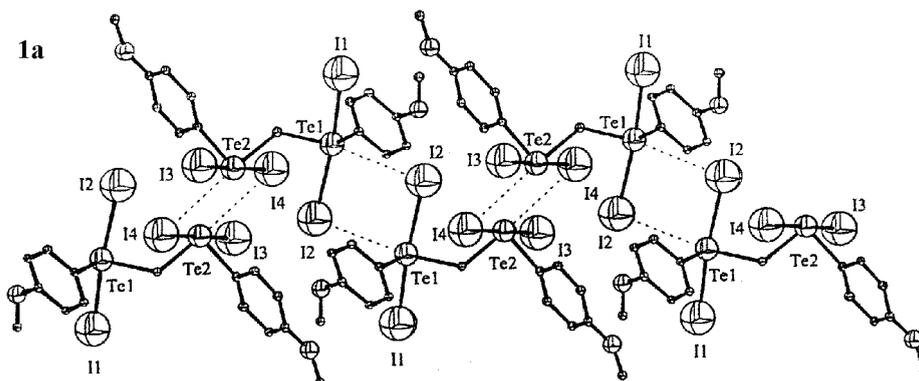

The complex *cis*-[Ru(DMSO)$_2$(Cl)$_2$(**1**)] (**11**) is formed by substitution of two DMSO molecules in *cis*-[Ru(DMSO)$_4$Cl$_2$] with **1**. The complex **11** is the first example of a ruthenium-ditelluroether complex[10] for which single crystal structure has been solved. The geometry of ruthenium in **11** is distorted octahedral. The bond lengths Ru(1)–Te(1) (2·599(5) Å) and Ru(1)–S(2) (2·244(1) Å), in which tellurium and sulphur atoms are *trans* to Cl, are both shorter than the corresponding Ru(1)–Te(2) (2·673 (5) Å) and Ru(1)–S(1) (2·314(1) Å) bond lengths, where the Te and S atoms are *trans* to each other. Both the Ru–Cl bond lengths are essentially identical with one Cl atom being *trans* to Te atom and the other *trans* to an S atom. The Te(1)–Ru(1)–Te(2) bite angle is 78·2(2)°, which can be compared to the values of 82·0(3) and 79·6(3)° for Te–Pd–Te angles in the complexes **9** and **10**. However in the complex **11** the ditelluroether ligand is not in *meso* form. The distortions from all 90° angles in the octahedron about ruthenium are apparently not equally shared between the two tellurium atoms. The angles involving Te(1) display much larger distortions of *cis* angles, 76·6(2)° for Te(1)–Ru(1)–Cl(2) to 99·6(3)° for Te(1)–Ru(1)–S(2) than those involving Te(2), 87·0(3)° for Te(2)–Ru(1)–Cl(2) to 93·5(3)° for Te(2)–Ru(1)–Cl(1). Further the 'plane' not involving Te(1), which

contains the five atoms, Te(2), Ru(1), S(1), S(2) and Cl(2) is planar within 0·008 Å while the one that includes Te(1) shows greater distortion from planarity, with Te(1), Te(2), Ru(1), S(1) and Cl(1) at 0·05 Å and Te(1), Ru(1), S(2), Cl(1) and Cl(2) at 0·07 Å. The Te–C(aromatic) distances, 2·120(5) and 2·124(5) Å are clearly shorter than those of Te–C(aliphatic) (2·145(5) and 2·146(5) Å), a general phenomenon reported earlier also[2]. However this is in contrast to free ligand in which all the Te–C bonds are essentially identical and also in contrast to what was observed for the two complexes of Pd(II) with **1**, but the bond lengths in these structures were less well-resolved. The value of Te–C–Te bond angle, 101·6(2)° in **11** concurs with no or little Te–C $p$bonding, but it is lower than those observed for Pd(II) complexes of **1**. The average C–Te–C angle 97·4° in **11** does not vary significantly from that of free **1** (98·1°). In the ^{1}H and ^{13}C NMR spectra of **11**, the CH_2 signals undergo deshielding (0·08 and 30 ppm respectively) consistent with its structure. In the ^{1}H NMR spectrum of crystals of **11** signals multiply after one hour of dissolution, indicating the formation of other *trans* isomers of **11**, complex species containing O–bonded DMSO (signal at *d* 2·90 ppm) and the presence of free DMSO (signal at *d* 2·61 ppm). The complex [(Ru(*p*-cymene)Cl$_2$).**1**] (**11a**) is also structurally characterized and has ligand **1** bonded in a bridging mode[10].


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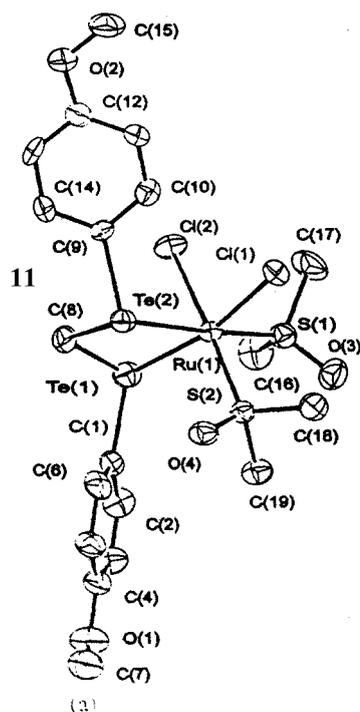
2.2 *Hybrid telluroethers*

In the last two decades, a few dozens of a variety of hybrid telluroether ligands have been explored for their ligation behaviour. Of these, a good number have been investigated in our research laboratory. Some very recent results are presented here. The common strategies used to design such ligands are the reactions of appropriate organic halides with ArTeNa, ArTeLi or Na_2Te. N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide (**2**)

$$\text{(1)}$$
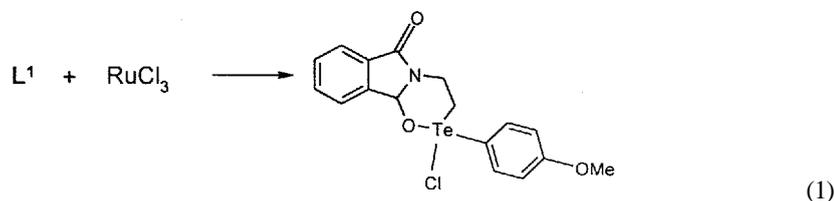
reacts with $RuCl_3 \cdot xH_2O$ resulting in a novel heterocycle as shown in (1). The heterocycle Te-chloro, Te-anisyl-1a-aza-4-oxa-3-tellura-1H, 2H, 4aH-9-fluorenone (**12**) is characterized structurally[11]. In the formation of **12** Te is oxidized to the + IV oxidation state as its electron pair geometry is typically that of a Te(IV) species, conforming to a trigonal bipyramidal arrangement by placing a lone pair at one corner of the trigonal plane. The oxygen and chlorine atoms are *trans* to each other. The C(1)–Te–C(8) angle (109·0(2)°) in **12** is a little higher than that of **2** (97·4(2)°). The Te–C bond lengths are also somewhat shortened on the formation of **12**. So far no tellurium heterocycle containing three heteroatoms is known and **12** is the first such example. Moreover, in the ^{13}C NMR spectrum of **12**, the signal due to $TeCH_2$ shows ~50 ppm downfield shift with respect to that of free **2**, concurring well with the formation of the Te(IV) species. The half sandwich compound [(*p*-cymene)$RuCl_2 \cdot$**2**] is also characterized structurally. In this half sandwich compound, *p*-cymene is in a H^6 bonding mode (Ru–C(av.) 2·192(1) Å) and Te–C(alkyl) has been found to be longer than Te–C(aryl).

N-{2-(4-methoxyphenyltelluro)-ethyl}morpholine (**3**) and *bis*{2-(N-morpholino) ethyl}-telluride (**4**) are potentially (Te, N) and (Te, N$_2$) type of ligands. Compound **4** is unstable but reaction of its freshly prepared sample with Pd(II) and Hg(II) in a 1:2 (metal:ligand) ratio stabilizes it. In the mass spectrum of **3** the molecular ion peak appears at *m/z* 351. CH_2N and CH_2Te signals in the ^{1}H NMR spectrum of **4** merge together, as supported by its HETCOR spectrum. The reactions of **3** and **4** with palladium(II) in a 1:1 molar ratio have resulted in insoluble materials which defy all attempts at characterization, probably due to their polymeric nature. The complexes of stoichiometry [Pd/PtCl$_2$ (**3/4**)$_2$] are characterized structurally[12,13]. There are many similarities in the structures of complexes of **3** and **4**. Both of them are *trans* square planar coordination compounds of the type [PdCl$_2$(RTeR′)$_2$] (R = R′ for **3**). There is no exact symmetry in either of them, however in the latter, the coordination plane is a pseudo mirror plane and there is a pseudo centre of symmetry at palladium position. The tellurium atoms in both the complexes have distorted pyramidal molecular geometry, the electron pair geometry of which may be described as distorted tetrahedral, if a lone pair presumably occupies one corner. The lone pairs on two Te atoms of these complexes have a *trans* orientation with respect to the linear Te–Pd–Te system. The organic groups present on the two tellurium atoms in each complex are in an orientation of least steric interaction. In the complex of **3** the two 4-MeOC$_6$H$_5$ groups present on different Te atoms are also *trans* to the Te–Pd–Te system.

The average values of Pd(II)–Te bond lengths in the complexes of **3** and **4** are very similar (2·596 and 2·600 Å, respectively). The sum of covalent radii of square planar Pd(II) (1·31 Å) and pyramidal Te(II) (1·32 Å) is 2·63 Å and comparable with the present averages. The Pd–Te bonds in these complexes are longer in comparison to those which are *trans* to Pd–Cl[7,8]. Thus the *trans* influence of Te has a very significant effect on the Pd–Te bond lengths of a *trans* Te–Pd–Te system.
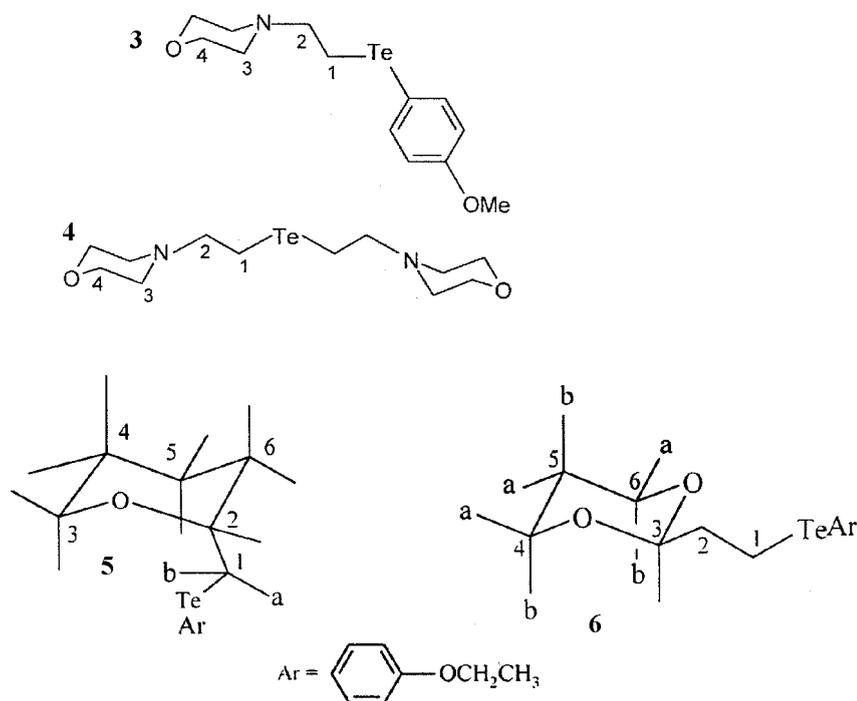
2-(4-Ethoxyphenlytelluromethyl)tetrahydro-2H-pyran (**5**), 2-(2-{4-ethoxyphenyl}-telluroethyl)-1,3-dioxane (**6**), and *bis*(2-{1,3-dioxan-2-yl}ethyl) telluride(**7**) are hemi-labile organotellurium ligands investigated in the recent past [14,15].

In the proton NMR spectrum of **5**, the H_4, H_5 and H_6 protons merge together and appear as a multiplet in the region of 1·24–1·96 ppm. The H_1 protons are not magnetically equivalent. The H_{1a}, H_{1b} and H_2 protons constitute an AA′B type spin system. Thus H_{1a} and H_{1b} protons appear as two multiplets of equal intensity in the regions 2·87–2·91 and 3·04–3·08 ppm respectively. The magnetic non-equivalence of H_{1a} and H_{1b} protons is supported by the HETCOR spectrum of **5**, in which both H_{1a} and H_{1b} appear as multiplets but have only one $^{13}C\{^1H\}$ cross peak. The diiodo derivative [**5**(I)$_2$] is formed through oxidative addition of iodine to tellurium of **5**. The ^1H NMR spectrum of this diiodo derivative is characteristic. The H_{1a} and H_{1b} signals, are deshielded (~0·6–0·8 ppm) with respect to those of free **5**. This concurs with the +IV oxidation state of its tellurium. The half sandwich Ru complexes of **5** and **6** in which the coordination sphere of metal is composed of two chloride ligands, H^6-bonded *p*-cymene ring and ligand **5/6** coordinated through Te are characterized structurally. The Ru-Te bond length (2·6197(8) Å) in the complex of **5** is consistent with the literature value 2·619(4)–2·650(1) Å reported for [Ru{PhTe(CH$_2$)$_3$TePh}$_2$Cl$_2$] and [Ru{MeTe(CH$_2$)$_3$TeMe}$_2$ClPPh$_3$]PF$_6$ [16]. The average value for Ru–C bond length is 2·189 Å and concurs with the values reported for **11a** [10]. The pyran ring has chair conformation as expected. The Ru–Cl bond distances 2·4205(12) and 2·4136(12) Å are normal and consistent with the literature values 2·4173(8) Å [17], reported for [RuCl{H^2–C,N–C$_6$H$_3$(CH$_2$NMe$_2$)$_2$–2,6}{H^6–C$_{10}$H$_{14}$}]. The aromatic ring of *p*-cymene ligand is almost planar (C–C–C bond angles vary from 116·8(3) to 122·3(4)°) and is perpendicular to Ru. The Ru–Te bond length in the complex of **6** is 2·642(1) Å and consistent with that of a similar complex of **5**. The dioxane ring

has chair conformation as expected. The Ru–Cl bond distances in the complex of **6** (2·404(3) and 2·415(3) Å) are normal. The potentially (Te, O_2) type of ligand **7** is stabilized on the formation of complexes [Ru(*p*-cymene)Cl$_2$.**7**] (**13**) and *trans*-[PdCl$_2$(**7**)$_2$] (**14**) which are characterized structurally[14]. The Ru–Te bond length in the half sandwich compound **13** is 2·6559(9) Å The geometry of Pd in **14** is square planar. The Pd–Te bond length in **14** is 2·5873(2) Å The **13** and **14** are the first examples of structurally
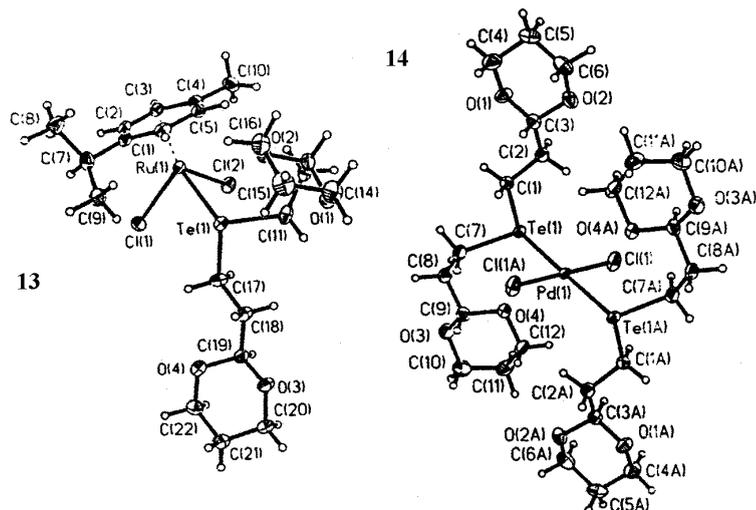
characterized complexes in which potentially (Te, O_2) type ligand molecules are present, and coordinate through Te. The reactions of ruthenium(II) complexes of hemilabile ligands of (Te, O_x) type ($x = 1$ or 2) with silver perchlorate result in species in which Ru is coordinated by ethereal oxygen. This Ru–O bond is found to be labile and is cleaved for several substrates easily.

2.3 *Trans-influence of tellurium ligands*

The *trans* influence of telluroether donor sites has been presumed most of the time as some what lower or at the most, nearly equal to that of thioether one. We have recently observed[18] that Pt–Cl *trans* to SMe is 2·324(4) Å, whereas in the same molecule of complex, [PtCl$_2$(4-EtOC$_6$H$_4$TeCH$_2$CH$_2$SMe)], 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 relative *trans* influence of telluro and thioethers. As suitable crystals of palladium(II) complex of 4-EtOC$_6$H$_4$TeCH$_2$CH$_2$SMe could not be grown, a similar ligand **8** having SEt and 4-MeOC$_6$H$_4$ groups was synthesized. Its palladium complex, [PdCl$_2$.**8**] (**15**) gives crystals suitable for X-ray diffraction[19]. The geometry of donor atoms around palladium is slightly distorted square planar. The Pd–Cl(2) is *trans* to the ArTe group and longer by 0·028 Å than Pd–Cl(1) which is *trans* to SEt. This suggests that *trans* influence of ArTe is probably greater in comparison to that of the thioether donor group SEt. The stronger s-donation[16] characteristic of Te in comparison to that of S seems to be responsible for its greater *trans* influence.

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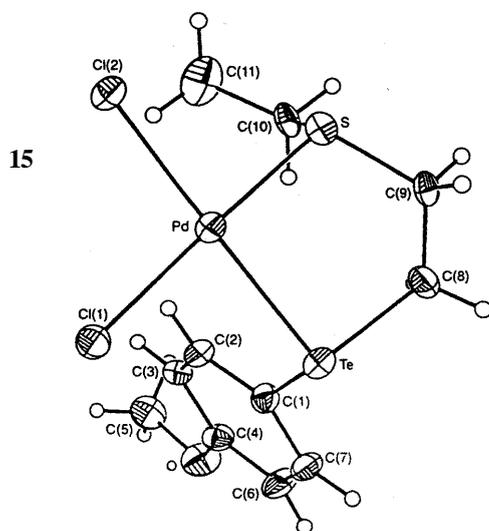
2.4 ^{125}Te NMR spectra

The ^{125}Te NMR of ligands **6** and **7** and their complexes [Pd/PtCl$_2$(**6/7**)$_2$] and [Pd/Pt (**6/7**)$_2$](ClO$_4$)$_2$ have been investigated the results are summarized in table 1. The chelate parameter for five-membered rings is positive and large in comparison to six-membered rings for which it is negative and small. Parallel behaviour of chelate parameters is well-known for ^{31}P NMR spectra.

2.5 *Reaction of complexes of Te-ligands with singlet oxygen*

The reaction of [Pd(phen)(**5/6**)$_2$](ClO$_4$)$_2$ with singlet oxygen has been followed in solution by monitoring the LLCT band of the complex at 450/452 nm, which disappears with time indicating that the Te atom is oxidized by the singlet oxygen resulting in the decomposition of the complex. The plots of log[complex] vs time are linear.

Table 1. ^{125}Te NMR data.

Ligand/complex	Chemical shift d (ppm)	Chelate parameter
5	489	
6	467	
[PdCl$_2$(**5**)$_2$]	642	
[PdCl$_2$(**6**)$_2$]	626	
[Pd(**5**)$_2$](ClO$_4$)$_2$	769	+127
[Pd/(**6**)$_2$](ClO$_4$)$_2$	607	−19
[PtCl$_2$(**5**)$_2$]	620	
[PtCl$_2$(**6**)$_2$]	618	
[Pt(**5**)$_2$](ClO$_4$)$_2$	732	+112
[Pt(**6**)$_2$](ClO$_4$)$_2$	602	−16

3. Conclusion

The reaction of chloroform with ArTe⁻ gives a very pure sample of *bis*(aryltelluro) methane which chelates in a bidentate mode more easily than dppm due to its bigger bite. Its bridging mode of coodination is also established. The tetraiodo derivative of *bis*(aryltelluro)methane has an interesting structure as Te···I secondary interactions result in a macromolecular framework in the solid state. [Ru(DMSO)$_2$Cl$_2$(**1**)] is the first example of a ruthenium-ditelluroether complex for which crystal structure has been solved. In this structure the geometry of Ru is distorted significantly indicating that if more than one molecule of **1** enters the coordination sphere of an octahedral complex, the probability of its acting in a chelating mode of coordination is much lower due to a limit on distortion tolerance and other steric reasons. The Te-chloro,Te-anisyl-1a-aza-4-oxa-3-tellura-1H, 2H, 4aH-9-fluorenone (**12**), is a unique example of a tellura heterocycle containing oxygen as well as nitrogen in the same ring, formed by oxidation of **2** with Ru(III) unexpectedly. The first tellurated derivatives of morpholine, N-{2-(4-methoxy-phenyltelluro) ethyl}morpholine and *bis*{2-(N-morpholino)ethyl}telluride are synthesized, which have a suitable bite for bi-/tri-dentate (Te, N)/(N, Te, N) ligation. However, donor capability of morpholine nitrogen seems to be weaker in comparison to those of other nitrogen donors studied in conjunction with Te as both the ligands prefer to coordinate only through the Te. The *trans* influence of Te shows a very significant effect on the Pd–Te bond lengths. The *trans* influence of ArTe is shown to be stronger than that of SEt. The potentially (Te, O) ligands, 2-(4-ethoxyphenlytelluromethyl) tetrahydro-2H-pyran and 2-(2-{4-ethoxyphenyl}telluroethyl)-1,3-dioxane, which like (P, O) ligands exhibit hemilability and thus can be of some importance in the context of catalytically active species, have been authenticated structurally in [RuCl$_2$(*p*-cymene).**5/6**]. The chelate parameter is found to behave in a manner similar to that of ^{31}P NMR. The Pd–Te bond is cleaved by singlet oxygen as Te is oxidized readily.

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