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SYNTHESIS AND LIGAND CHEMISTRY OF BIS[(2-ARYLTELLURO)ETHYL]AMINE AND BIS[(2-ARYLTELLURO)ETHYL]METHYLAMINE—NOVEL (Te, N, Te) DONORS

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Abstract—New tridentate ligands, bis[(2-aryltelluro)ethyl]amine (**1** and **2**) and bis[(2-aryltelluro)ethyl]methylamine (**3** and **4**) (aryl = 4-MeOC_6H_4 or 4-EtOC_6H_4) were synthesized by the reaction of sodium aryltellurolate with bis(2-chloroethyl)amine and bis(2-chloroethyl)methylamine, respectively, and characterized by molecular weight measurements, elemental analyses, IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectra. Complexes of the type $MCl_2 \cdot L$ (L = **1** or **2**; M = Hg, Pd or Pt) were synthesized by reacting the ligand with $HgCl_2$, $(C_6H_5CN)_2PdCl_2$ and K_2PtCl_4. Mercury complexes were found to be non-ionic and monomeric. ^{1}H and $^{13}C\{^1H\}$ NMR spectra suggest that the ligands in these complexes coordinate only through two tellurium atoms. Palladium and platinum complexes of **1** and **2** were found to be diamagnetic, monomeric and non-ionic in nitrobenzene. However, they exhibit conductance in acetonitrile and methanol due to solvolysis. ^{1}H and $^{13}C\{^1H\}$ (recorded for **1** only) NMR spectra suggest that **1** and **2** act as a tridentate ligand in palladium and platinum complexes. On considering their electronic and IR spectral data in conjunction with the various properties, a square pyramidal structure with two chlorine atoms *trans* to each other seems to be most plausible for palladium/platinum complexes.

Bidentate or polydentate hybrid telluride ligands are somewhat rare.[1–3] We have reported recently[4] novel (Te, N) ligands, *viz.* 1-(NMe_2)-2-(TeAr)-4-MeC_6H_3 (Ar = C_6H_5, 4-MeOC_6H_4, or 4-EtOC_6H_4), and their complexation with palladium(II) and platinum(II). They also behave as unidentate ligands (coordinating through tellurium only) in mercury(II) complexes.[5] In continuation of our studies on the syntheses and ligation of (Te, N) donors we have synthesized bis[(2-aryltelluro)ethyl]amine and bis[(2-aryltelluro)ethyl]methylamine (**1**–**4**). It was thought worthwhile to explore their complexation with metal ions in detail because their phosphorus analogues have been found to give interesting structures[6] and induce catalytic activities[7] in platinum metal complexes. In the present paper the syntheses of **1**–**4** and the ligational behaviour of **1** and **2** with mercury(II), palladium(II) and platinum(II) are reported.

EXPERIMENTAL

Published methods were used to synthesize the ditellurides, $(4\text{-MeOC}_6H_4)_2Te_2$ and $(4\text{-EtOC}_6H_4)_2Te_2$,[8] bis(2-chloroethyl)amine and bis(2-chloroethyl)methylamine.[9] Chloride, mercury and tellurium were estimated by standard methods.[10] The C, H and N analyses were carried out with a Perkin–Elmer elemental analyser 240C. ^{1}H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ were recorded at 25°C on a JEOL FX100 FT-NMR spectrometer at 99.55 and 25 MHz, respectively. IR spectra (Nujol mulls between CsI windows or CsI/KBr discs) in the range 4000–200 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrometer. Electronic spectra in chloroform were recorded on a Hitachi 300 UV–vis spectrometer. The conductivity measurements were made on *ca* 1 mM solutions in acetonitrile, methanol and nitrobenzene with a Metrohm 660 conductometer. The molecular weights were determined in chloroform solution (~ 10 mmolal) with a Knauer vapour pressure osmometer.

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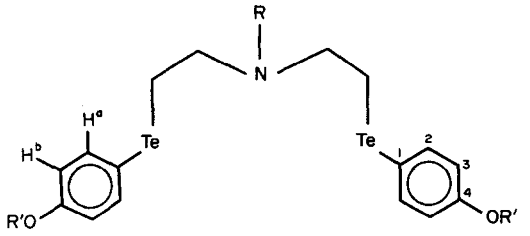


R'	R	
Me	H	**(1)**
Et	H	**(2)**
Me	Me	**(3)**
Et	Me	**(4)**

Synthesis of bis[(2-aryltelluro)ethyl]amine and bis[(2-aryltelluro)ethyl]methylamine

Diaryl ditelluride (2.5 mmol) was refluxed in ethanol (30 cm^3) under a nitrogen atmosphere. Sodium borohydride (0.2 g in 2 cm^3 of 1 M NaOH) was added to it dropwise until the refluxing solution became colourless. Bis(2-chloroethyl)amine or bis(2-chloroethyl)methylamine (2.5 mmol) dissolved in ethanol (10 cm^3) was added dropwise to this refluxing solution of sodium aryl tellurolate with vigorous stirring. The resulting pale yellow mixture was further refluxed for 1 h, cooled to room temperature and poured into 200 cm^3 of water. The ligand (**1**–**4**) was extracted into chloroform (200 cm^3) from this aqueous mixture. The extract was washed with water, dried over anhydrous sodium sulphate and concentrated to ~5 cm^3 under vacuum. The precipitated pale yellow–white crystalline solid was recrystallized from a chloroform–hexane (70 : 30) mixture to give the white crystalline ligand (**1**–**4**). The yield, melting point, molecular weight, results of elemental analyses, characteristic IR bands, ^1H and $^{13}C\{^1H\}$ NMR data for **1**–**4** are given below.

Ligand **1**. Yield 75%; m.p. 78°C. Analysis: Found: C, 39.5; H, 4.1; N, 2.5; Te, 46.6. Calc. for $C_{18}H_{23}NO_2Te_2$: C, 40.0; H, 4.3; N, 2.6; Te, 47.2%. Mol. wt: Found: 522.8; Calc.: 540.2. IR (cm^{-1}): 1180m [ν(C—N)]; 3261m [ν(N—H)]; 268mb, 297mb [ν(Te—C(Ar))]. NMR [^1H]: δ, 1.65 (bs, 1H, NH); 2.92 (bs, 8H, NCH_2CH_2Te); 3.78 (s, 6H, OMe); 6.69–6.78 (d, 4H, H^b of phenyl ring -*m* to Te); 7.62–7.71 (d, 4H, H^a of phenyl ring -*o* to Te); [$^{13}C\{^1H\}$]: δ, 10.5 ($TeCH_2$); 49.5 (NCH_2); 55.1 (OMe); 100.4 (C_1); 115.0 (C_3); 140.8 (C_2); 159.6 (C_4).

Ligand **2**. Yield 80%; m.p. 85°C. Analysis: Found: C, 41.7; H, 4.1; N, 2.4; Te, 43.8. Calc. for $C_{20}H_{27}NO_2Te_2$: C, 42.2; H, 4.8; N, 2.5; Te, 44.9%. Mol. wt: Found: 547.0; Calc.: 568.2. IR (cm^{-1}): 1180m [ν(C—N)]; 3261bm [ν(N—H)]; 270mb, 315mb [ν(Te—C(Ar))]. NMR [^1H]: δ, 1.65 (bs, 1H, NH); 2.83 (bs, 8H, NCH_2CH_2Te); 3.80–4.10 (q, 4H, OCH_2); 1.32–1.46 (t, 6H, CH_3); 6.67–6.76 (d, 4H, H^b of phenyl ring); 7.58–7.66 (d, 4H, H^a of phenyl ring); [$^{13}C\{^1H\}$]: δ, 10.4 ($TeCH_2$); 14.7 (CH_3); 49.5 (NCH_2); 63.2 (OCH_2); 100.1 (C_1); 115.5 (C_3); 140.8 (C_2); 158.9 (C_4).

Ligand **3**. Yield 85%; m.p. 58°C. Analysis: Found: C, 40.2; H, 4.2; N, 2.7; Te, 45.7. Calc. for $C_{19}H_{25}NO_2Te_2$: C, 41.1; H, 4.5; N, 2.5; Te, 46.1%. Mol. wt: Found: 530.5; Calc.: 554.2. IR (cm^{-1}): 1180m [ν(C—N)]; 280m, 245m [ν(Te—C(Ar))]. NMR [^1H]: δ, 2.23 (s, 3H, NMe); 3.77 (s, 6H, OMe); 2.78–2.84 (unresolved triplet, 4H, $TeCH_2$); 2.91–2.97 (unresolved triplet, 4H, NCH_2); 6.69–6.78 (d, 4H, H^b of phenyl ring); 7.61–7.69 (d, 4H, H^a of phenyl ring); [$^{13}C\{^1H\}$]: δ, 8.6 ($TeCH_2$); 40.9 (NMe); 55.0 (OMe); 58.0 (NCH_2); 101.3 (C_1); 114.9 (C_3); 140.4 (C_2); 159.3 (C_4).

Ligand **4**. Yield 87%; m.p. 62°C. Analysis: Found: C, 42.5; H, 4.7; N, 2.3; Te, 42.6. Calc. for $C_{21}H_{29}NO_2Te_2$: C, 43.3; H, 5.0; N, 2.4; Te, 43.8%. Mol. wt: Found: 562.4; Calc.: 582.2. IR (cm^{-1}): 1180m [ν(C—N)]; 250w, 280m [ν(Te—C(Ar))]. NMR [^1H]: δ, 2.23 (s, 3H, NMe); 2.78–2.84 (unresolved triplet, 4H, $TeCH_2$); 2.91–2.98 (unresolved triplet, 4H, NCH_2); 1.32–1.46 (t, 6H, CH_3); 3.89–4.10 (q, 4H, OCH_2); 7.60–7.69 (d, 4H, H^a of phenyl ring); 6.81–6.90 (d, 4H, H^b of phenyl ring); [$^{13}C\{^1H\}$]: δ, 8.13 ($TeCH_2$); 14.7 (CH_3); 41.0 (NMe); 58.2 (NCH_2); 63.3 (OCH_2); 101.1 (C_1); 115.6 (C_3); 140.5 (C_2); 158.9 (C_4).

Synthesis of mercury complexes (**5** *and* **6**)

To a solution of $HgCl_2$ (0.3 mmol) in acetone (5 cm^3) was added the solution of the ligand (**1**, **2**) (0.3 mmol) in acetone (5 cm^3) with stirring at room temperature. Hexane was added to precipitate the complex (**5** or **6**) as a pale yellow solid which was filtered, washed with acetone (2 cm^3) and dried *in vacuo*. These complexes are soluble in $CHCl_3$, CH_2Cl_2 and CH_3CN. The physical and spectral data are recorded below.

$HgCl_2 \cdot$**1** (**5**). Yield 67%; m.p. 70°C. Analysis: Found: C, 26.6; H, 2.8; N, 1.7; Cl, 8.7; Te, 31.4; Hg, 24.7. Calc. for $C_{18}H_{23}NO_2Te_2 \cdot HgCl_2$: C, 26.0; H, 2.7; N, 1.7; Cl, 8.1; Te, 30.5; Hg, 24.1%. Mol. wt: Found: 830.8; Calc.: 811.7. IR (cm^{-1}): 1180m [ν(C—N)]; 250m, 290w [ν(Te—C(Ar))]; 3261bw [ν(N—H)]; 325wb (ν(Hg—Cl)]. NMR [^1H]:

δ, 3.76 (s, 6H, OMe); 3.12 (bs, 4H, $TeCH_2$); 3.40 (bs, 4H, NCH_2); 1.67 (bs, 1H, NH); 7.79–7.87 (d, 4H, H^a of phenyl ring); 6.78–6.87 (d, 4H, H^b of phenyl ring); [$^{13}C\{^1H\}$]: δ, 24.8 ($TeCH_2$); 46.1 (NCH_2); 55.2 (OMe); 103.2 (C_1); 115.8 (C_3); 139.6 (C_2); 161.0 (C_4).

$HgCl_2 \cdot$**2** (**6**). Yield 63%; m.p. 80°C. Analysis: Found: C, 28.5; H, 3.2; N, 1.7; Cl, 8.5; Te, 30.4; Hg, 23.9. Calc. for $C_{20}H_{27}NO_2Te_2 \cdot HgCl_2$: C, 27.7; H, 3.2; N, 1.6; Cl, 7.9; Te, 29.4; Hg, 23.0%. Mol. wt: Found: 855.0; Calc.: 839.7. IR (cm^{-1}): 1180m [ν(C—N)]; 3282bw [ν(N—H)]; 265m, 290w [ν(Te—C(Ar))]; 315m [ν(Hg—Cl)]. NMR [^1H]: δ, 2.00 (bs, 1H, NH); 3.14 (bs, 4H, $TeCH_2$); 3.37 (bs, 4H, NCH_2); 1.30–1.43 (t, 6H, CH_3); 3.84–3.98 (q, 4H, OCH_2); 7.73–7.82 (d, 4H, H^a of phenyl ring); 6.73–6.82 (d, 4H, H^b of phenyl ring); [$^{13}C\{^1H\}$]: δ, 14.6 (CH_3); 24.5 ($TeCH_2$); 46.2 (NCH_2); 63.4 (OCH_2); 103.1 (C_1); 116.3 (C_3); 139.5 (C_2); 160.3 (C_4).

Synthesis of palladium complexes (**7** *and* **8**)

Bis(benzonitrile)palladium dichloride (0.5 mmol) dissolved in chloroform (20 cm^3) was stirred at room temperature with **1** or **2** (0.5 mmol) (added as solid) for 2 h. The resulting orange–yellow solution was mixed with hexane (50 cm^3) with stirring. The orange coloured precipitate of the complex (**7** or **8**) was filtered, washed with hexane, dried *in vacuo* and recrystallized from a chloroform–hexane (75:25) mixture. These complexes are soluble in a wide range of polar organic solvents, *vis.* CH_2Cl_2, $CHCl_3$, CH_3CN, MeOH, EtOH, DMF and DMSO, as well as in H_2O. The physical and spectral data for **7** and **8** are recorded below.

$PdCl_2 \cdot$**1** (**7**). Yield 75%; m.p. 125°C. Analysis: Found: C, 30.6; H, 3.4; N, 1.8. Calc. for $C_{18}H_{23}NO_2Te_2 \cdot PdCl_2$: C, 30.1; H, 3.2; N, 2.0%. Mol. wt: Found: 698.2; Calc.: 717.6. IR (cm^{-1}): 3028.8 [ν(N—H)]; 1112m [ν(C—N)]; 270w, 240w [ν(Te—C(Ar))]; 320bw [ν(Pd—Cl)]. NMR [^1H]: δ, 3.83 (s, 6H, OMe); 5.39 (bs, 1H, NH); 2.60–3.70 (broad unresolved multiplet, 8H, NCH_2CH_2Te); 6.90–6.98 (d, 4H, H^b of phenyl ring); 7.97–8.06 (unresolved doublet, 4H, H^a of phenyl ring); [$^{13}C\{^1H\}$]: δ, 16.1 ($TeCH_2$); 55.4 (OMe); 59.1 (NCH_2); 105.6 (C_1); 116.2 (C_3); 138.6 (C_2); 161.6 (C_4).

$PdCl_2 \cdot$**2** (**8**). Yield 80%; m.p. 155°C. Analysis: Found: C, 31.3; H, 4.1; N, 1.7. Calc. for $C_{20}H_{27}NO_2Te_2 \cdot PdCl_2$: C, 32.2; H, 4.2; N, 1.9%. Mol. wt: Found: 730.4; Calc.: 754.6. IR (cm^{-1}): 3071bw [ν(N—H)]; 1112m [ν(C—N)]; 275w, 243w [ν(Te—C(Ar))]; 320bw [ν(Pd—Cl)]. NMR [^1H]: δ, 5.39 (bs, 1H, NH); 3.95–4.15 (q, 4H, OCH_2); 1.36–1.50 (t, 6H, CH_3); 2.67–3.75 (broad unresolved multiplet, 8H, NCH_2CH_2Te); 7.95–8.01 (unresolved doublet, 4H, H^a of phenyl ring); 6.88–6.96 (d, 4H, H^b of phenyl ring).

Synthesis of platinum complexes (**9** *and* **10**)

To a solution of K_2PtCl_4 (0.5 mmol) in water (15 cm^3) was added **1** or **2** (0.5 mmol) in acetone (10 cm^3). The resulting solution was stirred for 3 h at room temperature and poured into water (100 cm^3). From an aqueous mixture the complex (**9** or **10**) was extracted into chloroform (150 cm^3). The chloroform extract was dried over anhydrous sodium sulphate and the solvent was reduced under vacuum to ~ 5 cm^3. The platinum complex **9** or **10** crystallized as pale yellow crystals on keeping the concentrated solution for 4–5 h at room temperature. They were recrystallized from a chloroform–hexane (80:20 mixture). In CH_2Cl_2, $CHCl_3$, CH_3CN, MeOH, EtOH, DMF and DMSO the platinum complexes are fairly soluble and sparingly in H_2O. The analytical and spectral data for these complexes are given below.

$PtCl_2 \cdot$**1** (**9**). Yield 80%; m.p. 75°C. Analysis: Found: C, 25.8; H, 2.4; N, 1.7. Calc. for $C_{18}H_{23}NO_2Te_2 \cdot PtCl_2$: C, 26.8; H, 2.9; N, 1.8%. Mol. wt: Found: 830.4; Calc.: 806.3. IR (cm^{-1}): 1110w [ν(C—N)]; 270m, 245m [ν(Te—C(Ar))]; 325m [ν(Pt—Cl)]; 2965.5bw [ν(N—H)]. NMR [^1H]: δ, 3.84 (s, 6H, OMe); 4.93 (bs, 1H, NH); 2.34–3.66 (broad unresolved multiplet, 8H, NCH_2CH_2Te); 6.88–9.97 (d, 4H, H^b of phenyl ring); 7.88–7.96 (d, 4H, H^a of phenyl ring).

$PtCl_2 \cdot$**2** (**10**). Yield 95%; m.p. 105°C. Analysis: Found: C, 27.6; H, 3.0; N, 1.4. Calc. for $C_{20}H_{27}NO_2Te_2 \cdot PtCl_2$: C, 28.7; H, 3.2; N, 1.7%. Mol. wt: Found: 856.4; Calc.: 834.3. IR (cm^{-1}): 1100m [ν(C—N)]; 285w, 250w [ν(Te—C(Ar))]; 330bm [ν(Pt—Cl)]; 2944.4bw [ν(N—H)]. NMR [^1H]: δ, 4.96 (bs, 1H, NH); 2.26–3.61 (broad unresolved multiplet, 8H, NCH_2CH_2Te); 3.95–4.15 (q, 4H, OCH_2); 1.34–1.48 (t, 6H, CH_3); 6.86–6.95 (d, 4H, H^b of phenyl ring); 7.98–8.15 (bd, 4H, H^a of phenyl ring).

The $^{13}C\{^1H\}$ NMR spectra of **8**, **9** and **10** could not be recorded due to an inadequate solubility problem.

RESULTS AND DISCUSSION

The ligands, bis[(2-aryltelluro)ethyl]amine and bis[(2-aryltelluro)ethyl]methylamine were synthesized by the reactions given in eqs (1)–(3):

$$RN(C_2H_4OH)_2 \xrightarrow[CHCl_3/Reflux]{SOCl_2} RN(C_2H_4Cl)_2 \cdot HCl$$

$$\xrightarrow{10\%\ NaOH} RN(C_2H_4Cl)_2 \quad (1)$$

$$(4\text{-}R'OC_6H_4)_2Te_2 \xrightarrow[NaOH/N_2\ atm.]{NaBH_4/EtOH} 4\text{-}R'OC_6H_4TeNa \quad (2)$$

$$4\text{-}R'OC_6H_4TeNa + RN(C_2H_4Cl)_2 \xrightarrow[N_2\ atm.,\ 1\ h]{EtOH/Reflux} RN(C_2H_4TeC_6H_4\text{-}4\text{-}OR')_2 \quad (3)$$

(1–4)

(R = H or Me; R′ = Me or Et).

Fig. 1.

The ligands, **1–4**, are white crystalline solids with low melting points. They are more soluble in $CHCl_3$, CH_2Cl_2 and Me_2CO than in MeOH and EtOH. Like other tellurides they also behave as non-electrolytes in solution. ^1H NMR spectra of **1**–**4** exhibit some interesting features. In the spectra of **1** and **2** a broad resonance at 1.65 ppm attributable to the NH group appears, whereas ligands **3** and **4** show a sharp singlet at 2.23 ppm due to the NMe group, concurring with earlier reported values.[11] In **1** and **2** the protons of the "NCH_2CH_2Te" bridge appear as a broad singlet at 2.92 and 2.83 ppm, respectively [Fig. 1(a)], contrary to the expected triplets for the $TeCH_2$ and NCH_2 protons. But in the spectra of **3** and **4** these CH_2 protons give two partly resolved triplets [Fig. 1(b)], centred at 2.94 and 2.81 ppm for the NCH_2 and $TeCH_2$ groups, respectively. The appearance of a broad singlet for the protons of the "NCH_2CH_2Te" bridge may be explained by considering the ^1H NMR spectrum of diethanolamine (precursor of these ligands) in which the NCH_2 and OCH_2 appear as triplets centred at 2.80 and 3.69 ppm, respectively. When oxygen is replaced by a less electronegative tellurium, the protons of the CH_2 group attached to it experience shielding and their signal probably merges with the NCH_2 signal, thereby giving a broad singlet. In **3** and **4** the protons of the NCH_2 group are shielded with respect to the similar protons of **1** and **2** due to the presence of the methyl group on nitrogen and, therefore, partly resolved signals [Fig. 1(b)] for the NCH_2 and $TeCH_2$ groups were observed. The ^1H NMR spectra of **1–4** were also recorded in CF_3COOD in which the ligands may exist as $D(R)N(C_2H_4TeAr)_2^+$. The "NCH_2CH_2Te" bridge in this medium has two magnetically non-equivalent groups of CH_2 protons, i.e. $CH_2(N)$ and $CH_2(Te)$, thereby showing the expected coupling of these protons in the spectra [Fig. 1(c)]. The merging of two CH_2 signals may be partly as a result of the weak N → Te interaction which is possible in ligands **1–4**. In acid solution such an interaction breaks down resulting in the expected ^1H NMR spectrum for the methylene groups. Moreover, the two tellurium atoms seem to be involved in a dynamic process fast enough on the ^1H NMR time scale, in which they interact alternatively with the nitrogen, otherwise protons of the CH_2 groups would have become magnetically non-equivalent, resulting in a complex ^1H NMR spectrum. The ring protons H^a and H^b appear as doublets, as expected for a 1,4-substituted phenyl ring. The $^{13}C\{^1H\}$ NMR spectra of **1–4** have been found to be in agreement with ^1H NMR spectra as the $CH_2(Te)$ resonances appear between 8 and 10.5 ppm in **1–4**, consistent with the earlier reported values,[12] supporting the shielding of carbon linked to tellurium. The carbon of $CH_2(N)$ in the spectra of these ligands appears between 50 and 58 ppm as reported for such carbons.[11] The carbons of the *p*-ethoxyphenyl and *p*-methoxyphenyl groups linked to tellurium also exhibit signals in agreement with the reported values for such moieties.[13] The two ν[Te—C(Ar)] vibrations in the IR spectra of **1–4** at 280–315 and 250–270 cm^{-1} are consistent with the earlier reports on tellurides.[14]

Complexation of **1** *and* **2** *with mercury*(II), *palladium*(II) *and platinum*(II)

The ligands **1** and **2** form complexes with bivalent mercury, palladium and platinum according to eqs

(4)–(6):

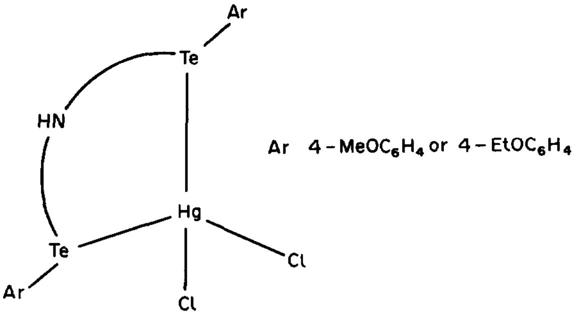
$$L + HgCl_2 \xrightarrow[\text{r.t.}]{\text{acetone}} \underset{(\mathbf{5},\mathbf{6})}{HgCl_2 \cdot L} \qquad (4)$$

$$L + (C_6H_5CN)_2PdCl_2 \xrightarrow[\text{r.t., 2 h}]{CHCl_3} \underset{(\mathbf{7},\mathbf{8})}{[PdCl_2 \cdot L]} \qquad (5)$$

$$L + K_2PtCl_4 \xrightarrow[\text{r.t., 3 h}]{\text{aq.-acetone}} \underset{(\mathbf{9},\mathbf{10})}{[PtCl_2 \cdot L]} \qquad (6)$$

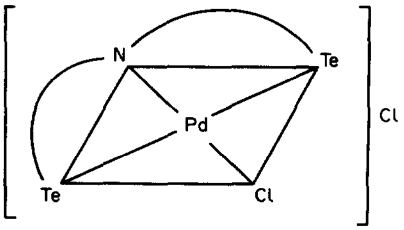
(L = **1** or **2**).

Molecular weights of mercury complexes indicate that they are monomeric. Their molar conductance values in acetonitrile indicate that they are non-ionic in nature. In the IR spectra of **5** and **6**, two ν[Te—C(Ar)] bands have been found at lower frequency (~ 15–30 cm^{-1}) in comparison to the similar bands of **1** and **2**. On coordination, ν(C—N) remains unaffected and the shift of ν(N—H) is too insignificant to conclude coordination of the NH group. Thus, probably two tellurium atoms are the only ligating site of **1** and **2** in the mercury complexes. The ^1H NMR spectra of **5** and **6** have two broad singlets due to NCH_2 and $TeCH_2$. This suggests that on coordination, these protons (almost similar in **1** and **2**) become magnetically non-equivalent and therefore appear as two broad singlets. The signal of the NH protons does not show any change in **5** and **6** when compared with that of free ligand, indicating the presence of an uncoordinated NH group in the mercury complexes. The H^a protons of the phenyl ring undergo a greater downfield shift (~ 0.15 ppm) than the H^b protons (~ 0.10 ppm). In the $^{13}C\{^1H\}$ NMR spectra of these mercury complexes, carbon signals of $CH_2(Te)$ and $C_1(Te)$ were found to be deshielded by ~ 14.3 and ~ 3.0 ppm, respectively, with respect to the corresponding signals of the free ligands. However, the carbon signal of $CH_2(N)$ appears around 3.5 ppm upfield relative to the free ligand, which supports the possibility of a weak $N \rightarrow Te$ interaction in **1** and **2**. If these spectral observations are considered together they indicate that **1** and **2** probably coordinate with mercury through their two tellurium atoms. On consideration of the spectral data in conjunction with molecular weight and molar conductance values, it is reasonable to presume that structure **A** is most plausible for **5** and **6**.

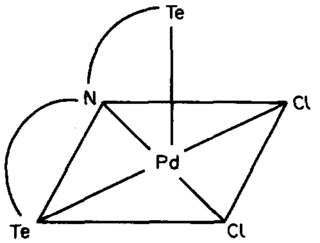


(A)

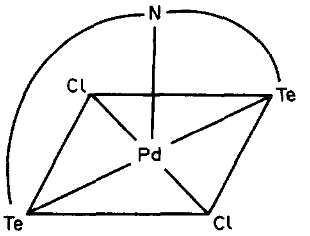
The molar conductances of the solutions of **7**–**10** in acetonitrile (~ 1 mM) were found in the range 30–40 Ω^{-1} cm^2 mol^{-1}. These values are lower than those expected for a 1 : 1 electrolyte.[15] The conductances (Λ_M = ~ 100 Ω^{-1} cm^2 mol^{-1}) of **7**–**10** in methanol (~ 0.1 mM solution) are very close to that of a 1 : 1 electrolyte and decrease on increasing the concentration (Λ_M for 1 mM solution is ~ 60 Ω^{-1} cm^2 mol^{-1}). In nitrobenzene the conductance is very low (Λ_M = ~ 4 Ω^{-1} cm^2 mol^{-1} at 1 mM concentration) compared to the value expected for a 1 : 1 electrolyte and does not change much on dilution (Λ_M = ~ 10 Ω^{-1} cm^2 mol^{-1} at 0.1 mM concentration). These observations suggest that conductance probably arises from solvolysis of $MCl_2 \cdot$ **1**/**2** (M = Pt or Pd), and to assume that these complexes are non-ionic is reasonable. Molecular weights of these complexes (**7**–**10**) in chloroform favour their monomeric and non-ionic nature. In the IR spectra of **7** and **8**, the ν(Te—C) consists of two bands with a red shift of the order of 27–35 cm^{-1}. The ν(C—N) and ν(N—H) are also red shifted by an order of ~ 70 and ~ 200 cm^{-1}, respectively, in comparison to the free ligand, which suggests that **1** and **2** coordinate with palladium through the nitrogen and tellurium atoms. A broad peak at 320 cm^{-1} in the IR spectra of **7** and **8** may be assigned to the ν(Pd—Cl) vibrations.[6,16] The assignment of ν(Pd—Cl) was confirmed by examining the IR spectra of $PdBr_2 \cdot$ **1**/**2** prepared by the metathetical reaction of $PdCl_2 \cdot$ **1**/**2** with KBr. The band assigned to ν(Pd—Cl) was absent in the spectra of $PdBr_2 \cdot$ **1**/**2**. In the ^1H NMR spectra of **7** and **8**, the NH signal was observed ~ 4.7 ppm downfield from its position in the spectra of the free ligand, indicating strong coordination of the NH group with palladium. The H^a protons of the phenyl ring were found to be more deshielded (0.35 ppm) than the H^B protons (0.20 ppm), on formation of palladium complexes. Only the $^{13}C\{^1H\}$ NMR spectrum of **7** could be recorded due to the low solubility of the other complexes. Complex **7** displays carbon signals for the $CH_2(Te)$ and $CH_2(N)$ groups at 5.6 and 9.5 ppm downfield, respectively, relative to the free ligand. The signal of $C_1(Te)$ also moves 5.2 ppm downfield on coordination. On considering the information derived from the IR and NMR spectra together, it appears that in palladium complexes (**7** and **8**) the ligands most probably coordinate through the nitrogen and two tellurium atoms. The



(B)



(C)



(D)

electronic spectra of the palladium complexes which are found to be diamagnetic have three bands at 33.3, 29.4 and 23.8 kK. The first band probably originates from intra-ligand transitions (the electronic spectra of **1** and **2** show only one band at 41.6 kK). The second and third bands suggest that palladium complexes have either square-planar or pyramidal geometry. The bands may be assigned to $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions.[17] In view of the non-ionic nature of the palladium complexes, the square-planar ionic structure **B** is ruled out. Of the two structures **C** and **D**, the value of ν(Pd—Cl) being somewhat lower than expected for a Cl *trans* to N, favours the *trans* structure **D**.[16] The trigonal bipyramidal geometry around palladium does not seem possible due to steric reasons also.

The IR spectra of **9** and **10** show two ν(Te—C) bands which are red shifted by the order of 20–30 cm^{-1}. The ν(C—N) and ν(N—H) are also red shifted by the order of $\sim$ 70 and $\sim$ 300 cm^{-1}, respectively. The ν(Pt—Cl) bond appears[6,16] around 330 cm^{-1} in the spectra of **9** and **10**, which is supported by the IR spectrum of $PtBr_2 \cdot 1/2$ (prepared by metathesis) as for the palladium complexes. In the ^{1}H NMR spectra of the platinum complexes (**9** and **10**) the "NCH_2CH_2Te" bridge protons appear as a broad unresolved multiplet compared to a broad singlet for the free ligands, indicating a strong involvement of the nitrogen and both the tellurium atoms of **1** and **2** in coordination to platinum. The signal for H^a protons also undergoes a downfield shift, 0.26 and 0.44 ppm for **9** and **10**, respectively. Similarly, H^b protons undergo a downfield shift of the order 0.20 ppm in **9** as well as in **10**. These trends in the "shifts" indicate that in platinum complexes **1** and **2** probably also coordinate through the nitrogen and two tellurium atoms. The electronic spectra of diamagnetic **9** and **10** show only one band at 29.8 kK which indicates that the platinum complexes are either square-planar or pyramidal. The band may be due to an $^1A_{1g} \rightarrow {}^1E_g$ transition.[17] On considering the above mentioned spectral data and the fact that the conductance behaviour of platinum complexes **9** and **10** is similar to that of palladium complexes, and that they are monomeric, it seems reasonable to presume that the platinum complexes also have a square-pyramidal structure **D** as proposed for palladium complexes (**7** and **8**).

Preliminary investigations have revealed that the palladium complexes (**7** and **8**) have good activity for the homogeneous catalytic hydrogenation of simple olefins, e.g. cyclohexene, which is like the palladium complexes of (P, N, P) ligands.[6]

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