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Synthesis and spectral studies of platinum(II) and palladium(II) complexes of bis(3-aminopropyl)telluride

Anju Khanna & B L Khandelwal*
Department of Chemistry, Indian Institute of Technology, New Delhi 110 016

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Bis(3-aminopropyl)telluride (**L**) and its complexes with platinum(II) and palladium(II) of the types $PtCl_2L(PhCN)_{1.25}$ (**1**), [PdClL]Cl (**2**) and [PdMeL]Cl (**3**) have been prepared and characterized by elemental analyses, molar conductance measurements, IR and multinuclear NMR (^1H, $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ data. The complexes have square planar geometry around the metal (Pt or Pd) with the (N, Te, N) ligand coordinated in a tridentate mode.

The chemistry of organotellurium compounds has received considerable attention in the recent past due to their potential applications in a wide range of areas such as organic[1-3], inorganic[4-6] and coordination[7,8] chemistry. The fact that the tellurium nuclei (^{125}Te, $I = 1/2$, natural abundance = 6.99%) provides a convenient probe to study the metal-tellurium bond in solution as well as in the solid state, has further facilitated developments in this field.

As a part of our continuing research in the area of hybrid organotellurium ligand complexes of the platinum metals[9-15], we describe herein the synthesis of bis(3-aminopropyl)telluride, a novel tridentate (N, Te, N) ligand and its complexes with platinum(II) and palladium(II). In view of the importance of the organopalladium complexes in carbonylation reactions[16], we also report a methylpalladium complex of the ligand.

Experimental

All the solvents were dried, distilled and degassed before use. Experimental manipulations were carried out under an atmosphere of dry oxygen-free dinitrogen. [PdCl(Me)(COD)] was prepared following the recently described method[9]. The elemental tellurium (Aldrich) and the compounds, 3-chloropropylamine hydrochloride (Fluka) and $(COD)PdCl_2$ (Aldrich) were used as received. IR spectra over the range of 4000-700 cm^{-1} were recorded on a Nicolet 5 DX FT spectrophotometer as nujol mulls. Far IR spectra were recorded on a Perkin-Elmer 1700 X FT instrument as polyethylene pellets. ^1H NMR spectra were obtained on a Jeol FX-100 FT instrument at 99.5 MHz using TMS as an internal standard. $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Brüker AMX 400 FT spectrometer at 126 and 86 MHz using Me_2Te and H_2PtCl_6 as external references, respectively. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Conductance measurement of ~ 1 m*M* solutions were made in appropriate solvents using Metrohm 660 conductometer. Molecular weights wherever possible were determining using Knauer vapour pressure osmometer.

Synthesis of bis(3-aminopropyl)telluride (L)

An alkaline solution of sodium borohydride (0.74 g, 19.5 mmol in 5 cm^3 of 1 *M* NaOH) was added dropwise to a suspension of elemental tellurium powder (1.00 g, 7.8 mmol) in deoxygenated water (10 cm^3) under dinitrogen with constant stirring at refluxing temperature till whole of the tellurium dissolved. The solution turned dark purple indicating the formation of Na_2Te_2. It was further refluxed for 2 h when the solution became colourless indicating the formation of Na_2Te. To this was added 3-chloropropylamine hydrochloride (2.039 g, 15.6 mmol) in deoxygenated water (10 cm^3) dropwise and the solution refluxed for another 1 h. It was cooled and the organic layer extracted into chloroform. The chloroform solution was dried over sodium sulphate under dinitrogen. On removal of excess solvent *in vacuo*, a viscous pale yellow liquid was obtained. It was thoroughly washed with hexane, dried *in vacuo* and stored under dinitrogen.

Yield: 60%; b.p. 180°C; mol. wt (in $CHCl_3$). Found, 220; Calcd. 243.6; IR (nujol, cm^{-1}), 3269 ν(N − H), 1599 δ(N − H), 1164 ν(C − N); far IR (polyethylene cm^{-1}), 474 ν (Te − C), 204 δ (C − Te − C); ^1H NMR ($CDCl_3$), δ 1.33 (s, 2 NH_2, 4H), 1.73-2.02 (m, 2 CH_2, 4H), 2.59-2.81 (m, 2 CH_2 − Te, 2 CH_2 − N, 8H); $^{125}Te\{^1H\}$ NMR ($CHCl_3$), δ 240.3 ppm.

Synthesis of $PtCl_2L.(PhCN)_x$ (1) and $PdCl_2L$ (2)

To a solution of bis(benzonitrile)platinum(II) chloride (0.47 g, 1 mmol) or bis(acetonitrile)palladium(II) chloride (0.26 g, 1 mmol) in CH_2Cl_2 (10 cm^3) cooled in an ice bath was added under dinitrogen atmosphere, the ligand (0.24 g, 1 mmol, in 5 cm^3 CH_2Cl_2) solution with constant stirring. A white (platinum) or yellow (palladium) coloured solid separated out. Stirring was continued for 1 h after which the precipitate was filtered, washed with dichloromethane and dried *in vacuo*.

$PtCl_2$.L. 1.25 PhCN: Yield, 65%; m.p., 172° (d); Anal. [Found: C, 30.2; H, 3.6; Reqd. for $C_6H_{16}N_2Cl_2TePt$. 1.25. C_6H_5CN, C, 29.3; H, 3.6%]; IR (nujol, cm^{-1}), 3240 ν(N – H), 1614 δ(N – H), 1155 ν(C – N); Far IR (polyethylene, cm^{-1}), 465 ν(Te – C), 332 ν(Pt – Cl), 215 δ(C – Te – C); ^{1}H NMR (MeOH-d_4), δ 1.92-2.52 (m, 2 NH_2, 2 CH_2, 8H), 2.64-3.12 (m, 2 CH_2 – N, 2 CH_2 – Te, 8H), 7.50 (bs, Ph); ^{125}Te{^{1}H} NMR (MeOH), δ 370.6 ($^1J_{Pt-Te}$, 884 Hz), 333.4 ($^1J_{Pt-Te}$, 631 Hz); ^{195}Pt{^{1}H} NMR (MeOH), δ 3400; λ_m (MeOH, ohm^{-1} cm^2 mol^{-1}), 81.6.

$PdCl_2$.L: Yield, 75%; m.p., 156° (d); Anal: [Found: C, 16.5; H, 3.4; Reqd. for $C_6H_{16}N_2Cl_2TePd$, C, 17.1; H, 3.8%]; IR (nujol, cm^{-1}), 3200 ν(N – H), 1610 δ(N – H), 1147 ν(C – N), Far IR (polyethylene, cm^{-1}), 444 ν(Te – C), 298 ν(Pd – Cl), 215 δ (C – Te – C); ^{1}H NMR (DMSO-d_6), δ 2.00-2.40 (m, NH_2, CH_2), other peaks merged with DMSO signals; λ_m (DMSO, ohm^{-1} cm^2 mol^{-1}), 48.3.

Synthesis of [*Pd*(*Me*)*L*]*Cl* (**3**)

To a solution of [PdCl(Me)(COD)] (0.26 g, 1 mmol) in CH_2Cl_2 (10 cm^3) cooled in an ice bath was added the ligand (0.24 g, 1 mmol, in 5 cm^3 CH_2Cl_2) solution with constant stirring under dinitrogen atmosphere, when a white solid separated out. It was further stirred for 1 h after which the precipitate was filtered, washed with dichloromethane and dried *in vacuo*.

Yield: 75% m.p., 145° (d); Anal: [Found: C, 20.7; H, 4.4; Reqd. for $C_{17}H_{19}N_2$ ClTePd, C, 20.9; H, 4.9], IR (nujol, cm^{-1}), 3220 ν(N – H); 1605 δ (N – H), 1155 ν(C – N), Far IR (polyethylene, cm^{-1}), 518 ν(Pd – C), 465 ν(Te – C), 211 δ(C – Te – C); ^{1}H NMR (DMSO-d_6), δ 0.51 (s, Me – Pd, 3H), 2.04-2.33 (m, 2 NH_2; 2 CH_2, 8H), other peaks merged with DMSO; ^{125}Te {^{1}H} NMR (DMSO), δ 418.7; λ_m(MeOH, ohm^{-1} cm^2 mol^{-1}), 91.6

Results and discussion

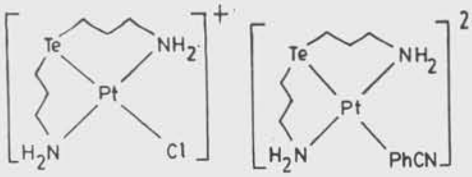
Bis(3-aminopropyl)telluride (*L*), a potentially tridentate (N, Te, N) ligand has been prepared from the reaction between Na_2Te, generated *in situ*, and 3-chloropropylamine hydrochloride. This symmetric telluride is a rather foul smelling liquid, soluble in a variety of solvents, e.g. chloroform, dichloromethane, acetonitrile, benzene etc., but insoluble in hexane and diethylether. It is somewhat unstable and undergoes aerial oxidation resulting in a white insoluble telluroxide, from which the telluride can be regenerated by reduction with hydrazine. The amino protons in its ^{1}H NMR spectrum as confirmed by deuterium exchange, resonate at δ 1.33 ppm. The signals of CH_2 – Te protons merge with those of CH_2 – N protons and appear upfield (δ 2.59-2.81 ppm) as compared to the signals of CH_2 – Cl protons (δ 3.73 ppm) in the precursor, 3-chloropropylamine hydrochloride, probably due to the replacement of an electronegative chlorine by an electropositive tellurium. The ^{125}Te {^{1}H} NMR exhibits a single signal at δ 240.3 ppm which is ~230 upfield compared to $PhTe(CH_2)_3NH_2$[9].

Bis(3-aminopropyl)telluride with Pt(II) and Pd(II) formed **1, 2** and **3** complexes having metal:ligand ratio as 1:1. These complexes are air-stable, almost insoluble in chlorinated solvents like $CHCl_3$, CH_2Cl_2 etc., but soluble in DMSO and methanol. They behave as 1:1 electrolytes in solution. However, their low solubility in suitable organic solvents precluded molecular weight measurements.

In all the three complexes, the amino protons are deshielded by ~0.7 ppm relative to the free ligand and merged with the CH_2(2) protons, which also get deshielded by ~0.3-0.5 ppm. The CH_2 – N and CH_2 – Te protons in **1** appear together, ~0.4 ppm downfield with respect to the corresponding ligand protons. All this data suggest the coordination of both N and Te with the metal atom. In the platinum complex **1**, the phenyl protons of benzonitrile also appear in the spectrum suggesting the role of the solvent in coordination. In the palladium complex **3**, a signal corresponding to methyl (attached to Pd) protons appear 0.5 ppm upfield relative to [PdCl(Me)(COD)]. This is indicative of the position of methyl group *trans* to Te in the complex.

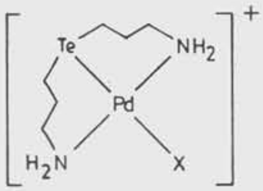
The ^{125}Te{^{1}H} NMR spectrum of **1** shows two peaks, associated with Pt satellites, one of high intensity at δ 370.5 ($^1J_{Pt-Te}$, 884 Hz) and the other of low intensity at δ 336 ppm ($^1J_{Pt-Te}$, 631 Hz). Both the peaks are deshielded with respect to the ligand resonance by 130 and 95 ppm respectively, indicating the coordination of Te to Pt. A comparison of the coupling constant values suggest that the resonance at δ 370.5 ppm corresponding to Te *trans* to Cl[17] (Structure **Ia**) the other could be attributed to the species where Te is *trans* to benzonitrile (Structure **Ib**). The presence of an additional band at 2360 cm^{-1} corresponding to ν(C – N) in its IR spectrum further support the coordinated aromatic nitrile[18].

The ^{195}Pt{^{1}H} NMR spectrum of **1**, however, shows a single peak of low intensity at δ 3400 ppm. The second peak (expected for **Ib** structure) is not clearly observed most probably because of its lower concentration and poor quality of spectrum.



(a) (b)

(I)



(X = Cl , Me)

(II)

The $^{125}Te\{^1H\}$ NMR spectrum of the palladium complex (recorded for **3** only) shows a single signal at δ 418.7 ppm, ~178 ppm downfield with respect to that of the ligand indicating the ligation of Te to Pd. The tentative structure of the complexes **2** and **3** having square planar arrangement of atoms around Pd and the ligand acting in a tridentate mode is depicted in Structure **II**.

The coordination of both N and Te to the metal atom is further supported by the IR data of the complexes which show red shifts in ν(N − H), ν(C − N) and ν(Te − C) by 30-70, 10-15 and 10-30 cm^{-1}, respectively, and blue shifts in δ(N − H) and δ(C − Te − C) by 5-15 and ~10 cm^{-1}, respectively. The presence of one band corresponding to ν(M − Cl) vibration in **1** and **2** is suggestive of the presence of one Cl inside the coordination sphere; the other Cl being outside as obvious from the conductance data. Attempts to grow single crystals for these complexes to undertake X-ray work have been unsuccessful.

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References

1 Gysling H J, *The chemistry of organic selenium and tellurium compounds*, Vol. 1, edited by S Pattai & Z Rappoport (Wiley, New York), 1986.
2 Segi M, Koyama T, Takata Y, Nakajima T & Suga S, *J Am chem Soc*, 111 (1989) 8749
3 Fujiwara S, Ike T S, Okada K, Aoki M, Kambe N & Sonoda N, *Tetrahedron Lett*, 33 (1992) 7021.
4 Jayatirtha H N, Handerson D O, Burger A & Volz M P, *Appl phys Lett*, 62 (1993) 573.
5 Zhang X H, Ma H L, Blanchtiere C & Lucas J, *J non-cryst solids*, 146(1992) 154.
6 Digiulo M, Manno D, Nicotra M C & Re M, *J non-cryst solids*, 155 (1993) 67.
7 Hope E G & Levason W, *Coord chem Rev*, 122 (1993) 109.
8 Gysling H J, *Coord chem Rev*, 42 (1982) 133.
9 Khanna A, Bala A & Khandelwal B L, *J organometal Chem*, 494 (1995) 199.
10 Khalid A, Khandelwal B L, Singh A K, Singh T P & Padmanabhan B, *J coord Chem*, 31 (1994) 19.
11 Srivastava V, Singh A K & Khandelwal B L, *Trans Met Chem*, 17 (1992) 177.
12 Singh A K, Thomas S & Khandelwal B L, *Polyhedron*, 10 (1991) 2693.
13 Khandelwal B L, Singh A K, Srivastava V, Povey D C & Smith G W, *Polyhedron*, 9(1990) 2041.
14 Singh A K, Vinod Srivastava & Khandelwal B L, *Polyhedron*, 9 (1990) 495.
15 Singh A K, Vinod Srivastava & Khandelwal B L, *Polyhedron*, 9 (1990) 851.
16 Rülke R E, Han I M, Elsevier C J, Vrieze K, Van Leeuwen P W N M, Roobeck C F, Zoutberg M C, Wang Y F & Stam C H, *Inorg chim Acta*, 169 (1990) 5.
17 Kemmitt T, Levason W & Webester M, *Inorg Chem*, 28 (1989) 692.
18 Silverstein R M, Bassler G C & Morill T C, *Spectrometric identification of organic compounds*, 5th Edn (John Wiley, New York), 1991.