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Inorganic Chemistry Communications 6 (2003) 1378–1381

INORGANIC CHEMISTRY COMMUNICATIONS

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First example of bimetallic complex of platinum(II) with a hybrid organotellurium ligand [(4-MeOC$_6$H$_4$Te)CH$_2$CH$_2$OCH$_2$CH$_2$CH$_2$ (2-C$_5$H$_4$N)] (L^1) containing 20-membered metallomacrocycle ring: synthesis and crystal structure

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Received 5 June 2003; accepted 28 August 2003

Abstract

1-(4-Methoxyphenyltelluro)-2-[3-(6 methyl-2 pyridyl)propoxy]ethane (**L^1**) and its complexes [MCl$_2$(**L^1**)]$_2$ (M = Pd or Pt) have been synthesized. The single crystal X-ray diffraction of [PtCl$_2$(**L^1**)]$_2 \cdot$2CHCl$_3$ shows a bimetallic complex of platinum(II) containing a 20-membered metallomacrocycle ring, which remains stable in solution as shown by molecular weight and conductance measurements. The Pt–Te and Pt–N bond lengths are 2.5409(3) and 2.087(5) Å, respectively. The protons of CH$_2$ linked to Te show a deshielding $>$ 1 ppm on the formation of the two complexes.

Keywords: Platinum; Complex; 1-(4-Methoxyphenyltelluro)-2-[3-(6 methyl-2 pyridyl)propoxy]-ethane; Hybrid organotellurium ligand; Crystal structure; Synthesis

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Mono and bi-nuclear metal complexes with nitrogen, oxygen, sulfur and phosphorus ligands containing large size chelate ring are not numerous[1–6]. The complexes [Cu$_2$(μ-dppy)$_3$(MeCN)][BF$_4$]$_2$ (where dppy = 2-(diphenylphosphino)pyridine), *trans*-[1,8-bis(diphenylphosphino)-3,6-dioxaoctane-*P,P*′] carbonyl(ethanol) rhodium(I) hexaflurophosphate [2], *trans*-[1,5-bis(diphenylphosphino)-3-oxapentane-*P,P*′]carbonylchlororhodium(I) dimer [2] di-μ-[glutaraldehydebis(dimethylhydrazone)]-bis[dichloropalladium(II)] [3] [{CoCl$_2$Ph$_2$CH$_2$CH$_2$P(O)Ph$_2$}$_2$][4] and dinuclear platinum(II) complex of the dithioether ligand 1,5-bis(*n*-propylthio)-pentane [5] are some examples containing 8 to 16-membered chelate ring. Two well known examples of metallomacrocycles containing telluroether ligands are the polymeric silver(I) complex of MeTe(CH$_2$)$_3$TeMe [6a] and the mononuclear Hg(II) complex of 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene [6b] with 24- and 13-membered rings, respectively. No example containing a macrocycle formed by a hybrid organotellurium ligand has been reported so far for platinum(II). Our interest in (Te$_x$, N$_y$) type hybrid organotellurium ligands [7a] has led us to explore macrocycle containing tellurium and nitrogen donor atoms and we have designed a 20-membered metallomacrocycle ring using the hybrid organotellurium ligand 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy] ethane (**L^1**) and platinum(II) for the first time. Palladium(II) complex of **L^1** appears to be a similar metallomacrocycle. Recently, a Pd(II) complex of a macrocyclic ligand having Te and

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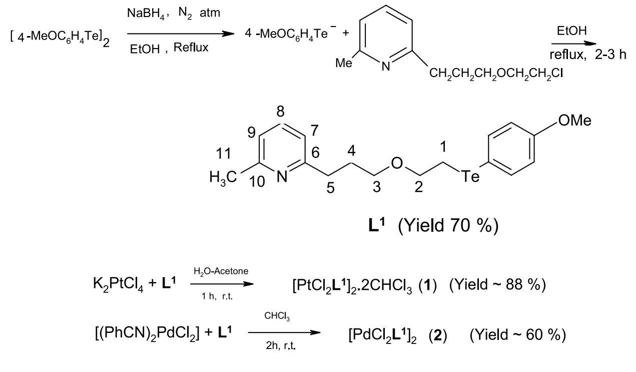
doi:10.1016/j.inoche.2003.08.020

N donor sites has been characterized structurally but the ligand breaks on complexation with Pt(II) [7b].

The ligand $\mathbf{L^1}$ (viscous oil) synthesized by the reactions given in Scheme 1 remains stable under ambient conditions for 3–4 months. The $\mathbf{L^1}$, **1** and **2** have good solubility in chloroform and dichloromethane. In methanol and hexane the solubility of $\mathbf{L^1}$was only moderate. The reactions of $\mathbf{L^1}$ with K_2PtCl_4 and $[(PhCN)_2PdCl_2]$ gave complexes having metal to ligand ratio as 1:1 (Scheme 1), which are stable under ambient conditions. Ligand $\mathbf{L^1}$ and its two complexes are authenticated [18–20] by elemental analyses, ^1H (and $^{13}C\{^1H\}$ also in the case of **1)** NMR spectra. The ^1H NMR spectra of the complexes **1** (single crystals) and **2** were found to be similar and somewhat complex in the alkyl region, indicating that the two complexes have structural similarity. In the spectrum of **1** the two singlets at 7.26–7.28 are due to two chloroform molecules identified in the lattice of its single crystal. The H_1 proton in the spectrum of **1** appears maximum deshielded (~1.14–1.41 ppm) with respect to that of free $\mathbf{L^1}$ as it coordinates through Te. Similarly, deshielding of H_5 with respect to that of free $\mathbf{L^1}$ is also large (~0.85 ppm) because the ligand also coordinates via pyridine nitrogen, which is also reflected in the deshielding of H_{11}. All other CH_2 protons also exhibit deshielding (0.1–0.3 ppm). Some of them become nonequivalent (viz. H_1, H_3 and H_5) also. Pyridine and aryl protons also appear deshielded (0.1–0.2 ppm). The rigidity in the structure of the complex in comparison to that of free ligand is probably responsible for the complexity observed in the proton NMR of the complexes **1** and **2**. On comparing the $^{13}C\{^1H\}$ NMR spectrum of the Pt complex with that of $\mathbf{L^1}$ it is apparent that the C_1 signal undergoes highest deshielding (~10 ppm), which concurs with the proton NMR spectrum. For all other carbon signals the deshielding is less than 4.0 ppm. In the IR spectrum of the Pt-complex the bands at 331 and 346 cm^{-1} may be assigned to symmetric and asymmetric stretching of the *trans* Cl–Pt–Cl system [13], respectively.



Scheme 1.

Table 1
Crystal data and structure refinement for $[PtCl_2L]_2 \cdot 2CHCl_3$

Empirical formula	$C_{19}H_{24}NO_2Cl_5PtTe$
Formula weight	798.33
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system [8]	Triclinic
Space group	*P*-1
a (Å)	8.9977(1)
b (Å)	9.0841(2)
c (Å)	15.2134(3)
α (°)	88.694(1)
β (°)	84.896(1)
γ (°)	81.391(2)
Volume $(Å)^3$	1224.54(4)
Z	2
Density (calculated) (g/cm^3)	2.165
Absorption coefficient (mm^{-1})	7.459
F(000)	752
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.15$
θ range for data collection (°)	2.98–27.48
Index ranges	$-10 \leqslant h \leqslant 11, -11 \leqslant k \leqslant 11, -19 \leqslant l \leqslant 19$
Reflections collected	18001
Independent reflections	5502 [$R_{int} = 0.0513$]
Max. and min. transmission	0.4008 and 0.3170
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5502/0/264
Goodness-of-fit on F^2	1.057
Final *R* indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0383$, $wR_2 = 0.0977$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.1000$
Largest diff. peak and hole (e $Å^{-3}$)	2.160 and −5.019

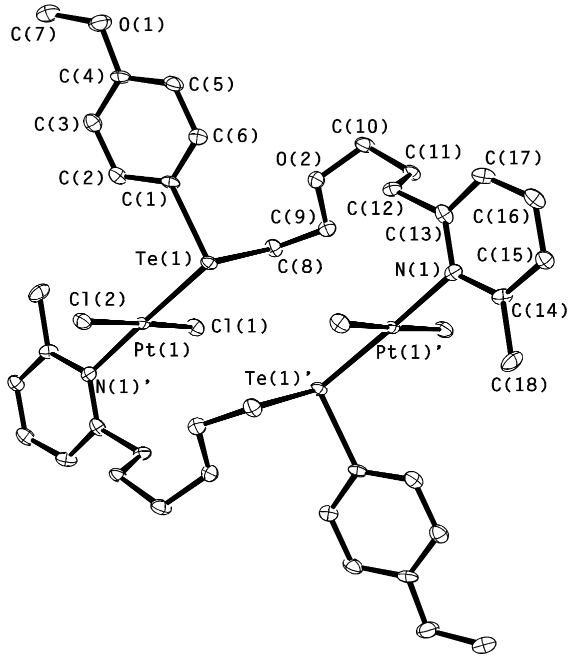


Fig. 1. ORTEP plot of the molecule $[PtCl_2\mathbf{L^1}] \cdot 2CHCl_3$. The atoms are drawn with 50% probability ellipsoids. The $CHCl_3$ molecule and all the H atoms are omitted for clarity.

The band at 480 cm^{-1} may be assigned to Te–C(alkyl) vibrations [14].

X-ray diffraction data were collected on an Enraf Nonius Kappa CCD area detector diffractometer at 120 K with ϕ and ω scans chosen to give a complete asymmetric unit. An absorption correction was applied [9]. The structure was solved by the use of the program DIRDIFF-99 [10] and refined using the WinGX version [11] of SHELXL-97 [12]. Crystallographic data are given with in Table 1. The molecule $[PtCl_2\mathbf{L^1}]_2 \cdot 2CHCl_3$ is shown in Fig. 1 and selected bond distances and bond angles are given in Table 2. Additional material is available from the Cambridge Crystallographic Data Centre (CCDC number 212111). This is the first example of the formation of a 20-membered metallomacrocycle ring by a hybrid organotellurium ligand. The bimetallic Pt complex also remains dimeric in solution as confirmed [19] by molecular weight (determined osmometrically) and conductance values. Platinum has square planar geometry with two Cl (*trans* to each other), Te and N atoms constituting its coordination sphere. The Pt–Cl bond lengths 2.319(1)/2.293(1) Å are consistent with the earlier reports of 2.297 (2) Å for a *trans* Cl–Pt–Cl system [15]. The Te–C(aryl) bond is shorter than that of Te–C(alkyl) as reported earlier [16]. The Pt–Te bond length of 2.5409(3) Å in the present complex is somewhat shorter than the Pt–Te bond length 2.583(2) Å observed for Pt complexes of monodentate tellurides [15]. By contrast, the Pt(1)–N(1) bond length of 2.087(5) Å is a little longer than the literature values 2.005(17) Å [16] and 2.05(1) Å [17], probably due to the *trans* influence of Te. However, crystal of **2** does not diffract and consequently structure of Pd-complex of $\mathbf{L^1}$ could not be confirmed. The molecular weight of **2** indicates its dimeric nature [20].

Table 2
Bond lengths [Å] and angles [°] for $[PtCl_2L]_2 \cdot 2CHCl_3$[a]

Pt(1)–Cl(1)	2.293(1)	Pt(1)–Cl(2)	2.319(1)
Pt(1)–Te(1)	2.5409(3)	Pt(1)–N(1)′	2.087(5)
Pt(1)–Cl(1)	2.293(1)	Pt(1)–Cl(2)	2.319(1)
Te(1)–C(1)	2.135(5)	Te(1)–C(8)	2.156(5)
O(1)–C(4)	1.366(6)	O(2)–C(9)	1.413(6)
O(1)–C(7)	1.437(7)	O(2)–C(10)	1.441(6)
N(1)–C(13)	1.335(7)	N(1)–C(14)	1.355(6)
C(1)–C(6)	1.379(7)	C(1)–C(2)	1.394(7)
C(2)–C(3)	1.405(7)	C(3)–C(4)	1.391(7)
C(4)–C(5)	1.394(8)	C(5)–C(6)	1.383(7)
C(8)–C(9)	1.518(7)	C(10)–C(11)	1.519(7)
C(11)–C(12)	1.534(7)	C(12)–C(13)	1.517(7)
C(13)–C(17)	1.406(7)	C(14)–C(15)	1.397(7)
C(14)–C(18)	1.487(7)	C(15)–C(16)	1.380(7)
C(16)–C(17)	1.368(8)		
Cl(3)–C(19)	1.759(6)	Cl(4)–C(19)	1.755(5)
Cl(5)–C(19)	1.758(5)	N(1)–Pt(1)′	2.087(5)
Cl(1)–Pt(1)–Cl(2)	177.67(4)	Te(1)–Pt(1)–N(1)′	177.2(1)
Cl(1)–Pt(1)–Te(1)	94.98(3)	Cl(2)-Pt(1)–Te(1)	87.34(3)
Cl(1)–Pt(1)–N(1)′	86.7(1)	Cl(2)–Pt(1)–N(1)′	91.0.(1)
C(1)–Te(1)–Pt(1)	103.6(1)	C(8)–Te(1)-Pt(1)	103.9(1)
C(1)–Te(1)–C(8)	98.8(2)	C(13)–N(1)–C(14)	120.3(5)
C(13)–N(1)–Pt(1)′	120.6(3)	C(14)–N(1)–Pt(1)′	118.9(3)
C(2)–C(1)–Te(1)	121.0(4)	C(6)–C(1)–Te(1)	118.3(4)
C(6)–C(1)–C(2)	120.5(4)	C(1)–C(2)–C(3)	119.9(5)
C(2)–C(3)–C(4)	119.1(5)	C(3)–C(4)–C(5)	120.2(5)
C(4)–C(5)–C(6)	120.5(5)	C(1)–C(6)–C(5)	119.8(5)
O(1)–C(4)–C(3)	124.6(5)	O(1)–C(4)–C(5)	115.2(5)
C(4)–O(1)–C(7)	117.8(4)	C(9)–O(2)–C(10)	113.8(4)
C(9)–C(8)–Te(1)	112.4(3)	O(2)–C(9)–C(8)	108.4(4)
O(2)–C(10)–C(11)	113.8(4)	C(10)–C(11)–C(12)	112.5(4)
C(13)–C(12)–C(11)	109.4(4)	N(1)–C(13)–C(12)	119.7(4)
N(1)–C(13)–C(17)	120.9(5)	C(17)–C(13)–C(12)	119.4(5)
N(1)–C(14)–C(15)	120.3(5)	N(1)–C(14)–C(18)	119.0(4)
C(15)–C(14)–C(18)	120.6(4)	C(14)–C(15)–C(16)	119.6(5)
C(17)–C(16)–C(15)	119.4(5)	C(13)–C(17)–C(16)	119.4(5)
Cl(3)–C(19)–Cl(4)	110.4(3)	Cl(3)–C(19)–Cl(5)	110.6(3)
Cl(4)–C(19)–Cl(5)	110.3(3)		

[a] Symmetry position $(-x, -y+2, -z+1)$ given by a prime.

Acknowledgements

M.B.H. thanks the UK Engineering and Physical Sciences Council for support of the X-ray facilities at Southampton. J.E.D. thanks the Natural Sciences and Engineering Research Council of Canada for financial support. AKS and SB thank Department of Atomic Energy (India) for financial support. P.S. is thankful to DGAPA,UNAM for financing sabbatical stay at IITD.

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[18] $\mathbf{L^1}$ (yellow viscous oil): Analyses: Found Te, 30.54%; Calc. for $C_{18}H_{23}NO_2Te$, Te, 30.92%. Yield, 70%; ^{1}H NMR ($CDCl_3$, 25 °C): δ (vs TMS): 1.91–2.01(m, 2H, H_4), 2.52 (s, 3H, H_{11}), 2.71–2.82 (t, 2H, H_1), 2.95–3.00 (t, 2H, H_5), 3.43–3.47 (t, 2H, H_3), 3.66–3.70 (t, 2H, H_2), 3.78 (s, 3H, OCH_3), 6.73–6.76 (d, 2H, *m* to Te), 6.93–6.96 (d, 2H, H_7 and H_9), 7.43–7.48 (t, 1H, H_8), 7.65–7.70 (d, 2H, *o* to Te); ^{13}C {^{1}H} NMR ($CDCl_3$, 25 °C): δ (vs TMS): 8.16 (C_1), 24.14 (C_{11}), 28.91(C_4), 54.78 (OCH_3), 69.48 (C_2), 71.85 (C_3), 99.81(ArTe–C), 114.83 (C_9), 119.37 (ArC *m* to Te), 120.19 (C_7), 136.44 (C_8), 140.62 (ArC *o* to Te), 157.35 (C_{10}), 160.52 (ArC *p* to Te), 161.15 (C_6).

[19] Complex **1:** m.p. (in open capillary) 126 °C; mol. wt. (microcrystalline sample): Found: 1324. 2; Calc.: 1357.3 Λ_M, 10.54 ohm^{-1} cm^2 mol^{-1}. Analyses (microcrystalline sample): Found C, 32.91; H, 3.80; N, 2.00; Te, 18.92 %. Calc. for $[C_{18}H_{23}O_2NTePtCl_2]_2$: C, 31.82; H, 3.38; N, 2.06; Te, 18.80 %. NMR of single crystals: ^{1}H ($CDCl_3$, 25 °C): δ (vs TMS): 2.22–2.30 (m, 2H, H_4), 3.26–3.32 (m, 4H, H_{11} + H_3), 3.55–3.67 (m, 2H, H_5 + H_3), 3.81–3.84 (m, 4H, CH_3O + H_5), 3.90–3.92 (t, 2H, H_2), 4.12–4.14 (m, 1H, H_1), 4.26–4.41 (m, 1H, H_1), 6.87–6.94 (m, 2H, *m* to Te), 7.10–7.13 (m, 2H, H_7 and H_9), 7.26–7.28 (bs, 2H, $CHCl_3$), 7.53–7.61 (m, 1H, H_8), 7.80–7.83 (d, 1H, ArH *o* to Te), 8.00–8.06 (m, 1H ArH *o* to Te); ^{13}C{^{1}H}-NMR($CDCl_3$, 25 °C: δ (vs TMS): 18.90 (C_1), 26.84 (C_{11}), 28.08 (C_4), 55.30 (OCH_3), 66.91 (C_2), 70.63 (C_3), 99.81 (ArTe-C), 115.21 (C_9), 122.70 (ArC *m* to Te), 123.88 (C_7), 138.49 (C_8), 140.60 (ArC *o* to Te), 160.00 (C_{10}), 160.62 (ArC *p* to Te), 161.20 (C_6).

[20] Complex **2**: m.p.(in open capillary) 125 °C(d) ; Mol. wt (microcrystalline sample): Found: 1144.6; Calc.: 1180. Analyses (microcrystalline sample): Found C, 36.24; H, 3.89; N, 2.31%. Calc. for $[C_{18}H_{23}O_2NTePdCl_2]_2$: C, 36.60; H, 3.97; N, 2.37%. NMR (microcrystalline sample): ^{1}H ($CDCl_3$, 25 °C): δ (vs TMS): 2.28 (bm, 2H, H_4), 3.23–3.26 (m, 1H, H_3), 3.30–3.31 (s, 3H, H_{11}) 3.59–3.66 (m, 3H, H_5 + H_3), 3.81–3.83 (m, 4H, CH_3O), 3.86–3.95 (t, 2H, H_2), 4.12–4.26 (m, 1H, H_1), 4.41 (m, 1H, H_1), 6.87–6.94 (m, 2H, *m* to Te), 7.10–7.12 (m, 2H, H_7 and H_9), 7.47–7.61 (m, 1H, H_8), 7.80–7.83 (d, 1H, ArH *o* to Te), 8.00–8.06 (m, 1H ArH *o* to Te).