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### Studies on some Platinum (II) complexes with Ditellura tetraazamacrocycles

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#### ABSTRACT

The synthesis of 10-membered and 12-membered tellurium containing tetraazamacrocyclic complexes of platinum (II) by template condensation of diaryltellurium dichlorides, (aryl = *p*-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, *p*-methoxyphenyl) with ethylenediamine and 1, 3-diaminopropane in the presence of platinum dichloride is reported. The resulting complexes have been subjected to elemental analyses, magnetic measurements, solution electronic absorption, infra-red, and proton magnetic resonance spectral studies. The formation of proposed macrocyclic skeletons and their donor sites have been identified on the basis of spectral studies. Square planer geometry has been assigned to all these platinum complexes.

**Keywords:** 10- and 12-Membered tetraazamacrocycles, Diaryltellurium dichlorides, Ethylenediamine-1, 3-diaminopropane, Platinum (II) complexes.

#### INTRODUCTION

The ligand chemistry of tellurium has developed quite rapidly during the last decade [1-7]. Also, the coordination chemistry of organotellurium ligands containing *hard* donor atoms such as nitrogen and oxygen along with *soft* tellurium is interesting as such ligand framework can provide 'insight' into competitive coordination behavior between the *hard* and *soft* donors towards a metal center [8,9]. In addition, macrocyclic complexes are significant as they are known to act as possible models for biochemically important proteins and enzymes [10,11]. Srivastava *et al* [12] reported the route of synthesis of metal complexes with tellurium containing macrocycles. Also, platinum complexes are widely used in today's anticancer therapy [13-15]. In view of this, and in continuation of our earlier work [16-20] on such macrocyclic complexes, we herein report the synthesis and characterization of platinum (II) complexes with six novel 10- and 12-membered ditellura tetraazamacrocycles, Te<sub>2</sub>N<sub>4</sub>Pt system.

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## MATERIALS AND METHODS

### Materials

The chemicals, tellurium tetrachloride, ethylenediamine and 1, 3-diaminopropane (Aldrich), PtCl<sub>2</sub> (Fluka), phenol, *o*-cresol and anisole (Loba Chemie) were of reagent grade. All the solvents were purified and dried before use by conventional methods.

### Preparation of Diaryltellurium dichlorides

Bis(*p*-hydroxyphenyl), bis(3-methyl-4-hydroxyphenyl) and bis(*p*-methoxyphenyl) tellurium dichlorides were prepared by direct reactions of TeCl<sub>4</sub> with phenol [21], *o*-cresol [22] and anisole [23] respectively as reported in the literature. All the preparations were carried out in an atmosphere of dry N<sub>2</sub>.

### Preparation of Platinum Complexes

The 10- and 12-membered ditellura tetraazamacrocyclic platinum (II) complexes have been synthesized by the template condensation reaction of PtCl<sub>2</sub> with diaryltellurium dichloride and ethylenediamine/1, 3-diaminopropane in 1: 2: 2 molar ratios.

A general method for the preparation of these 1, 6-diaryltellura-2, 5, 7, 10-tetraaza cyclodecane and 1, 7-diaryltellura – 2, 6, 8, 12-tetraazacyclododecane platinum complexes is given below:

A saturated solution of 4.0 mmol of diaryltellurium dichloride (1.536 g, 1.648 g, 1.648 g respectively, for *p*-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, *p*-methoxyphenyl derivatives) in methanol was added slowly and with constant stirring to a methanolic (~ 5 mL) solution of 0.240 g, 4.0 mmol of ethylenediamine or 0.296 g, 4.0 mmol of 1,3-diaminopropane taken in a R.B. flask. A distinct change in color with slight turbidity was observed. The contents were refluxed for 2-3 h followed by an addition of a saturated methanolic solution of 0.532 g, 2.0 mmol of PtCl<sub>2</sub>. This mixture was further refluxed for 3-4 h and concentrated to about one third of its original volume and cooled. This resulted in the separation of a yellow to reddish brown solid, which was filtered, washed with benzene/petroleum ether and dried in a vacuum desiccator over P<sub>4</sub>O<sub>10</sub>.

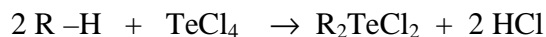
### Physical Measurements

Elemental analyses for C, H, N for these complexes were obtained from SAIF, Panjab University, Chandigarh on a CARLO ERBA Model 1106. Platinum was estimated gravimetrically [24], and tellurium and chlorine contents were determined volumetrically [24]. The magnetic susceptibility data were obtained from National Physical Laboratory, New Delhi on a Gouy's balance (Model Johnson Matthey Alfa Products) using glycerin as a calibrant. The electronic spectra were recorded in dimethylsulphoxide at 25 ± 2°C on a Thermo Spectronic UV-1 Spectrophotometer. The IR spectra (4000-400 cm<sup>-1</sup>) were recorded as KBr pellets on a Perkin Elmer Model 2000 FTIR Spectrometer at SAIF, Panjab University, Chandigarh. <sup>1</sup>H NMR spectra were recorded at Kurukshetra University, Kurukshetra in DMSO – d<sub>6</sub> on BRUKER XWIN – NMR AVANCE 300 operating at 300.13 MHz, using tetramethylsilane as an internal reference.

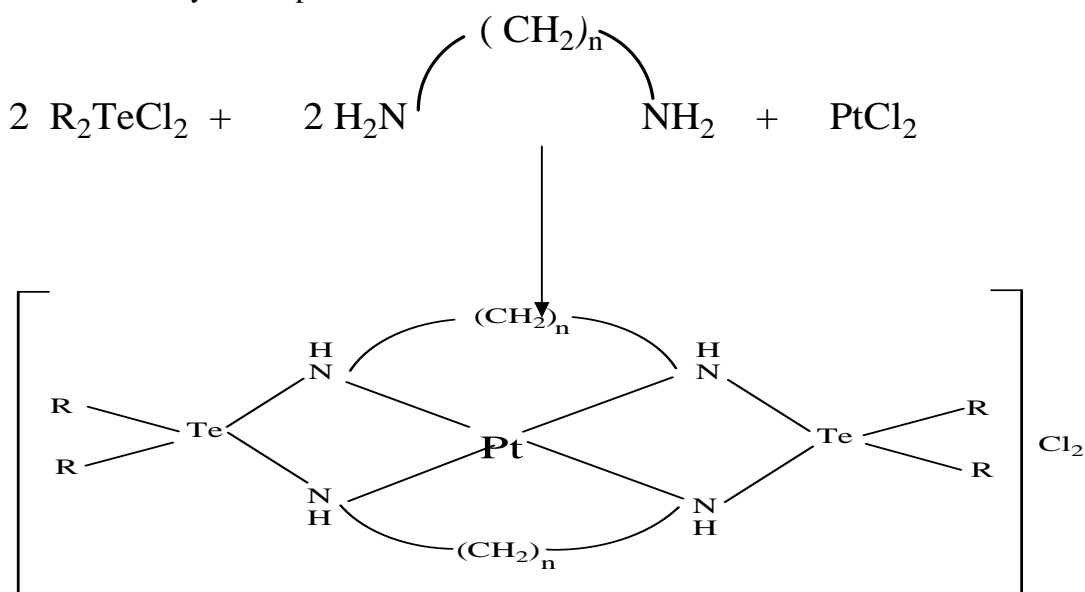
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**RESULTS AND DISCUSSION**

Tellurium tetrachloride when heated with arene, R-H (phenol, *o*- cresol, and anisole) gives diaryltellurium dichlorides [21-23] as per equation:



These diaryltellurium dichlorides and ethylenediamine/1, 3-diaminopropane when refluxed in the presence of PtCl<sub>2</sub>, yield the complexes of 10- and 12-membered tellurium containing tetraazamacrocycles as per Scheme-1



Where,

- L<sup>1</sup>; R = *p*-hydroxyphenyl, n = 2
- L<sup>2</sup>; R = 3-methyl-4-hydroxyphenyl, n = 2
- L<sup>3</sup>; R = *p*-methoxyphenyl, n = 2
- L<sup>4</sup>; R = *p*-hydroxyphenyl, n = 3
- L<sup>5</sup>; R = 3-methyl-4-hydroxyphenyl, n = 3
- L<sup>6</sup>; R = *p*-methoxyphenyl, n = 3

**Scheme 1. Formation of Platinum Complexes**

The analytical data for these platinum complexes are compiled in Table 1, which confirms their formulation as Pt L Cl<sub>2</sub>. These complexes are yellow to reddish brown, air stable crystalline solids which are soluble only in polar donor organic solvents.

***Electronic Absorption Spectra and Magnetic Measurement Studies***

The present platinum (II) complexes show two bands at 23,580 – 25,667 cm<sup>-1</sup> and 27,980 – 30,215 cm<sup>-1</sup> (Table 2) which may be assigned to <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub> and CT bands [25-27], respectively. These transitions in platinum (II) complexes establish square planer coordination

around the metal ion [25-27]. The observed diamagnetic behavior of these complexes further supports their square planer structure.

**Table.1: Analytical data, physical properties and yields for platinum (II) complexes**

Complex	Empirical formula (Formula weight)	Color	mp, °C (dec.)	Yield (%)	Elemental analysis found (calculated) %					
					C	H	N	Cl	Te	M
[PtL <sup>1</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1009.8)	Red brown	216-220	65	33.06 (33.30)	2.94 (3.19)	5.12 (5.55)	6.98 (7.02)	25.10 (25.27)	18.94 (19.32)
[PtL <sup>2</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1065.9)	Light yellow	148-150	63	35.80 (36.06)	3.29 (3.78)	5.02 (5.26)	6.79 (6.65)	23.55 (23.94)	17.93 (18.30)
[PtL <sup>3</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1065.9)	Yellow	158-160	59	35.88 (36.06)	3.59 (3.78)	5.11 (5.26)	6.54 (6.65)	23.82 (23.94)	18.02 (18.30)
[PtL <sup>4</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>30</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1037.8)	Brown red	92-95	67	34.20 (34.72)	3.13 (3.50)	5.17 (5.40)	6.83 (6.74)	24.59 (25.15)	18.50 (18.81)
[PtL <sup>5</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1093.9)	Dark yellow	110-112	64	37.11 (37.33)	3.84 (4.05)	4.83 (5.12)	6.33 (6.48)	23.13 (23.33)	17.58 (17.83)
[PtL <sup>6</sup> ] <sub>2</sub> Cl <sub>2</sub>	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Te <sub>2</sub> Pt (1093.9)	Yellow	177-180	66	37.16 (37.33)	3.96 (4.05)	4.97 (5.12)	6.37 (6.48)	23.12 (23.33)	17.67 (17.83)

**Table.2: Electronic Absorption Spectral data for platinum (II) complexes**

Complex	Absorption, cm <sup>-1</sup>	
	Assignment	
[PtL <sup>1</sup> ] <sub>2</sub> Cl <sub>2</sub>	23580 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	29569 CT
[PtL <sup>2</sup> ] <sub>2</sub> Cl <sub>2</sub>	25400 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	30211 CT
[PtL <sup>3</sup> ] <sub>2</sub> Cl <sub>2</sub>	24406 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	29446 CT
[PtL <sup>4</sup> ] <sub>2</sub> Cl <sub>2</sub>	23795 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	27989 CT
[PtL <sup>5</sup> ] <sub>2</sub> Cl <sub>2</sub>	25667 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	30149 CT
[PtL <sup>6</sup> ] <sub>2</sub> Cl <sub>2</sub>	24875 <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	28816 CT

### IR Spectra

The important IR bands and their assignments are compiled in Table 3. The spectra are quite complex and an attempt has therefore been made to draw the conclusions by comparing the spectra of platinum complexes with those of corresponding constituent diaryltellurium dichlorides and ethylenediamine or 1, 3-diaminopropane.

The platinum (II) macrocycles under study did not show bands characteristic of free NH<sub>2</sub> group, instead the entire complexes exhibit a single sharp absorption band at around 3170-3272 cm<sup>-1</sup> attributed to ν<sub>N-H</sub> vibration. The assignment of this sharp band is based on the fact that macrocyclic ligands which have coordinated secondary amino group have bands in the vicinity [12,16-19, 28-30] of 3200 cm<sup>-1</sup>. This contention finds support [28] from appearance of bands of medium to strong intensity at 1630-1654 cm<sup>-1</sup> and 812-829 cm<sup>-1</sup> assigned as N-H deformation coupled with N-H out of the plane bending vibrations. Bands at ~1180 cm<sup>-1</sup> may be reasonably assigned to C-N stretching vibration [12, 31, 32]. The above observations strongly suggest [12,

28, 31, 32] that proposed macrocyclic framework is formed. The formation of tellurium containing macrocyclic ring is also supported by appearance of new weak intensity bands around 420-410  $\text{cm}^{-1}$  due to Te-N [12,33]. The Pt-N however could not be ascertained due to non-availability of far infrared data.

**Table. 3: Important IR data ( $\text{cm}^{-1}$ ) for platinum (II) complexes**

Complex	$\nu_{\text{N-H}}$	N-H def.	N-H out of the plane bending	$\nu_{\text{C-N}}$
[PtL <sup>1</sup> ]Cl <sub>2</sub>	3190 m	1635 m	827 vs	1172 s
[PtL <sup>2</sup> ]Cl <sub>2</sub>	3170 m	1635 m	813 s	1189 m
[PtL <sup>3</sup> ]Cl <sub>2</sub>	3272 m	1654 m	818 s	1176 s
[PtL <sup>4</sup> ]Cl <sub>2</sub>	3210 m	1640 m	829 s	1172 s
[PtL <sup>5</sup> ]Cl <sub>2</sub>	3220 m	1630 m	812 s	1180 m
[PtL <sup>6</sup> ]Cl <sub>2</sub>	3230 m	1653 m	821 s	1177 vs

*s = strong, m = medium, vs = very strong.*

### <sup>1</sup>H NMR Spectra

The proton chemical shifts for some representative complexes which have sufficient solubility in DMSO -d<sub>6</sub> are presented in Table 4.

The phenyl protons in platinum complexes resonate at slightly upfield side (6.94-7.83  $\delta$  ppm) as compared to parent diaryltellurium dichlorides [21,22,34] due to an increase in electron density at the tellurium atom as a result of replacement of 2 Cl by 2 N atoms. Ethylenediamine, H<sub>2</sub>N-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>2</sub> shows [35] two sets of four equivalent protons each at (a) = 1.19  $\delta$  ppm and (b) = 2.74  $\delta$  ppm. [PtL<sup>1</sup>]Cl<sub>2</sub> does not show any signal attributable to free -NH<sub>2</sub>, instead a broad singlet at 1.80  $\delta$  ppm, which may be assigned to coordinated secondary amino group [36] is observed. This confirms the formation of proposed 10-membered macrocycle skeleton. The deshielding of -NH- protons further suggests the donation of electron density to the Pt atom. The methylene protons in this complex resonate at 2.61  $\delta$  ppm, as a multiplet as reported [12,16,18,30,32] for other tetraazamacrocycles derived from ethylenediamine.

1, 3-diaminopropane, NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>, exhibits [37] protons resonances at 1.15 (4H), 2.76 (4H) and 1.59 (2H)  $\delta$  ppm. due to amino, methylene (adjacent to N) and middle methylene groups, respectively. The [PtL<sup>5</sup>]Cl<sub>2</sub> does not show any signal due to free amino group. Instead, a broad singlet at 1.92  $\delta$  ppm assignable to coordinated secondary amino group [36], confirms the formation of 12-membered tellurium containing tetraazamacrocycles skeleton. The middle methylene protons and those adjacent to N-atoms resonate at 2.11 and 2.88  $\delta$  ppm, respectively. This behavior of platinum complex under study is quite similar to those of other tetraazamacrocycles [12,17,19,38,39] derived from 1, 3-diaminopropane. Further, aryl proton chemical shifts of platinum complexes are similar to tellurium containing tetraazamacrocyclic complexes of other metal - ions [16-20]. This observation indicates the non-involvement of tellurium atoms of the macrocycles in coordination with the platinum atom in these complexes. Thus, <sup>1</sup>H NMR studies on these platinum complexes support the formation of 10- and 12-membered tellurium tetraazamacrocycles and their tetra dentate ligation behavior as predicted by IR studies.

**Table.4:**  $^1\text{H}$  NMR Data ( $\delta$  ppm) for platinum (II) complexes in DMSO –  $d_6$ 

Complex	–NH–	–CH <sub>2</sub> – (middle)	–CH <sub>2</sub> – (adjacent to N)	–CH <sub>3</sub> <sup>*</sup>	Phenyl	–OH
[PtL <sup>1</sup> ]Cl <sub>2</sub>	1.80 <sup>s</sup> (4H)	---	2.61 <sup>m</sup> (8H)	---	7.01 <sup>d</sup> ( <i>J</i> =8.7 Hz), (8H) 7.83 <sup>d</sup> ( <i>J</i> =8.7 Hz), (8H)	6.30 <sup>b</sup> (4H)
[PtL <sup>5</sup> ]Cl <sub>2</sub>	1.92 <sup>s</sup> (4H)	2.11 <sup>m</sup> (4H)	2.88 <sup>m</sup> (8H)	2.50 <sup>s</sup> (12H)	6.94 <sup>d</sup> ( <i>J</i> =8.4 Hz) (4H) 7.56 <sup>d</sup> ( <i>J</i> =8.4 Hz), 7.66 <sup>s</sup> (8H)	8.10 <sup>b</sup> (4H)

\* May be mixed with solvent peak, s = singlet, d = doublet, m = multiplet, b = broad.

Based on analyses, magnetic, electronic, infra-red and proton magnetic resonance spectral studies, a square planer geometry involving four N atoms of tetraazamacrocyclic may be proposed for these platinum complexes.

### CONCLUSION

Platinum (II) macrocyclic complexes have been prepared by condensation of diaryltellurium dichlorides with ethylenediamine / 1, 3-diaminopropane in the presence of platinum dichloride. These complexes have been characterized using elemental analyses, magnetic measurements, electronic absorption, infra-red and proton magnetic resonance spectral techniques. All the platinum complexes have been assigned a square planer stereochemistry on the bases of these studies.

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