



Synthesis, Characterization and Antimicrobial Studies of Nitrogen-Sulphur Donor Tellurium Containing Macrocyclic Complexes of Ni^{II}, Pd^{II} and Pt^{II}

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ABSTRACT

Some new tellurium containing dithiadiazia macrocyclic complexes of Ni^{II}, Pd^{II} and Pt^{II} have been synthesized via template condensation of 2-aminoethanethiol and diaryltellurium dichlorides, R₂TeCl₂ (R = *p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl) in presence of divalent metal chlorides. On the basis of elemental analyses, magnetic moment measurement, ¹HNMR, Infrared and electronic absorption spectroscopy their structures have been elucidated. Based on these studies a distorted octahedral geometry to Ni^{II} complexes while a square planar geometry to Pd^{II} and Pt^{II} complexes have been assigned with the macrocycles coordinating through two S and two N atoms. These metal complexes have also been screened for their antimicrobial activity against some bacteria and fungi.

Keywords: Dithiadiazia macrocycles; 2-Aminoethanethiol; Antimicrobial activity; *p*-Hydroxyphenyl; 3-Methyl-4-hydroxyphenyl

INTRODUCTION

During the last decade, the ligand chemistry of tellurium has developed quite swiftly [1-7]. The macrocyclic complexes have various applications as, in industrial and synthetic process such as catalysis, photochemistry and biological systems [8-10], dyes and pigments [11], models for biologically important proteins and enzymes [12-16]. Palladium and platinum complexes are also biologically important due to their carcinostatic activity [17,18]. Some macrocyclic complexes have received special attention due to their mixed hard-soft donor character and versatile coordination behavior [19] and also due to their pharmacological properties [20].

Template synthetic route for transition metal complexes of dithiadiazia [21] and tellurium containing tetraaza [22-25] macrocycles have been reported. In view of this and in continuation to our earlier research work [26,27], we report the synthesis, characterization and antimicrobial activity of some Ni^{II}, Pd^{II} and Pt^{II} complexes with two new 10-membered tellurium containing dithiadiazia macrocycles (Te₂N₂S₂ system) in the present paper.

EXPERIMENTAL SECTION

Materials and methods

The chemicals used for synthesis and recrystallization were of reagent grade. The solvents, phenol and *o*-cresol were purified and dried by standard methods [28,29] before use. Moisture sensitive reactions are carried out under an inert atmosphere of dry nitrogen. Carbon, hydrogen and nitrogen analyses for these metal complexes were obtained from SAIF, Panjab University; Chandigarh on a Microprocessor based Thermo Scientific (FLASH 2000) CHNS-O Organic Elemental Analyser. Chlorine and tellurium contents were determined volumetrically [30a] while Palladium and Platinum gravimetrically [30b]. Atomic absorption spectrophotometer (ECIL Model No.4129) was used to estimate nickel. IR (4000-400 cm⁻¹) spectra were recorded on Bruker (Alpha), software; OPUS 7.2.139.1294 Spectrometer. ¹H NMR Spectra were obtained from SAIF, Panjab University, Chandigarh on BRUKER AVANCE II 400 NMR spectrometer in DMSO-d₆ using TMS as reference.

Electronic spectra were recorded on a UV-VIS-NIR Spectrophotometer; model UV-3600 Plus (SHIMADZU) in BaSO₄ at 25±2 °C. Magnetic mass susceptibility data were obtained from NPL, New Delhi on a Gouy's balance (model Johnson Matthey Alfa products) using glycerin as a calibrant. Melting points were determined in open capillary tube and are uncorrected.

The antifungal and antibacterial activity of the synthesized macrocyclic metal complexes and their precursors were tested against fungal strains: *Candida albicans* (MTCC 227), *Aspergillus niger* (MTCC 8189) and *Aspergillus fumigatus* (ITCC 4517); Gram +ve bacteria: *Staphylococcus aureus* (MTCC 2901), *Bacillus subtilis* (MTCC 2063) and *Bacillus cereus* (MTCC 7350) and Gram -ve bacteria: *Escherichia coli* (MTCC 1652) and *Salmonella typhi* (ATCC 15499) using tube dilution method [31]. The test and standard compounds were both serially diluted in Double strength nutrient broth- I.P for bacteria and Sabouraud Dextrose Broth –I.P for fungi [32]. Fluconazole (antifungal) and Cefadroxil (antibacterial) were taken as standard drugs.

Preparation of diaryltellurium dichlorides

Bis(3-methyl-4-hydroxyphenyl) and bis(*p*-hydroxyphenyl)tellurium dichlorides were prepared by reactions of tellurium tetrachloride with *o*-cresol [33] and phenol [34] respectively as reported in the literature.

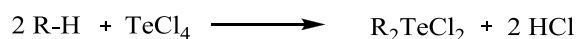
Synthesis of Metal Complexes with 10-Membered Tellurium Dithiadiazia Macrocycles (Te₂N₂ S₂M System)

The metal complexes were synthesized by template condensation of 2-aminoethanthiol and diaryltellurium dichlorides with divalent metal chlorides in 2: 2: 1 molar ratio, as given below:

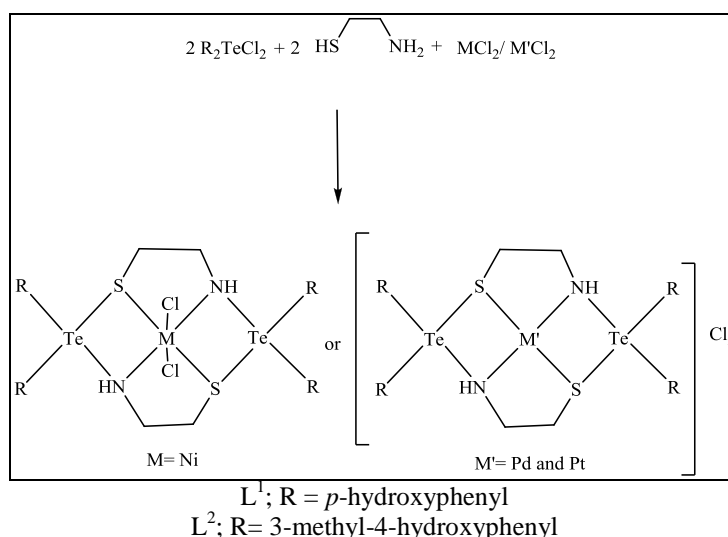
A saturated and hot solution (4.0 mmol) of diaryltellurium dichloride in dry methanol was added dropwise with stirring to a hot methanolic solution of 2-aminoethanthiol (4.0 mmol) taken in a round bottom flask. An immediate change in colour was observed. The contents were refluxed for 4-5 h, followed by the addition of methanolic solution of metal chlorides (2.0 mmol). Again a change in colour was observed. The mixture was then further refluxed for about 7-8 h. The small amount of precipitated solid was filtered off and the filtrate was kept in refrigerator after concentrating it to about one third of original volume to obtain second crop of crystalline product. This was filtered, washed with petroleum ether and dried in vacuum desiccator over P₄O₁₀.

RESULTS AND DISCUSSION

When tellurium tetrachloride is heated with arene, R-H (*o*-cresol and phenol) gives diaryltellurium dichlorides [33,34] as per the equation:



These diaryltellurium dichlorides when heated with 2-aminoethanthiol in presence of PtCl₂/ PdCl₂/ NiCl₂.6H₂O in 2:2:1 molar ratios yield the desired complexes as shown in Scheme-1.



Scheme 1: Formation Ni^{II}, Pd^{II} and Pt^{II} complexes

The analytical data for these complexes, compiled in Table 1 are in good agreement with the proposed stoichiometry. These newly synthesized metal complexes are colored, crystalline solids which are soluble in polar donor organic solvents.

Table 1: Analytical data and physical properties for metal complexes

Complex	Empirical formula (FW)	Color (Yield %)	M.P. °C	Analysis found (calculated), %					
				C	H	N	Cl	Te	M
[NiL ¹ Cl ₂]	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Ni (907.48)	Light brown (78)	110-112	36.88 (37.06)	3.54 (3.33)	2.88 (3.09)	7.74 (7.81)	28.32 (28.12)	6.22 (6.47)
[PdL ¹ Cl ₂]	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Pd (955.20)	Yellowish green (65)	152-154*	35 (35.21)	2.8 (3.17)	2.72 (2.93)	6.99 (7.42)	26.36 (26.72)	10.98 (11.14)
[PtL ¹ Cl ₂]	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Pt (1058.90)	Brown (60)	110-112	32.54 (32.89)	3.34 (3.14)	2.46 (2.65)	6.35 (6.70)	23.8 (24.10)	18.12 (18.42)
[NiL ² Cl ₂]	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Ni (963.58)	Yellowish green (72)	140-143	39.43 (39.89)	3.67 (3.97)	2.69 (2.91)	7.21 (7.36)	26.18 (26.48)	5.88 (6.09)
[PdL ² Cl ₂]	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Pd (1011.31)	Light yellow (65)	175-177*	37.77 (38)	3.55 (3.79)	2.52 (2.77)	6.78 (7.01)	25.03 (25.33)	10.3 (10.52)
[PtL ² Cl ₂]	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Pt (1099.97)	Brown (59)	198-200*	34.74 (34.94)	3.6 (3.48)	2.36 (2.55)	6.31 (6.45)	22.97 (23.20)	17.42 (17.73)

* Decomposition temperature

Infrared spectra

The important IR data along with their assignments are presented in Table 2. The metal complexes under study did not show any band corresponding to free amino group; instead a new single sharp band appeared in the region 3166-3291 cm⁻¹ (sometimes mixed with O-H) assignable to ν_{N-H} vibration [25,35-37], provide an evidence for the skeleton of the macrocyclic moiety and appearance of medium to strong intensity band at 1615-1651 cm⁻¹ and 810-825 cm⁻¹ attributed to N-H deformations coupled with N-H out of plane bending vibrations also support this contention [37]. Medium to weak intensity bands at ~1175 cm⁻¹ and 458-509 cm⁻¹ may be assigned to C-N stretching vibration [24,38,39] and M-N stretching [21,24,40,41] respectively.

Formation of tellurium containing macrocyclic ring [22,25,42] is also supported by appearance of new weak intensity bands at 403- 433 cm⁻¹ due to Te-N vibrations. The spectra of 2-aminoethanethiol show band at around 2400 cm⁻¹ due to S-H stretching vibration while the metal complexes show complete absence of the band in this range which supports deprotonation of Sulphur. Two new medium intensity bands in the region 325-339 cm⁻¹ and 700-759 cm⁻¹ assigned to ν(M-S) and ν(C-S) vibrations respectively [43-45] are consistent with metal-sulfur co-ordination. Further, Nickel complexes show presence of medium to weak intensity bands in the region 295-320 cm⁻¹ assigned to ν(Ni-Cl) vibration [38,46,47].

Table 2: Important IR data (cm-1) for metal complexes

Complex	ν _{N-H}	N-H def.	N-H out of plane bending	ν _{X-N}	ν _{X-S}	ν _{M-N}	ν _{M-S}	ν _{Te-N}
[NiL ¹ Cl ₂]	*	1626 m	825 s	1173 s	700 w	470 w	328 w	403 w
[PdL ¹ Cl ₂]	3291 s	1644 s	822 s	1171 m	754 m	458 w	335 w	420 w
[PtL ¹ Cl ₂]	3166 sb	1615 s	823 s	1181 s	754 m	509 w	325 w	428 w
[NiL ² Cl ₂]	3209 m	1626 m	810 s	1176 m	753 m	475 w	339 w	426 w
[PdL ² Cl ₂]	3227 s	1630 s	811 m	1175 m	759 m	470 w	330 w	432 w
[PtL ² Cl ₂]	3218 m	1651 s	812 s	1176 m	752 m	473 w	334 w	433 w

m= medium, b= broad, s= strong, w= weak, *mixed with ν_{O-H}

Proton magnetic resonance spectra

The proton chemical shifts for the metal complexes in DMSO-d₆ are presented in Table 3. In the metal complexes, the phenyl protons resonate at slightly upfield side (6.68-7.78 δ ppm) as compared to the parent diaryltellurium dichlorides [33,34] due to replacement of 2 chlorine by 2 nitrogen atoms and hence increase in electron density at the tellurium atom. 2-Aminoethanethiol, H₂N-CH₂-CH₂-SH, exhibits proton chemical shifts at 1.45 (2H), 2.50 (1H), 2.75 (2H) and 2.87 (2H) δ ppm due to amino, thiol, methylene (adjacent to N) and methylene (adjacent to S) groups respectively [48,49].

The synthesized metal complexes do not show any signal due to free amino group. Instead, a broad singlet at 1.62-215 δ ppm assignable to coordinated secondary amino group [21-23] confirms the formation of macrocyclic skeleton. All the complexes show presence of triplets (slightly downfield side) at 2.95-3.07 and 3.12-3.19 δ ppm corresponding to (S-CH₂; 4H) and (N-CH₂; 4H) respectively, of the 2-aminoethanethiol moiety.

However, no band could be assigned for free amino or thiol protons, suggesting that proposed macrocyclic complexes are formed by the condensation reaction. Further, the independence of chemical shifts of aryl protons on the metal ions, hints at non-participation of Te atoms of the macrocycle in coordination with the metal ions. Thus, proton NMR studies support the formation of 10-membered tellurium containing dithiadiazia macrocycles and their quadridentate behavior as predicted by IR studies.

Based on elemental analyses, magnetic, infrared, electronic and proton magnetic resonance spectral studies, a distorted octahedral geometry involving two N and two S of the dithiadiazia macrocycle and 2 Cl may be proposed for these metal complexes.

Table 3: ¹H-NMR spectral data (δ ppm) for the metal complexes in dmsO-d6

Complex	Chemical Shift, δ ppm
[NiL ¹ Cl ₂]	1.62 (s, 2H, -NH-), 2.95 (t, 4H, -CH ₂ -S-), 3.15 (t, 4H, -CH ₂ -N-), 6.68 ^d & 7.67 ^d (16H, phenyl), 8.21 (s, 4H, OH)
[PdL ¹ Cl ₂]	1.99 (s, 2H, -NH-), 3.03 (t, 4H, -CH ₂ -S-), 3.15 (t, 4H, -CH ₂ -N-), 6.92 ^d & 7.77 ^d (12H, phenyl), 8.27 (s, 4H, OH)
[PtL ¹ Cl ₂]	2.15 (s, 2H, -NH-), 3.07 (t, 4H, -CH ₂ -S-), 3.19 (t, 4H, -CH ₂ -N-) 6.92 ^d & 7.78 ^d (16H, phenyl), 8.31 (s, 4H, OH)
[NiL ² Cl ₂]	1.85 (s, 2H, -NH-), 2.96 (t, 4H, -CH ₂ -S-), 3.13 (t, 4H, -CH ₂ -N-) 2.49 (s, 12H, phenyl -CH ₃), 6.77 ^d , 7.51 ^d & 7.60 ^s (12H, phenyl), 8.27 (s, 4H, OH)
[PdL ² Cl ₂]	1.98 (s, 2H, -NH-), 2.97 (t, 4H, -CH ₂ -S-), 3.12 (t, 4H, -CH ₂ -N-), 2.50* (s, 12H, phenyl -CH ₃), 6.93 ^d , 7.56 ^d & 7.66 ^s (16H, phenyl), 8.1 (s, 4H, OH)
[PtL ² Cl ₂]	2.04 (s, 2H, -NH-), 3.00 (t, 4H, -CH ₂ -S-), 3.13 (t, 4H, -CH ₂ -N-) 2.52* (s, 12H, phenyl -CH ₃) 6.93 ^d , 7.57 ^d & 7.67 ^s (12H, phenyl), 8.23 (s, 4H, OH)

(s=singlet, d= doublet, t= triplet, m= multiplet); * may be mixed with solvent peak

Magnetic moment and electronic spectra

The electronic absorption and magnetic moment data for the complexes are presented in Table 4. Ni(II) complexes exhibited three spin allowed transitions from ³A_{2g} → ³T_{2g}, ³T_{1g}(F), and ³T_{1g}(P), which appeared 9989–10101 cm⁻¹, 12870–14388 cm⁻¹ and 24390–28640 cm⁻¹, respectively corresponding to an octahedral/distorted octahedral geometry [24,25,50,51]. Also, the ratio of ν₂/ν₁ ≈ 1.4 is indicative [52,53] of an octahedral stereochemistry for Ni(II) complexes. The magnetic moment values of the studied Ni(II) complexes (2.94–3.12 B.M.) also suggest an octahedral stereochemistry for these complexes and rules out the possibility of a square-planar geometry [54,55].

The Pd(II) complexes displayed two bands at 20888–20918 cm⁻¹ and 27777–28499 cm⁻¹, which may be assigned to ¹A_{1g} → ¹A_{2g}, and ¹A_{1g} → ¹B_{1g}. These transitions in the Pd(II) complexes establish a square-planar coordination around palladium [50,56]. This was further supported by their diamagnetic nature.

Table 4: Electronic absorption spectra and magnetic moment data for the metal complexes

Complex	Band Position (cm ⁻¹)	Assignments	Observed magnetic moment, μ _B
[NiL ¹ Cl ₂]	10101	³ A _{2g} → ³ T _{2g} (F)	3.12
	12870	³ A _{2g} → ³ T _{1g} (F)	
	24390	³ A _{2g} → ³ T _{1g} (P)	
[NiL ² Cl ₂]	9989	³ A _{2g} → ³ T _{2g} (F)	2.94
	14388	³ A _{2g} → ³ T _{1g} (F)	
	28640	³ A _{2g} → ³ T _{1g} (P)	
[PdL ¹ Cl ₂]	20888	¹ A _{1g} → ¹ A _{2g}	Diamagnetic
	27777	¹ A _{1g} → ¹ B _{1g}	
[PdL ² Cl ₂]	20918	¹ A _{1g} → ¹ A _{2g}	Diamagnetic
	28499	¹ A _{1g} → ¹ B _{1g}	
[PtL ¹ Cl ₂]	23464	[¹ A _{1g} → ¹ B _{1g}]	Diamagnetic
	32011	CT	
[PtL ² Cl ₂]	21710	¹ A _{1g} → ¹ B _{1g}	Diamagnetic
	33246	CT	

In case of Pt(II) complexes, bands in the region 21710–23464 cm⁻¹ and 32011–33246 cm⁻¹ may be assigned to ¹A_{1g} → ¹B_{1g} and CT bands [56–58] respectively, corresponding to a square planar geometry of these complexes. The observed diamagnetic behavior of these complexes further supports their square planar structure.

Thus based on the analyses and spectral studies, nickel appears to be hexa-coordinated in a distorted octahedral fashion involving 2 N and 2 S of the macrocycle and 2 Cl atom whereas palladium and platinum are tetra-coordinated in a square planar arrangement involving 2 N and 2 S atom of the macrocycle.

Antimicrobial studies

The MIC values of the synthesized complexes against the growth of microorganisms are summarized in table 5 and 6. The determination of the MIC involves a semi quantitative test procedure, which gives an approximation to the least concentration of an antimicrobial needed to prevent microbial growth. It is observed that the complexes used for the experiment exhibited good activities than their precursors towards the inhibition of test fungi and bacteria. Platinum complexes are found to be more powerful bacteriostatic and fungistatic agents

which show very good activity against all the test bacteria (MIC = 3.12 $\mu\text{g ml}^{-1}$) except *S. typhi* and *S. aureus* (MIC= 6.25 $\mu\text{g ml}^{-1}$) and fungi (MIC= 3.12-6.25 $\mu\text{g ml}^{-1}$).

Table 5: Minimum inhibitory concentration (mic) of the complexes against bacteria

Complex	MIC($\mu\text{g ml}^{-1}$)				
	<i>Salmonella typhi</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Bacillus cereus</i>	<i>Staphylococcus aureus</i>
$\text{NH}_2(\text{CH}_2)_2\text{SH}$	12.5	12.5	25	12.5	12.5
R_2TeCl_2 (p-hydroxyphenyl)	25	25	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5	25	25
$[\text{NiL}^1\text{Cl}_2]$	12.5	12.5	12.5	12.5	12.5
$[\text{PdL}^1]\text{Cl}_2$	12.5	6.25	12.5	12.5	12.5
$[\text{PtL}^1]\text{Cl}_2$	6.25	3.12	12.5	3.12	6.25
$[\text{NiL}^2\text{Cl}_2]$	12.5	12.5	12.5	6.25	12.5
$[\text{PdL}^2]\text{Cl}_2$	6.25	3.12	6.25	6.25	6.25
$[\text{PtL}^2]\text{Cl}_2$	3.12	3.12	3.12	3.12	6.25
Cefadroxil	3.12	1.56	3.12	1.56	3.12

Table 6: Minimum inhibitory concentration (mic) of the complexes against fungi

Complex	MIC($\mu\text{g ml}^{-1}$)		
	<i>Aspergillus niger</i>	<i>Aspergillus fumigatus</i>	<i>Candida albicans</i>
$\text{NH}_2(\text{CH}_2)_2\text{SH}$	12.5	12.5	25
R_2TeCl_2 (p-hydroxyphenyl)	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5
$[\text{NiL}^1\text{Cl}_2]$	12.5	12.5	12.5
$[\text{PdL}^1]\text{Cl}_2$	12.5	6.25	12.5
$[\text{PtL}^1]\text{Cl}_2$	3.12	3.12	6.25
$[\text{NiL}^2\text{Cl}_2]$	12.5	12.5	6.25
$[\text{PdL}^2]\text{Cl}_2$	6.25	6.25	3.12
$[\text{PtL}^2]\text{Cl}_2$	3.12	6.25	3.12
Fluconazole	3.12	3.12	1.56

CONCLUSION

Ni(II), Pd(II) and Pt(II) complexes have been prepared by template condensation of diaryltellurium(IV) dichlorides with 2-aminoethanethiol in presence of divalent transition metal chlorides and characterized by elemental analyses, electronic absorption, IR and proton magnetic resonance spectral studies. Based on these studies, a distorted octahedral structure has been assigned to Ni(II) complexes while Pt(II) and Pd(II) complexes are found to have square planar structures. Pt and Pd complexes show very good antimicrobial activity against some pathogenic bacteria and fungi while others are moderately active.

ACKNOWLEDGEMENT

The authors are thankful to M. D. University, Rohtak for providing the necessary facilities. We also thank SAIF, Panjab University Chandigarh for providing the CHN analyses and spectral data.

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