



*J. Serb. Chem. Soc.* 77 (3) 325–333 (2012)  
JSCS–4271

## Studies on nickel(II) and palladium(II) complexes with some tetraazamacrocycles containing tellurium

NITU RATHEE and KRISHAN KUMAR VERMA\*

*Department of Chemistry, Maharshi Dayanand University, Rohtak – 124001, Haryana, India*

(Received 11 December 2010, revised 13 July 2011)

**Abstract:** The synthesis of 10-membered and 12-membered tellurium-containing tetraazamacrocyclic complexes of divalent nickel and palladium by template condensation of diaryltellurium dichlorides, (aryl = *p*-hydroxyphenyl, 4-hydroxy-3-methyl-phenyl, *p*-methoxyphenyl) with 1,2-diaminoethane and 1,3-diaminopropane in the presence of metal dichloride is reported. The resulting complexes were subjected to elemental analyses, magnetic measurements, and electronic absorption, infrared, and proton magnetic resonance spectral studies. The formation of the proposed macrocyclic skeletons and their donor sites were identified based on the spectral studies. A distorted octahedral structure for the nickel complexes and a square-planar structure for the palladium complexes in the solid state are suggested.

**Keywords:** tetraazamacrocycles; diaryltellurium dichlorides; template condensation; ethylenediamine; 1,3-diaminopropane.

### INTRODUCTION

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 the competitive coordination behavior between hard and soft donors towards a metal center.<sup>1,2</sup> Such molecular systems may be important in transition metal catalyzed asymmetric synthesis,<sup>3,4</sup> and as single source precursors in metal–organic chemical vapor deposition processes.<sup>5–7</sup> In addition, macrocycle complexes are significant as they have been found to act as possible models for biochemically important proteins and enzymes.<sup>8–12</sup>

Some recent publications<sup>13–15</sup> show the development of tellurium-containing macrocycles. Srivastava *et al.*<sup>16</sup> reported the route to the synthesis of metal complexes with tellurium-containing macrocycles. In continuation of earlier work,<sup>17,18</sup>

\* Corresponding author. E-mail: vermakk123@rediffmail.com  
doi: 10.2298/JSC101211200R

herein the synthesis and characterization of divalent nickel and palladium complexes with six novel tellurium tetraazamacrocycles ( $\text{Te}_2\text{N}_4$  system) are reported.

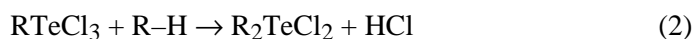
### RESULTS AND DISCUSSION

The formation of diaryltellurium(IV) dichlorides by the reactions of  $\text{TeCl}_4$  with phenol,<sup>19</sup> *o*-cresol<sup>20</sup> and anisole<sup>21</sup> involves two-step reactions. The first step is an electrophilic substitution of the phenyl ring by a trichlorotellurium moiety at the *para* position to the hydroxyl or the methoxy groups. This can be represented by the following equation:

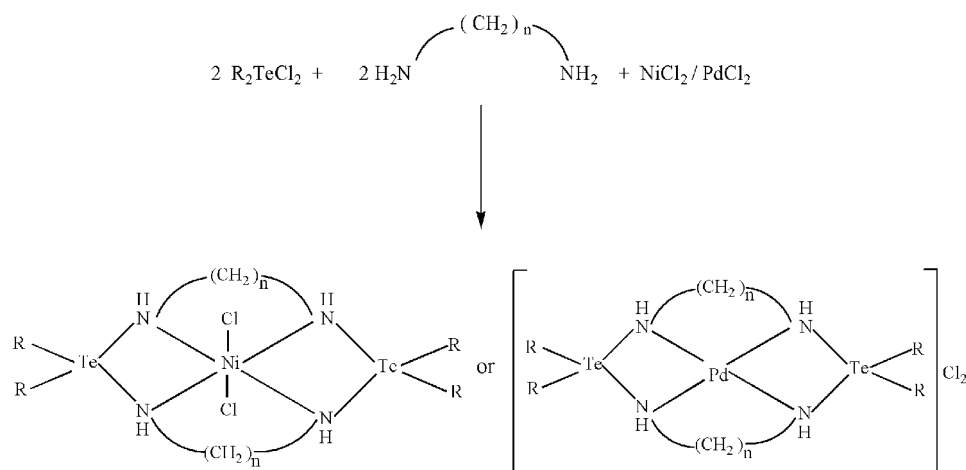


(R = *p*-hydroxyphenyl, *p*-methoxyphenyl or 4-hydroxy-3-methyl-phenyl).

In the second step, these aryltellurium trichlorides further react with phenol/*o*-cresol or anisole to give the diaryltellurium(IV) dichlorides as per the following equation:



These diaryltellurium dichlorides when refluxed with 1,2-diaminoethane or 1,3-diaminopropane in presence of  $\text{NiCl}_2/\text{PdCl}_2$  in 2:2:1 molar ratios yielded 10-membered and 12-membered tetraazamacrocyclic complexes, respectively, as shown in Scheme 1.



where: L<sup>1</sup>; R = *p*-hydroxyphenyl, *n* = 2, L<sup>2</sup>; R = 4-hydroxy-3-methyl-phenyl, *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 = 4-hydroxy-3-methyl-phenyl, *n* = 3 and L<sup>6</sup>; R = *p*-methoxyphenyl, *n* = 3.

Scheme 1. Formation of the Ni(II) and Pd(II) complexes.

These complexes are colored, crystalline solids, fairly stable in dry air and soluble only in polar donor organic solvents. The analytical data and physical properties of the complexes are presented in Table I.

TABLE I. Physical characteristics and analytical results of the metal complexes

Complex	Empirical formula (FW)	Color	M.p. °C	Yield %	Found (Calcd.), %					
					C	H	N	Cl	Te	M
[NiL <sup>1</sup> Cl <sub>2</sub> ]	C <sub>28</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (873.4)	Pink	85– 88	70	38.15 (38.51)	3.37 (3.69)	6.11 (6.41)	8.15 (8.12)	28.81 (29.22)	6.45 (6.51)
[NiL <sup>2</sup> Cl <sub>2</sub> ]	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (929.5)	Red brown	145– 147	81	40.95 (41.35)	3.87 (4.34)	6.11 (6.03)	7.61 (7.63)	26.71 (27.46)	6.18 (6.31)
[NiL <sup>3</sup> Cl <sub>2</sub> ]	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (929.5)	Light brown	157– 160	68	41.30 (41.35)	4.44 (4.34)	6.26 (6.03)	7.59 (7.63)	26.97 (27.46)	6.06 (6.31)
[NiL <sup>4</sup> Cl <sub>2</sub> ]	C <sub>30</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (901.4)	Light orange	150– 152	70	39.52 (39.97)	3.89 (4.03)	5.99 (6.22)	7.85 (7.87)	28.22 (28.31)	6.45 (6.51)
[NiL <sup>5</sup> Cl <sub>2</sub> ]	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (957.5)	Red brown	135– 138	78	42.26 (42.65)	4.33 (4.63)	5.37 (5.85)	7.43 (7.41)	26.10 (26.65)	6.04 (6.13)
[NiL <sup>6</sup> Cl <sub>2</sub> ]	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> NiO <sub>4</sub> Te <sub>2</sub> (957.5)	Light green	177– 180	69	42.37 (42.65)	4.41 (4.63)	5.68 (5.85)	7.27 (7.41)	27.19 (26.65)	5.88 (6.13)
[PdL <sup>1</sup> ]Cl <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (921.1)	Dark brown	155– 158	55	36.12 (36.51)	3.21 (3.50)	5.78 (6.08)	7.65 (7.70)	27.70 (27.71)	11.18 (11.55)
[PdL <sup>2</sup> ]Cl <sub>2</sub>	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (977.2)	Orange	210– 212	68	39.03 (39.33)	3.93 (4.13)	5.24 (5.73)	7.38 (7.26)	26.40 (26.12)	10.62 (10.89)
[PdL <sup>3</sup> ]Cl <sub>2</sub>	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (977.2)	Orange	118– 120	50	39.16 (39.33)	3.98 (4.13)	5.44 (5.73)	7.14 (7.26)	25.94 (26.12)	10.66 (10.89)
[PdL <sup>4</sup> ]Cl <sub>2</sub>	C <sub>30</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (949.2)	Brown	168– 170	75	37.67 (37.96)	3.53 (3.82)	5.46 (5.90)	7.47 (7.41)	26.09 (26.27)	10.83 (11.21)
[PdL <sup>5</sup> ]Cl <sub>2</sub>	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (1005.3)	Dark orange	222– 225	66	40.22 (40.62)	4.11 (4.41)	5.17 (5.57)	7.09 (7.05)	24.90 (25.39)	10.21 (10.59)
[PdL <sup>6</sup> ]Cl <sub>2</sub>	C <sub>34</sub> H <sub>44</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> PdTe <sub>2</sub> (1005.3)	Orange	87– 90	53	40.46 (40.62)	4.23 (4.41)	5.29 (5.57)	6.97 (7.05)	25.11 (25.39)	10.25 (10.59)

### Infrared spectra

The important IR bands and their assignments are reported in Table II. The spectra are quite complex and an attempt has thus been made to draw the conclusions by comparing the spectra of metal complexes with those of corresponding constituent diartellurium dichlorides and diaminoalkanes.

The metal complexes 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 3180–3250 cm<sup>-1</sup> (sometimes overlapped with O–H) attributed to ν<sub>N–H</sub> vibrations. The assignment of this sharp band is based on the fact that macrocyclic ligands that have a coordinated secondary amino group have bands<sup>18,22–24</sup> in the vicinity of 3200 cm<sup>-1</sup>. This contention finds support<sup>22</sup> from appearance of bands of medium to strong intensity at 1627–1655 cm<sup>-1</sup> and 809–827 cm<sup>-1</sup>, assigned as N–H deformation coupled with N–H out-of-plane bending vibrations.

The bands at 1156–1185  $\text{cm}^{-1}$  may reasonably be assigned to C–N stretching vibrations.<sup>18,25,26</sup> The above observation strongly suggests<sup>18,22,25,26</sup> that the proposed macrocyclic framework was formed. The formation of a tellurium-containing macrocyclic ring is supported by appearance of new weak intensity bands around 420–410  $\text{cm}^{-1}$  due to Te–N.<sup>18,27</sup> Evidence for the formation of proposed macrocycles and coordination through N atoms is further supported by new medium to weak intensity bands at around 480–450  $\text{cm}^{-1}$ , assignable to Ni–N stretching.<sup>28</sup> The M–Cl and Pd–N vibrations could not be ascertained due to the non-availability of far-infrared data.

TABLE II. Important IR data ( $\text{cm}^{-1}$ ) for the metal complexes (mixed with moisture band; *s* – strong, *m* – medium, *vs* – very strong)

Complex	$\nu_{\text{N-H}}$	N–H Def.	N–H Out-of-plane bending	$\nu_{\text{C-N}}$
[NiL <sup>1</sup> Cl <sub>2</sub> ]	3180 <i>m</i>	1630 <i>m</i>	825 <i>s</i>	1185 <i>m</i>
[NiL <sup>2</sup> Cl <sub>2</sub> ]	3191 <i>m</i>	1640 <i>m</i>	812 <i>s</i>	1176 <i>m</i>
[NiL <sup>3</sup> Cl <sub>2</sub> ]	3210 <i>m</i>	1649 <i>m</i>	819 <i>vs</i>	1176 <i>vs</i>
[NiL <sup>4</sup> Cl <sub>2</sub> ]	3250 <i>m</i>	1635 <i>m</i>	827 <i>s</i>	1173 <i>s</i>
[NiL <sup>5</sup> Cl <sub>2</sub> ]	3250 <i>m</i>	1630 <i>m</i>	813 <i>s</i>	1178 <i>m</i>
[NiL <sup>6</sup> Cl <sub>2</sub> ]	3215 <i>m</i>	1645 <i>m</i>	822 <i>s</i>	1176 <i>vs</i>
[PdL <sup>1</sup> Cl <sub>2</sub> ]	3210 <i>m</i>	1640 <i>m</i>	824 <i>vs</i>	1172 <i>s</i>
[PdL <sup>2</sup> Cl <sub>2</sub> ]	3180 <i>m</i>	1635 <i>m</i>	809 <i>vs</i>	1173 <i>m</i>
[PdL <sup>3</sup> Cl <sub>2</sub> ]	3230 <i>m</i>	1650 <i>m</i>	816 <i>s</i>	1176 <i>s</i>
[PdL <sup>4</sup> Cl <sub>2</sub> ]	3190 <i>s</i>	1630 <i>m</i>	825 <i>m</i>	1156 <i>vs</i>
[PdL <sup>5</sup> Cl <sub>2</sub> ]	3210 <i>m</i>	1627 <i>m</i>	809 <i>s</i>	1172 <i>m</i>
[PdL <sup>6</sup> Cl <sub>2</sub> ]	3210 <i>m</i>	1655 <i>m</i>	822 <i>s</i>	1177 <i>vs</i>

#### Proton magnetic resonance spectra

The proton chemical shifts for metal complexes with 10-membered and 12-membered tetraazamacrocycles that are soluble in DMSO-*d*<sub>6</sub> are presented in Tables III and IV, respectively.

TABLE III. <sup>1</sup>H-NMR data ( $\delta$  / ppm) for the 10-membered macrocyclic metal complexes in DMSO-*d*<sub>6</sub> (*s* – singlet, *d* – doublet, *m* – multiplet, *b* – broad)

Complex	–NH–	–CH <sub>2</sub> –	–OCH <sub>3</sub>	Phenyl	–OH
[NiL <sup>1</sup> Cl <sub>2</sub> ]	1.45 (4H, <i>s</i> )	2.17 (8H, <i>m</i> )	–	6.93 (8H, <i>d</i> , <i>J</i> = 8.7 Hz) 7.83 (8H, <i>d</i> , <i>J</i> = 8.7 Hz)	9.85 (4H, <i>b</i> )
[PdL <sup>1</sup> Cl <sub>2</sub> ]	1.40 (4H, <i>s</i> )	2.50 (8H, <i>m</i> )	–	6.91 (8H, <i>d</i> , <i>J</i> = 8.7 Hz) 7.74 (8H, <i>d</i> , <i>J</i> = 8.7 Hz)	8.35 (4H, <i>b</i> )
[PdL <sup>3</sup> Cl <sub>2</sub> ]	1.75 (4H, <i>s</i> )	2.50 (8H, <i>m</i> )	3.78 (12H, <i>s</i> )	7.11 (8H, <i>d</i> , <i>J</i> = 8.4 Hz) 7.87 (8H, <i>d</i> , <i>J</i> = 8.4 Hz)	–

The phenyl protons in metal complexes resonated slightly upfield (6.89–7.88 ppm) from those of the parent diaryltellurium dichlorides,<sup>19,20,29</sup> due to an increase in electron density at the tellurium atom as a result of the replacement of 2

Cl by 2 N atoms. Ethylenediamine,  $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2$  shows<sup>30</sup> two sets of four equivalent protons each at 1.19 (a) and 2.74 ppm (b). The metal complexes did not show any signal attributable to free  $-\text{NH}_2$  groups, instead a broad singlet at around 1.74–2.04 ppm, which may be assigned to coordinated secondary amino group,<sup>31</sup> was observed. This confirms the formation of the proposed 10-membered macrocycle skeleton. The deshielding of the  $-\text{NH}-$  protons further suggests the donation of electron density to the metal ions. The methylene protons in these metal complexes resonated at 2.17–2.50 ppm, as a multiplet as reported for other tetraazamacrocycles derived from ethylenediamine.<sup>18,24,26</sup>

TABLE IV.  $^1\text{H-NMR}$  data ( $\delta$  / ppm) for 12-membered macrocyclic metal complexes in  $\text{DMSO-}d_6$  (*s* – singlet, *d* – doublet, *m* – multiplet, *b* – broad)

Complex	$-\text{NH}-$	$-\text{CH}_2-$ (middle)	$-\text{CH}_2-$ (adjacent to N)	$-\text{CH}_3^a$	$-\text{OCH}_3$	Phenyl	$-\text{OH}$
$[\text{NiL}^4\text{Cl}_2]$	1.89 (4H, <i>s</i> )	2.27 (4H, <i>m</i> )	2.86 (8H, <i>m</i> )	–	–	6.89 (8H, <i>d</i> , $J = 8.7$ Hz) 7.77 (8H, <i>d</i> , $J = 8.7$ Hz)	8.63 (4H, <i>b</i> )
$[\text{PdL}^4\text{Cl}_2]$	1.91 (4H, <i>s</i> )	2.50 (4H, <i>m</i> ) <sup>a</sup>	2.88 (8H, <i>m</i> )	–	–	6.92 (8H, <i>d</i> , $J = 8.7$ Hz) 7.74 (8H, <i>d</i> , $J = 8.7$ Hz)	8.14 (4H, <i>b</i> )
$[\text{NiL}^5\text{Cl}_2]$	1.91 (4H, <i>s</i> )	2.06 (4H, <i>m</i> )	2.90 (8H, <i>m</i> )	2.49 (12H, <i>s</i> )	–	6.92 (4H, <i>d</i> , $J = 8.4$ Hz) 7.34 (4H, <i>s</i> ) 7.64 (4H, <i>d</i> , $J = 8.4$ Hz)	8.10 (4H, <i>b</i> )
$[\text{NiL}^6\text{Cl}_2]$	1.78 (4H, <i>s</i> )	2.01 (4H, <i>m</i> )	3.33 (8H, <i>m</i> )	–	3.72 (12H, <i>s</i> )	6.89 (8H, <i>d</i> , $J = 8.7$ Hz) 7.88 (8H, <i>d</i> , $J = 8.7$ Hz)	–

<sup>a</sup>May be overlapped with the solvent peak

1,3-Diaminopropane,  $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , exhibited<sup>32</sup> protons resonances at 1.15 (4H), 2.76 (4H) and 1.59 (2H) ppm due to amino, methylene (adjacent to N) and middle methylene groups, respectively. The metal complexes did not show any signal due to free amino groups. Instead, a broad singlet at 1.78–1.91 ppm, assignable to a coordinated secondary amino group,<sup>31</sup> confirms the formation of a 12-membered tellurium-containing tetraazamacrocycle skeleton. The middle methylene protons and those adjacent to the N-atoms resonate at 2.01–2.50 ppm and 2.86–3.33 ppm, respectively. This behavior of the complexes under study is quite similar to those of other tetraazamacrocycles derived from 1,3-diaminopropane.<sup>18,24,33</sup>

Furthermore, the independence of aryl proton chemical shifts on the nature of metal ions precludes the possibility of a Te–M bond. The proton magnetic resonance studies on these Ni(II) and Pd(II) complexes support the tetradentate nature of these ligands through four N-atoms, as predicted by infrared studies.

#### Electronic absorption spectra and magnetic studies

The electronic absorption and magnetic moment data for the complexes are presented in Table V.

TABLE V. Electronic absorption spectra and magnetic moment data for the metal complexes

Nickel(II) complex	Absorption, cm <sup>-1</sup>			Observed magnetic moment, $\mu_B$
	${}^3A_{2g} \rightarrow {}^3T_{2g}$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
[NiL <sup>1</sup> Cl <sub>2</sub> ]	9994	14500	29740	3.44
[NiL <sup>2</sup> Cl <sub>2</sub> ]	9850	14040	24096	2.99
[NiL <sup>3</sup> Cl <sub>2</sub> ]	10100	13600	25700	3.19
[NiL <sup>4</sup> Cl <sub>2</sub> ]	10700	14525	28668	3.10
[NiL <sup>5</sup> Cl <sub>2</sub> ]	10428	15052	27689	3.00
[NiL <sup>6</sup> Cl <sub>2</sub> ]	9941	13855	26550	2.90
Palladium(II) complex	${}^1A_{1g} \rightarrow {}^1A_{2g}$	${}^1A_{1g} \rightarrow {}^1B_{1g}$		
[PdL <sup>1</sup> Cl <sub>2</sub> ]	24500 <sup>a</sup>	27737		Diamagnetic
[PdL <sup>2</sup> Cl <sub>2</sub> ]	21700	28490		Diamagnetic
[PdL <sup>3</sup> Cl <sub>2</sub> ]	24752 <sup>a</sup>	26815		Diamagnetic
[PdL <sup>4</sup> Cl <sub>2</sub> ]	22026	27600		Diamagnetic
[PdL <sup>5</sup> Cl <sub>2</sub> ]	20829	28800		Diamagnetic
[PdL <sup>6</sup> Cl <sub>2</sub> ]	21100	26900		Diamagnetic

<sup>a</sup> ${}^1A_{1g} \rightarrow {}^1E_g$

The electronic spectral data of all the six Ni(II) complexes exhibited three spin allowed transitions from  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3T_{1g}(F)$ , and  ${}^3T_{1g}(P)$ , which appeared 9850–10700 cm<sup>-1</sup>, 13600–15052 cm<sup>-1</sup> and 24096–28668 cm<sup>-1</sup>, respectively. This spectral pattern corresponds to an octahedral/distorted octahedral geometry<sup>16,34,35</sup> Also, the ratio of  $\nu_2/\nu_1 \approx 1.4$  is indicative<sup>36,37</sup> of an octahedral stereochemistry for all these Ni(II) complexes. The third spin allowed d–d transitions appeared as a broad shoulder on the CT bands and extended up to  $22 \times 10^3$  cm<sup>-1</sup>, as reported<sup>38</sup> for other tetraazamacrocyclic complexes of Ni(II). The magnetic moment values of the studied Ni(II) complexes (2.90–3.44  $\mu_B$ ) also suggest an octahedral stereochemistry for these complexes and rules out the possibility of a square-planar geometry.<sup>39,40</sup> The Pd(II) complexes under study displayed two bands at 20829–24752 cm<sup>-1</sup> and 26900–28800 cm<sup>-1</sup>, which may be assigned to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$ , and  ${}^1A_{1g} \rightarrow {}^1B_{1g}$ . These transitions in the Pd(II) complexes establish a square-planar coordination around palladium.<sup>34,41</sup> This was further supported by their diamagnetic nature.

Based on the above studies, nickel appears to be hexa-coordinated, especially in the solid state, presumably in a distorted octahedral fashion involving four N atoms of the tetraazamacrocycles and two chlorine atoms, whereas palladium is tetra-coordinated in a square-planar arrangement involving four N atoms of the macrocyclic ring. However, the proton magnetic resonance spectral pattern of the nickel complexes also indicated<sup>42</sup> the presence of diamagnetic square-planar configuration. Probably, dissociation of the chloride anions occurs in solution and the nickel (II) complexes form an equilibrium of octahedral (paramagnetic) and square-planar (diamagnetic) species.

#### EXPERIMENTAL

All the preparations were performed under a dry N<sub>2</sub> atmosphere and the solvents were dried and purified by standard methods before use.

##### *Preparation of diaryltellurium dichlorides*

The bis(*p*-hydroxyphenyl), bis(4-hydroxy-3-methyl-phenyl), and bis(*p*-methoxyphenyl) tellurium dichlorides were prepared by the reactions of tellurium tetrachloride with phenol, *o*-cresol, and anisole, respectively.<sup>19-21</sup>

##### *Synthesis of metal complexes with tellurium containing 10-membered and 12-membered tetraazamacrocycles*

The complexes were prepared by template condensation of the diaryltellurium dichlorides with diaminoalkanes in the presence of metal dichlorides in 2:2:1 molar ratio. A general procedure is given below.

A saturated methanolic solution of 4.0 mmol of diaryltellurium dichloride (1.538 g, 1.650 g for bis(*p*-hydroxyphenyl), bis(4-hydroxy-3-methyl-phenyl) and bis(*p*-methoxyphenyl) tellurium dichlorides, respectively) was added to ethylenediamine (0.240 g, 4.0 mmol) or 1,3-diaminopropane (0.296 g, 4.0 mmol) in about 10 mL dry methanol under constant stirring. An immediate change in color was observed along with a little turbidity. The contents were stirred and refluxed for about 3 h. This was followed by addition of a solution of 2.0 mmol of metal dichloride (0.575 g and 0.355 g for NiCl<sub>2</sub>·6H<sub>2</sub>O and PdCl<sub>2</sub>, respectively) in about 10 mL methanol. This resulted in a distinct color change along with slight precipitation of a solid product. The solution was then refluxed for about 6 h and cooled. The small amount of colored solid that separated was filtered off and the filtrate was concentrated to about one third of its original volume and kept in a freezer (0 °C) overnight to obtain a second crop of the crystalline product. This was filtered and washed with benzene and dried in a vacuum desiccator over P<sub>4</sub>O<sub>10</sub>. The purity of these compounds was controlled by TLC using silica gel-G.

##### *Analytical methods and physical measurements*

Carbon, hydrogen, and nitrogen analyses were obtained micro-analytically from the Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh. The tellurium and chlorine contents were determined volumetrically<sup>43</sup> and palladium gravimetrically.<sup>43</sup> Nickel was estimated by atomic absorption spectrophotometry. The IR spectra were recorded in the region 4000–400 cm<sup>-1</sup> at the SAIF on a Perkin Elmer Model 2000 FTIR spectrometer using the KBr pellet technique. The <sup>1</sup>H-NMR spectra were recorded at the Kurukshetra University, Kurukshetra on a Bruker XWIN-NMR Avance 300 operating at 300.13 MHz in DMSO-*d*<sub>6</sub> using tetramethylsilane as an internal reference. The magnetic suscepti-

bility data were obtained from National Physical Laboratory, New Delhi on a Gouy balance (model Johnson Matthey Alfa products) using glycerin as a calibrant. The electronic spectra were recorded in dimethyl sulphoxide on a Thermo Spectronic UV-1 UV-Vis spectrophotometer (Electron Corporation, India).

### CONCLUSIONS

Nickel (II) and palladium (II) complexes have been prepared by condensation of diaryltellurium dichlorides with diaminoalkanes in the presence of metal chlorides. These metal complexes have been characterized using elemental analyses, magnetic measurements, and electronic absorption, infrared and proton magnetic resonance spectral techniques. A distorted octahedral structure for the Ni (II) complexes in the solid state and a square-planar structure for the Pd (II) complexes were assigned based on these studies. The Ni(II) complexes probably form an equilibrium of octahedral and square-planar species in solution.

*Acknowledgments.* The authors are thankful to Maharshi Dayanand University, Rohtak, India for providing the necessary facilities.

### ИЗВОД

#### ИСПИТИВАЊЕ КОМПЛЕКСА НИКЛА(II) И ПАЛАДИЈУМА(II) СА НЕКИМ ТЕРААЗАМАКРОЦИКЛИЧНИМ ЛИГАНДИМА КОЈИ САДРЖЕ ТЕЛУР

NITU RATHEE и KRISHAN KUMAR VERMA

*Department of Chemistry, Maharshi Dayanand University, Rohtak – 124001, Haryana, India*

Темплатном кондензационом реакцијом полазећи од диарилтелур-дихлорида (арил = *p*-хидроксифенил, 4-хидрокси-3-метил-фенил, *p*-метоксифенил) и 1,2-диаминоетана и 1,3-диаминопропана у присуству одговарајућег хлорида метала (Ni(II) и Pd(II)) синтетизовани су комплекси никла(II) и паладијума(II) са десеточланим и дванаесточланим тетраазамакроцикличним лигандима који садрже телур. Синтетисани комплекси су окарактерисани на основу резултата елементарне микроанализе, магнетних мерења, UV-Vis, IR и <sup>1</sup>H-NMR спектара. Грађење макроцикличног скелета са одговарајућим донорским атомима је праћено на основу спектроскопских мерења. На основу ових резултата је нађено да комплекси никла(II) имају дисторговану октаедарску, док комплекси паладијума(II) имају квадратно-планарну геометрију.

(Примљено 11. децембра 2010, ревидирано 13. јула 2011)

### REFERENCES

1. P. G. Jones, M. Carman, R. D. Arellano, *J. Chem. Soc. Dalton Trans.* (1996) 2713
2. C. O. Kienitz, C. Thone, P. G. Jones, *Inorg. Chem.* **35** (1996) 3990
3. Y. Nishibayashi, K. Segawa, J. D. Singh, S. I. Fukuzawa, K. Ohe, S. Uemura, *Organometallics* **15** (1996) 370
4. Y. Nishibayashi, J. D. Singh, Y. Arikawa, S. Uemura, M. Hidai, *J. Organomet. Chem.* **531** (1997) 13
5. Y. Chang, T. Emge, J. G. Brennan, *Inorg. Chem.* **35** (1996) 7339
6. M. L. Steigewald, C. R. Sprinkle, *J. Am. Chem. Soc.* **109** (1987) 7200



7. W. Hirpo, S. Dhingra, A. C. Sutorik, M. G. Kanatzidis, *J. Am. Chem. Soc.* **115** (1993) 1597
8. R. R. Gagne, J. L. Allison, R. S. Gall, C. A. Koval, *J. Am. Chem. Soc.* **99** (1977) 7170
9. J. W. L. Martin, J. H. Johnson, N. F. Curtis, *J. Chem. Soc. Dalton Trans.* (1978) 68
10. M. N. Hughes, *Inorganic Chemistry of Biological Processes*, 2<sup>nd</sup> ed., Wiley, New York, 1981
11. L. Casella, M. Gullotii, L. D. Gioia, M. Monzani, F. Chillemi, *J. Chem. Soc. Dalton Trans.* (1991) 2945
12. S. R. James, D. W. Margerum, *Inorg. Chem.* **19** (1980) 2784
13. W. Levason, S. D. Orchard, G. Reid, *Coord. Chem. Rev.* **225** (2002) 159
14. A. K. Singh, S. Sharma, *Coord. Chem. Rev.* **209** (2000) 49
15. A. Panda, *Coord. Chem. Rev.* **253** (2009) 1947
16. S. Srivastava, A. Kalam, *J. Indian Chem. Soc.* **83** (2006) 563
17. Nitu, K. K. Verma, *J. Chem. Pharm. Res.* **2**(4) (2010) 793
18. Nitu, K. K. Verma, *Int. J. Chem. Sci.*, **9**(1) (2011) 229
19. B. L. Khandelwal, K. Kumar, F. J. Berry, *Inorg. Chim. Acta* **47** (1981) 135
20. B. L. Khandelwal, K. Kumar, K. Raina, *Synth. React. Inorg. Met.-Org. Chem.* **11** (1981) 65
21. J. Bergman, *Tetrahedron* **28** (1972) 3323
22. V. B. Rana, P. Singh, D. P. Singh, M. P. Teotia, *Polyhedron* **1** (1982) 377
23. D. A. House, N. F. Curtis, *J. Am. Chem. Soc.* **86** (1964) 1331
24. M. Shakir, S. P. Varkey, P. S. Hameed, *Polyhedron* **13** (1994) 1355
25. A. K. Panda, A. Panda, S. Sutar, P. Mishra, S. Pradhan, S. Ghos, S. Pany, *J. Indian Chem. Soc.* **86** (2009) 908
26. S. Srivastava, A. Kalam, *Synth. React. Inorg. Met.-Org. Chem.* **34** (2004) 1529
27. Y. D. Kulkarni, S. Srivastava, *Indian J. Chem., A* **24** (1985) 429
28. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part-B, 5<sup>th</sup> ed., Wiley, New York, 1997, p. 15
29. K. Raina, B. L. Khandelwal, *Indian J. Chem., Sect A* **14** (1976) 63
30. *Handbook of Proton NMR Spectra and Data*, Vol. 1, Ed. Asahi Research Centre, Academic Press, New York, p. 47
31. S. C. Menon, H. B. Singh, R. P. Patel, S. K. Kulshreshtha, *J. Chem. Soc. Dalton Trans.* (1996) 1203
32. K. Kawakami, M. Miya-Uchi, T. Tanaka, *J. Inorg. Nucl. Chem.* **33** (1971) 3773
33. M. G. B. Drew, F. S. Esho, S. M. Nelson, *J. Chem. Soc. Dalton Trans.* (1983) 1653
34. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968
35. T. M. Dunn, in *Modern Coordination Chemistry*, J. Lewis, R. G. Wilkins, Eds., Interscience, New York, 1960, p. 230
36. K. Abe, K. Matsufuji, M. Ohba, H. Okawa, *Inorg. Chem.* **41** (2002) 4461
37. M. J. M. Campbell, R. Grzeskowiak, *J. Chem. Soc. A* (1967) 396
38. S. Chandra, K. Gupta, S. Sharma, *Synth. React. Inorg. Met.-Org. Chem.* **31** (2000) 1205
39. M. L. Dianu, A. Kriza, N. Stanica, A. M. Musuc, *J. Serb. Chem. Soc.* **75** (2010) 1515
40. Y. Baran, L. Yilmaz, *Transition Met. Chem.* **26** (2001) 36
41. S. Chandra, S. Verma, P. Meera, *J. Indian Chem. Soc.* **85** (2008) 896
42. A. Dei, *Inorg. Chem.* **18** (1979) 891
43. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, 3<sup>rd</sup> ed., Longman, London, 1975, pp. 266, 324, 511.