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Synthesis and Characterization of Palladium(II) Complexes with Substituted Dihydrobenzoimidazoquinazoline Derivatives

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Abstract

A series of palladium(II) halo complexes of the types **[PdX_2L_2].nH_2O** {n = 0, X = Cl, L = $L^4$and L^6; X = Br, L = L^3, L^4, L^5 and L^6; n = 2, X = Cl, L = $L^3$and L^7, X = Br, L = L^1}; **$Pd_2X_4L_2$** {X = Cl, Br, L = L^2 and L^8} and **$Pd_2X_4L_3$** [X = Cl, L = L^1; X = Br, L = L^7] were prepared where L is 6-R-5,6-dihydrobenzoimidazo quinazoline (R-Diq; where R = phenyl: L^1/furyl: L^2/thiophenyl: L^3/o- or p-hydroxyphenyl: L^4, L^5/o- or p-chlorophenyl: L^6, L^7/dimethylaminophenyl: $L^8$and characterized by elemental analyses, molar conductivity measurements, TGA, infrared, electronic, NMR and mass spectral techniques. Based on these studies, monomeric/dimeric structure with a square planar geometry around the metal ion was proposed for these complexes. Anti-microbial activity for some of the synthesized complexes were investigated.

Keywords: dihydrobenzoimidazoquinazoline, palladium(II), thermal analysis, mass spectra, biological activity.

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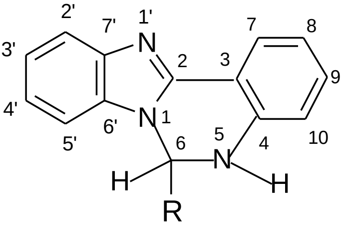
1. Introduction

N-heterocycles like imidazoles, benzimidazoles and quinazolines have the ability to stabilize various oxidation states of transition metals. Complexes of divalent palladium find application in catalysis [1,2], in biochemical reactions [3], in environment related studies [4] , as anticancer drugs [5] and in antimicrobial studies [6].



R-Diq; R = phenyl: L^1/furyl: L^2/thiophenyl: L^3/o- or p-hydroxyphenyl: L^4, L^5/o- or p-chlorophenyl: L^6, L^7/dimethylaminophenyl: L^8

2. Experimental

2.1Reagents

All the reagents were of analar grade. The solvents used were purified according to standard procedure. Palladiumchloride was obtained from Arora Matthey, Kolkata, India. N-heterocycles were prepared according to the published procedures [7 - 10].

2.2Measurements

Microanalyses were obtained from 240B Perkin – Elmer elemental analyzer. IR (nujol mull) spectra were recorded on Shimadzu FTIR 8400s and far-ir spectra were recorded on a Bruker IFS 66 v/S instrument. Electronic spectra were recorded in DMF on Shimadzu UV 3101PC. FAB mass spectra were recorded on a JEOL SX102 Mass Spectrometer at room temperature using Argon/Xenon as the FAB gas and m-nitrobenzyl alcohol as the matrix. NMR spectra were recorded on a Bruker WH 270 MHz and Bruker AMX 400

MHz (both equipped with Aspect 2000 computers) NMR Spectrometers in the solvent DMSO-d_6. Molar conductivity measurements were made on a Systronic conductivity meter 304 - cell type CD-10.

2.3Preparationof 6-R-5,6-dihydrobenzoimidazo[1,2-c] quinazoline derivatives ($L^1$to L^8)

Synthesis and single crystal X – ray structural studies of the ligands L^1, L^2, $L^5$and L^8 were reported earlier [7 - 10]. Similar procedure was adopted for synthesis of other 6-R-5,6-dihydrobenzoimidazo [1,2-c] quinazoline derivatives (L^3, L^4,L^6, andL^7). These were synthesized as follows. A mixture of 2-aminophenylbenzimidazole (0.05mol) in 200 ml alcohol and the corresponding aldehydes (0.05 mol) (thiophenaldehyde/) – hydroxybenzaldehyde /o-orp-chlorobenzaldehyde) were refluxed for 5 hours. The resulting solution was concentrated under reduced pressure to a small volume to obtain a yellow compound. It was filtered and recrystallised from alcohol to get cream/white crystalline compound (yield: 60 -70 %).

2.4Synthesis of the complexes

The N-heterocycles L^1 to L^8 (1 mmol)were reacted with palladium halide (1 mmol) (chloro and bromo) in presence of the respective halo acid in acetone in 1:2 ratio at refluxing temperature to afford complexes of the types**$[PdX_2L_2].nH_2O$** {n = 0, X = Cl, L = L^4 and L^6; X = Br, L = L^3, L^4, L^5 and L^6; ; n = 2, X = Cl, L = L^3 and L^7, X = Br, L = L^1}; **$Pd_2X_4L_2$** {X = Cl, Br, L = L^2 and L^8} and **$Pd_2X_4L_3$** [X = Cl, L = L^1; X = Br, L = L^7] as yellow solids. Yield (45 – 50%). The chloro complex of L^5 could not be isolated. The complexes were insoluble in common organic solvents but soluble in DMF and DMSO in which they behaved as non-electrolytes.

The physical properties and analytical data of the complexes are compiled in table 1.

Table 1: The physical properties and analytical data of Pd(II) complexes of L^1– L^8.

Complex	Colour	D.Pt (^oC)	$\Lambda^\#$	Analytical data (%)*		
				C	H	N
$PdCl_2L^1_{1.5}$	Yellow	295	24	58.78 (57.79)	2.82 (3.64)	10.26 (10.11)
$[PdBr_2L^1_2]\cdot 2H_2O$	Bright yellow	270	25	53.45 (53.56)	2.68 (3.82)	9.39 (9.36)
$PdCl_2L^2$	Pale yellow	248	28	46.12 (46.53)	2.73 (2.82)	9.07 (9.04)
$PdBr_2L^2$	Bright yellow	286	16	50.53 (51.42)	2.72 (3.12)	10.25 (9.95)
$[PdCl_2L^3_2]\cdot 2H_2O$	Yellow	287	21	52.79 (52.72)	3.61 (3.44)	10.61 (10.60)
$PdBr_2L^3_2$	Yellow	303	12	50.44 (49.53)	3.58 (3.00)	9.99 (9.63)
$PdCl_2L^4_2$	Yellow	252	17	59.71 (59.75)	3.78 (3.76)	10.68 (10.45)
$PdBr_2L^4_2$	Yellow	260	22	53.16 (53.80)	3.89 (3.38)	9.67 (9.41)
$PdBr_2L^5_2$	Dark yellow	271	20	53.63 (53.80)	3.14 (3.39)	9.04 (9.41)
$PdCl_2L^6_2$	Yellow	310	16	56.91 (57.13)	3.99 (3.36)	10.42 (9.99)
$PdBr_2L^6_2$	Yellow	302	17	51.86 (51.67)	3.69 (3.04)	9.60 (9.04)
$[PdCl_2L^7_2]\cdot 2H_2O$	Brownish yellow	255	29	54.47 (54.79)	3.52 (3.22)	8.83 (9.58)
$PdBr_2L^7_{1.5}$	Dark yellow	286	31	48.53 (48.83)	2.59 (3.48)	8.86 (8.54)
$PdCl_2L^8$	Dark yellow	312	16	51.98 (51.03)	3.16 (3.89)	10.88 (10.82)
$PdBr_2L^8$	Dark yellow	273	22	43.52 (43.55)	3.33 (3.50)	9.24 (9.29)

$^\#$: $\Omega^{-1}cm^2mol^{-1}$; (in DMF) *: calculated values are in parentheses.

3.1 Infrared spectral studies

IR spectra of the complexes were recorded as nujol mull and the Far-IR spectra were recorded as polyethylene pellets. IR spectra of the complexes (Table 2) were similar to those of the ligands L^1 to L^8 except for minor shifts in the position of the bands implying coordination of the N-heterocycles to the palladium(II) ion [11, 12]. The spectra of the chloro complexes of L^3 and L^7 and the bromo complex of L^1 exhibited peaks at 3406, 3475, 3475 cm^{-1} respectively which can be attributed to the presence of lattice water in the molecule. The $\upsilon_{C=N}$ of benzimidazole and $\upsilon_{C=C}$ of benzimidazole and quinazoline groups were observed in the region 1616 – 1618 cm^{-1} for the complexes as compared to the 1612 – 1620 cm^{-1} exhibited by the ligands. υ_{N-H} of quinazoline ring was observed in the range 3240–3321 cm^{-1}. The complexes exhibited υ_{N-H} in-plane bending vibration in the region 1577–1596 cm^{-1} and υ_{C-N} and δ_{NH} in the range 1330–1346 cm^{-1}. $\upsilon_{C=C}$ and δ_{CH} appeared in the region 1504–1527cm^{-1}. The complexes exhibited in–plane CH deformation and ring breathing modes between 1225 and 1269 cm^{-1} and CH out–of–plane deformation of quinazoline ring vibrations were observed in the range 1141–1189 cm^{-1}. The Far-IR spectra of the complexes revealed the presence of stretching vibrations of the terminal Pd-Cl bond in the range 329-333 cm^{-1}. The stretching frequencies of terminal Pd- Br bond was observed as twin forked peaks in the region 245–282 cm^{-1}. The bridging Pd–Cl stretching vibrations of the chloro complexes of L^2 and L^8were observed at 265 and 294 cm^{-1} and for the bromo complexes at 370 and 366 cm^{-1}.

3.2Electronic spectral studies

The electronic spectra of the quinazoline derivatives and their complexes were recorded in DMF. They displayed bands (Table 2) in the region 27,000 and 38,000 cm^{-1} assignable to the $\pi - \pi^*$ and $n-\pi^*$ transitions of the N-heterocycles. The metal-to-ligand charge transfer transitions were observed in the region 22,200 to 28,000 cm^{-1}. They also exhibited weak bands in the range 19,200 to 22,700 cm^{-1} assignable to the ${}^1B_{1g} \rightarrow {}^1A_{1g}$ transitions which are characteristic of a palladium(II) square planar complex [13 – 16].

Table 2: Electronic spectral data of the complexes (cm^{-1})*.

Complex	Ligand transitions		MLCT	d-d
	n → π*	π → π*	dπ → pπ	$^1B_{1g} \rightarrow A_{1g}$
$Pd_2Cl_4L^1_3$	36603(13182) 34060(14868)	32960(15427)	27473(8196)	22665(306)
$[PdBr_2L^1_2]\cdot 2H_2O$	34083(22004)	33025(22859)	27518(9983)	21777(261)
$PdCl_2L^2$	35236(22078) 33135(21077)	30854(12177)	22442(1152)	20350(241)
$PdBr_2L^2_2$	33944(14446)	32895(14221)	27609(7585)	22371(322)
$[PdCl_2L^3_2]\cdot 2H_2O$	33933(18024)	32960(18249)	27405(6482)	23256(245)
$PdBr_2L^3_2$	33289(27949)	32830(27210)	27518(8369)	22599(354)
$PdCl_2L^4_2$	34200(37054)	32895 (31699)	26853(6914)	21524(666)
$PdBr_2L^4_2$	34153(16135)	33003(14305)	26939(7097)	22163(397)
$PdBr_2L^5_2$	37878(18077) 33829(13941)	32851(13868)	26969(6732) 25075(4228)	22634(434)
$PdCl_2L^6_2$	35236(26163) 34083(27672)	32895(25879) 27042(10189)	22242(2002)	21368(67)
$PdBr_2L^6_2$	35361(26210) 33967(28499)	32895(26567) 26969(14305)	22272(421)	20956(139)
$[PdCl_2L^7_2]\cdot 2H_2O$	34412(13280)	33047(13749)	27996 (8042)	21749(193)
$Pd_2Br_4L^7_3$	37565(14939) 35638(14303)	34341(14959) 33047(15416)	27870(8561)	20408(186)
$PdCl_2L^8$	37908(12786)	32873(13013)	25393(2035) 25075(2598)	19268(121)
$PdBr_2L^8$	37936(13154) 33025(15111)	31566(14166)	26154(2685)	19223(153)

* in DMF

3.3 NMR spectral studies

The proton and ^{13}C NMR spectra of the complexes were recorded in DMSO-d_6. The spectra of the complexes resembled the spectra of the free N-heterocycles except for some minor shifts implying coordination of ligand to the metal ion. Ligand–to-metal σ–donation and metal-to-ligand π–back donation give rise to positive and negative coordination induced shifts (c.i.s.) of the peaks in the NMR spectra of metal complexes [17 – 19].

a) ^{1}HNMR spectral studies

The ^1H NMR spectral patterns of the complexes of L^1 to L^8 were comparable to their respective ligands except for the resonance signals due to the substituted R groups (Tables 3 and 4). The resonance peak due to the NH of the quinazoline ring was observed as a singlet in the range 14.28 – 7.22 ppm and this was found to disappear in the spectra of the deuterated samples confirming it to be the NH proton. The CH of the quinazoline moiety was observed as a singlet in the range 7.60 – 7.00 δ was shifted by -0.41 to 0.34 ppm on complexation. The benzimidazole ring protons H-2′, 3′ 4′ and 5′ were found to resonate as multiplets in the range 8.09 – 6.92 ppm with c.i.s. of -0.59 – 0.36 ppm. The resonance signals of quinazoline ring protons H – 7, 8, 9 and 10 were well resolved and appeared in the region 8.70 – 6.66 δ and were shifted by -0.33 to 0.76 δ on complexation. The phenyl protons of the substituted R group in the Pd(II) complex of L^1 appeared in the range 7.54 – 7.20 δ with the H-3′ proton being most deshielded. The complexes of L^2 and L^3 contain O and S in the substituted R group respectively and the H-4 proton attached to the carbon atom bonded to the O/S were more deshielded and shifted downfield as compared to the H-2″ and 3″. These signals were found in the region 7.68 - 6.38 ppm with c.i.s of 0.03 – 0.88 ppm. The Pd(II) complexes of L^4 and L^5 were found to resonate in the region 7.83 - 6.75 δ and were shifted by 0.12 to 0.71 ppm on complexation. The hydroxyl proton appeared as an intense singlet in the downfield region of 10.20 and 9.66 δ for L^4 and L^5respectively and it was seen between 10.20 – 10.30 δ on complexation. The Pd(II) complexes of L^6 and L^7 exhibited peaks in the range 7.66 – 6.62 δ with positive and negative shifts in the range -0.62 to 0.65 δ. The protons of the complexes of L^8 were found to resonate in the region 7.35 – 6.68 ppm and were shifted by ~ 0.20 δ. The methyl protons in dimethyl amino group appeared around 1.88ppm and underwent a shift of 0.94 ppm on complexation. The ^1H NMR spectral data of the ligands L^1 to L^8 and their complexes are complied in tables 3 and 4.

b) ^{13}C NMR spectral studies

The ^{13}C NMR spectral pattern was similar for the complexes of L^1 – L^8except for the substituted R groups, table 3 and 4the carbon atom C-2 was found to be most deshielded being bonded to two nitrogen atoms and appeared in the downfield region between 154.80 – 140.15 ppm. It exhibited an enormous shift of -5.88 – 7.06 ppm on complexation. C-4 of the heterocycles which is bonded to one nitrogen gave a signal in the downfield region 144.96 – 133.91 δ with c.i.s. of -10.76 to 2.39 ppm. C-6 ′ and 7 ′ of the benzimidazole moiety being bonded to one nitrogen each were shifted down field in the ranges 139.14 – 127.87 δ and 145.26 - 138.66 δ respectively. The C-7 ′ is more deshielded of the two as it is bonded to tertiary nitrogen and appeared around 12 ppm. The benzimidazole carbons C – 3, 7, 8, 9 and 10 gave resonance signals in the range 134.51 - 110.00 δ and exhibited large shifts in the range -8.88 – 8.55 δ on complexation. The benzimidazole ring carbons C - 2′, 3′, 4′ and 5′ are seen in the region 132.44 – 108.51 δ with c.i.s. of -3.18 – 3.42 ppm. The resonance signal of C- 6 was observed in the range 73.77 – 56.02 δ with c.i.s. of -11.09 to 6.94 ppm on complexation.

3.4 Mass spectral studies

Electrospray mass spectrum of the complex $Pd_2Cl_4L^1_3$ was carried out by dissolving the sample in acetonitrile. The ESI capillary was set at 3.5 kV and the cone voltage was 40V. Mass spectrum of the complex has revealed a molecular ion peak at 1248 which may be attributed to the dimeric molecular mass of the complex. Elemental composition of ions and their m/z values coincide with peaks produced by ESI - MS of $Pd_2Cl_4L^1_3$ and thereby support the dimeric nature of the complex [20]. The data are compiled in the table 7.

Table 7: Elemental composition of the ions and their m/z values produced by ESI-MS of $Pd_2Cl_4L^1_3$.

Complex/complex ions	m/z	Complex/complex ions	m/z
$Pd_2Cl_4L_3$	1248	$PdClL_2$	737
$Pd_2Cl_3L_3$	1211	PdL_2	702
$Pd_2Cl_3L_2$	913	PdL(L - CH)	687
$Pd_2Cl_2L_2$	878	PdL	404
Pd_2ClL_2 – 2H	841	L	298

3.5 Thermogravimetric analysis

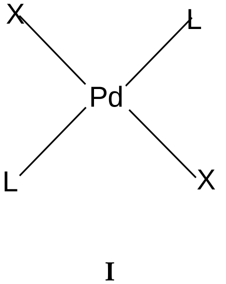
Thermogravimetric analysis was carried out for the complexes $[PdBr_2L^1_2]\cdot 2H_2O$, $[PdCl_2L^3_2]\cdot 2H_2O$ and $[PdCl_2L^7_2]\cdot 2H_2O$ with heating rate of 15 °C/min (Table 8). The water molecules were lost below 100°C which suggest the lattice nature of water. The chloride ions were lost in the range 230 – 285 °C followed by N-heterocycles which decomposed beyond 345 °C.

Table 8: TGA data of the complexes

Complex	TGA data		
	Temp. at which species lost (ºC) / % Weight loss (calculated)		
	H_2O	Cl/Br	L
$[PdBr_2L^1{}_2]\cdot 2H_2O$	72 / 4.4 (4.5)	230 – 269 / 13.2 (13.2)	345 / 50.1 (50.2)
$[PdCl_2L^3{}_2]\cdot 2H_2O$	48 / 4.5 (4.4)	260 – 285 / 13.1(13.0)	364 / 49.9 (50.0)
$[PdCl_2L^7{}_2]\cdot 2H_2O$	74 / 4.0 (4.1)	248 - 269 / 12.2 (12.2)	492 / 50.1(50.0)

4. Stereochemistry

The coordination of the heterocycles to the Pd(II) ions were confirmed by the physical and analytical data, molar conductivity measurements, IR and ^1H and ^{13}C NMR spectral results. The electronic spectral results imply the presence of a square planar geometry around the metal ion. The far IR spectra reveal the presence of terminal and bridging halogens in the complexes with L^2 and L^8. TGA studies show the presence of lattice water in the chloro complexes of L^3 and L^7 and bromo complex of L^1. Mass spectral data reveal the dimeric nature of the complex $\mathbf{Pd_2Cl_4L^1{}_3}$. From the above mentioned studies it can be inferred that the heterocycles behave as monodentate ligands except for chloro complex of L^1 and bromo complex of L^2 wherein they act as a bridging bidentate ligands. A monomeric structure **I** for the $PdX_2L_2.nH_2O$ type of complexes and a binuclear structure **II** and **III** for the $Pd_2X_4L_2$ and $Pd_2X_4L_3$ type of complexes respectively were proposed.

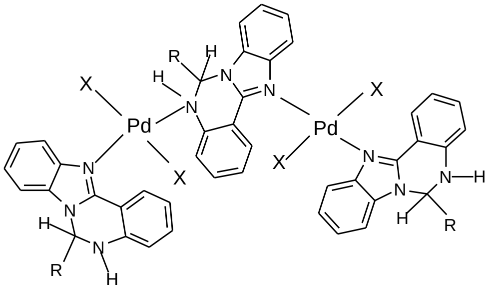


I

PdX_2L_2

X = Cl, L = L^3, , L^6, L^7 ,L^9

X = Br, L = L^1, L^3 – L^6

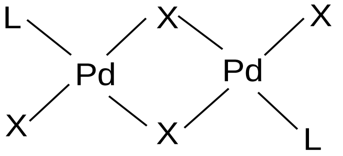


II

$Pd_2X_4L_3$

X = Cl, R = Ph; L^1

X = Br; R = p-chlorophenyl; L^7



III

$Pd_2X_4L_2$

X = Cl, Br; L = L^2, L^8

5. Biological activities

The test solutions containing palladium(II) complexes exhibited good antimicrobial properties at 100 ppm concentration for both strains of bacteria and the fungi *Yeast*. Six of the quinazoline derivatives L^1– $L^5$and L^8 and their chloro complexes of Pd(II) were tested for in vitro growth inhibitory activity against *Bacillus subtilis, E.coli* and *Yeast* by cup - plate method (Table 9). Septran and ampicillin were used as the standard antibiotics for *Bacillus subtilis* and *E.coli* respectively while grissoflumin was used as the standard antifungal agent. The toxicity of the quinazoline derivatives against the microbes was found to be effective at 50 ppm concentration against *Bacillus subtilis* and *Yeast* and 100 ppm against *E.coli*. The Pd(II) complexes were found to be effective against the microbes at

100 ppm concentration. It was observed that the Pd(II) complexes exhibited lower inhibitory activity as compared to those of the quinazoline derivatives. Though the metal complexes and quinazoline derivatives proved to be toxic against microorganisms, the standard drugs were found to be more toxic. The ligands L^2 and L^8 were found to be ineffective against the microbe *E.coli* while ligandsL^5 and L^8 were found to be ineffective against the microbe *Bacillus subtilis*. The palladium complex $PdCl_2(L^8)$ was found to be ineffective against the microbe *Bacillus subtilis*. The ligands and their complexes were moderately effective against *Yeast*.

Table 9: Antimicrobial activity of the quinazoline derivatives and their complexes.*

Compound ‡	*Yeast*	*E.coli*	*Bacillus subtilis*	Pd complex†	*Yeast*	*E.coli*	*Bacillus subtilis*
(L^1)	40	45	46	$PdCl_2(L^1)_{1.5}$	50	50	10
(L^2)	50	Nd	46	$PdCl_2(L^2)_2$	50	57	31
(L^3)	50	75	50	$PdCl_2(L^3)_2.H_2O$	55	57	18
(L^4)	65	76	40	$PdCl_2(L^4)_2$	45	67	18
(L^5)	70	50	Nd	$PdCl_2(L^5)_2$	55	50	18
(L^8)	70	Nd	Nd	$PdCl_2(L^8)$	55	26	Nd
Standard	67	76	76	$PdCl_2$	63	75	47

*: (%inhibition); nd: not detected; ‡: concentration: 50 ppm for *Bacillus subtili*,*Yeast* and 100 ppm for *E.coli*; †: concentration: 100 ppm.

Conclusion

In conclusion, synthesis of chloro and bromo complexes of palladium(II) with dihydrobenzoimidazo quinazoline derivatives L^1 – L^8 were carried out and characterised by various physicochemical techniques. Based on these studies monomeric/dimeric structures with a square planar geometry around the palladium(II) ion have been proposed. Some of the complexes were tested for antimicrobial activity and were found to be moderately active.

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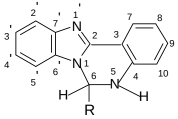
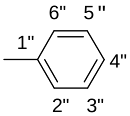
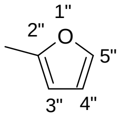
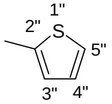
Table 3: ^{1}H NMR spectra of Pd(II) complexes with L^1 –L^5 (in ppm).

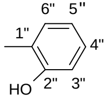
Compound / Complex	Quinazoline						Benzimidazole				R-Group				
	NH	CH	7	8	9	10	2′	3′	4′	5′	2″	3″	4″	5″	6″
(L^1)	7.62s	7.08s	7.95 d	7.27 m	6.82 t	6.86 d	7.65 d	7.25 m	7.18 m	7.10 d	7.29 m	7.33 m	7.15 m	7.33 m	7.29 m
$PdCl_2(L^1)_{1.5}$	14.08s	7.34m	8.12d	7.53m	6.87t	7.04m	7.62m	7.45t	7.28m	7.28m	7.34m	7.54m	7.20t	7.34m	7.34m
c.i.s	6.46	0.26	0.17	0.26	0.05	0.18	-0.03	-0.02	0.10	0.18	0.05	0.21	0.05	0.01	0.05
$PdBr_2(L^1)_2{\cdot}2H_2O$	8.12m	7.32m	8.12m	7.52m	6.92t	7.02d	7.64m	7.32m	7.32m	7.32m	7.32m	7.42m	7.25m	7.42m	7.32m
c.i.s	0.50	0.24	0.17	0.25	0.10	0.16	-0.01	0.07	0.14	0.22	0.03	0.09	0.10	0.09	0.03
(L^2)	7.63s	7.54s	7.94d	7.29t	6.86t	6.94d	7.67d	7.24m	7.22m	7.20m	–	6.34m	6.36m	7.46d	–
$PdCl_2(L^2)$	7.66s	7.60s	8.38m	7.49m	6.99t	7.04d	7.08d	7.50m	7.50m	7.44m	–	6.50m	6.50m	7.49m	–
c.i.s	0.03	0.06	0.44	0.20	0.13	0.10	-0.59	0.26	0.28	0.24	–	0.14	0.20	0.03	–
$PdBr_2(L^2)$	7.63m	7.59m	8.70m	7.59m	7.36t	7.10d	8.09d	7.48m	7.48m	7.48m	–	6.38m	6.40m	7.68m	–
c.i.s	0.03	0.05	0.76	0.30	0.50	0.10	0.42	0.24	0.26	0.28	–	0.04	0.04	0.22	–
(L^3)	7.57 s	7.44 s	7.95 d	7.30 t	6.87 t	6.93 d	7.65 d	7.22m	7.23m	7.19m	–	6.34 d	6.34m	7.47 d	–
$PdCl_2(L^3)_2{\cdot}2H_2O$	14.06s	7.60m	8.34d	7.63m	7.36m	7.36m	7.91d	7.52m	7.52m	7.36m	–	7.22m	7.22m	7.60m	–
c.i.s	6.49	0.16	0.39	0.33	0.49	0.43	0.26	0.30	0.29	0.17	–	0.88	0.88	0.13	–
$PdBr_2(L^3)_2$	7.66m	7.47m	8.18m	7.58m	7.18m	7.10d	7.75t	7.39m	7.47m	7.18m	–	6.93m	6.93m	7.66m	–
c.i.s	0.09	0.03	0.23	0.28	0.31	0.17	0.10	0.17	0.24	-0.01	–	0.59	0.59	0.19	–
(L^4)	7.26 s	7.09 s	7.96 d	7.26 t	6.64 t	6.68 d	7.66 d	7.06 t	6.87 t	6.90 d	10.20 s OH)	7.12m	6.80 t	7.19m	7.17m
$PdCl_2(L^4)_2$	14.28s	7.23m	8.24d	7.64m	6.90m	6.90m	7.97d	7.37m	7.23m	7.37m	10.30s	7.52m	7.23m	7.66m	7.62m
c.i.s	7.02	0.14	0.28	0.38	0.26	0.22	0.31	0.31	0.36	0.47	0.10	0.40	0.43	0.47	0.45
$PdBr_2(L^4)_2$	7.56s	7.28m	8.02m	7.52m	6.82t	6.92m	8.02m	7.24m	6.92m	7.28m	10.25s	7.83d	6.92m	7.43m	7.43m
c.i.s	0.30	0.19	0.06	0.26	0.18	0.24	0.36	0.18	0.05	0.38	0.05	0.71	0.12	0.24	0.26
(L^5)	7.46 s	6.89 s	7.96 d	7.25 t	6.83 t	6.89 d	7.64d	7.16 t	7.06 t	6.96 d	7.02d	6.75 d	9.66 d OH)	6.74 d	7.20 d
$PdBr_2(L^5)_2$	7.22s	7.08m	7.96d	7.13t	6.61t	6.66d	7.64d	7.06m	6.79m	7.06m	7.26m	6.90m	10.20s	6.87m	7.26m
c.i.s	-0.24	0.14	0.00	-0.12	-0.22	-0.23	0.00	-0.10	-0.27	0.10	0.24	0.15	0.54	0.13	0.06











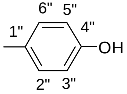
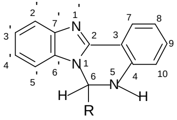
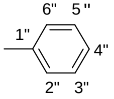
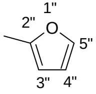


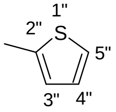
Table 4: ^1H NMR spectra of Pd(II) complexes with L^6 – L^8 (in ppm).

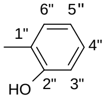
Compound/ Complex	Quinazoline						Benzimidazole				R-Group				
	NH	CH	7	8	9	10	2′	3′	4′	5′	2″	3″	4″	5″	6″
(L^6)	7.56 s	7.41 s	8.02 d	7.38 t	6.85m	6.89m	7.69 d	7.19 t	7.08 t	6.90 m	-	7.58 d	7.26 m	7.24 m	6.97 m
$PdCl_2(L^6)_2$	14.06s	7.20m	8.35d	7.53m	7.20m	7.20m	7.93d	7.38m	7.38m	7.53m	-	7.62m	7.62m	7.62m	7.62m
c.i.s	6.50	-0.21	0.33	0.15	0.35	0.31	0.24	0.19	0.30	0.04	-	0.36	0.38	0.05	0.65
$PdBr_2(L^6)_2$	11.18m	7.00m	7.99m	7.35m	6.88m	7.00m	7.99m	7.16m	7.16m	7.35m	-	7.62m	7.62m	6.62m	7.62m
c.i.s	3.62	-0.41	-0.03	-0.03	0.03	0.11	0.30	-0.03	0.08	0.45	-	0.04	0.36	-0.62	0.65
(L^7)	7.69 s	7.16 s	8.20 d	7.27 m	6.86 t	6.91 d	7.71d	7.22 m	7.14 m	7.25 m	7.42 d	7.31	-	7.31 d	7.42 d
$PdCl_2(L^7)_2\cdot 2H_2O$	14.07s	7.21m	8.35d	7.54m	7.21m	7.21m	7.93d	7.38m	7.38m	7.54m	7.63m	7.63m	-	-7.63m	7.63m
c.i.s	6.34	0.05	0.15	0.27	0.35	0.30	0.23	0.16	0.14	0.29	0.21	0.32	-	0.32	0.21
$PdBr_2(L^7)_{1.5}$	14.07s	7.41m	7.87m	7.87m	7.46m	7.07d	7.87m	7.46m	7.46m	7.46m	7.58m	7.66d	-	7.73d	7.58m
c.i.s	6.38	0.25	-0.33	0.60	0.60	0.16	0.16	0.24	0.32	0.21	0.16	0.35	-	0.42	0.16
(L^8)	7.40 s	6.86 s	7.96 d	7.24 t	6.81m	6.87m	7.62 d	7.06 t	7.02t	7.12 d	7.15 d	6.63 d	2.82 s $(CH_3)_2$	6.63 d	7.15d
$PdCl_2(L^8)$	14.09s	7.20m	7.92m	7.65m	7.20m	7.00m	7.92m	7.30t	7.30t	7.46m	7.34m	6.83m	1.88m	6.83m	7.34m
c.i.s	6.69	0.24	-0.04	0.41	0.39	0.13	0.30	0.24	0.28	0.34	0.19	0.20	-0.94	0.20	0.19
$PdBr_2(L^8)$	14.08m	7.20m	7.93m	7.66m	7.20m	7.00m	7.93m	7.30m	7.30m	7.44m	7.35m	6.83m	1.89m	6.83m	7.35m
c.i.s	6.68	0.34	-0.03	0.42	0.13	0.31	0.24	0.28	-0.02	0.20	0.20	0.20	-0.93	0.20	0.20











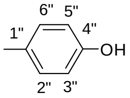
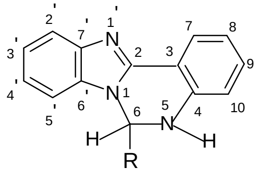
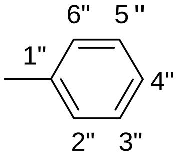
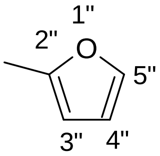


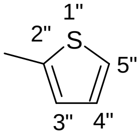
Table 5: ^{13}C NMR for the ligands L^1 to L^4 and their Pd(II) complexes (in ppm).

Compound/ complex	Quinazoline								Benzimidazole						R-Group					
	2	3	4	7	8	9	10	CH	2′	3′	4′	5′	6′	7′	1″	2″	3″	4″	5″	6″
(L^1)	146.80	111.80	143.11	124.59	131.61	118.13	114.76	67.80	118.55	122.13	121.98	110.47	140.31	143.80	132.78	128.88	125.94	128.88	125.94	128.88
$PdCl_2(L^1)_{1.5}$	146.40	111.42	143.51	124.93	133.73	118.23	114.96	67.93	118.55	124.04	124.04	111.02	139.10	144.36	134.52	128.90	126.05	129.26	125.83	128.90
c.i.s	-0.40	-0.38	2.39	0.34	2.12	0.10	0.20	0.13	0.00	1.91	2.06	-0.45	-1.21	0.56	1.74	0.02	0.11	0.38	-0.11	0.02
$PdBr_2(L^1)_2{\cdot}2H_2O$	146.50	111.84	144.12	125.41	133.72	118.57	115.64	68.12	118.82	124.03	124.03	111.43	139.14	144.28	134.36	128.91	126.23	129.58	125.41	128.91
c.i.s	0.10	0.04	1.01	0.82	2.12	0.44	0.88	-0.32	0.27	1.90	2.05	0.96	-1.17	0.48	1.58	0.03	-0.29	0.70	-0.53	0.03
(L^2)	147.20	112.29	143.40	125.14	132.19	118.94	110.62	61.83	119.14	122.93	122.83	108.37	132.89	143.74	-	152.36	110.83	110.83	115.42	-
$PdCl_2(L^2)$	149.65	114.15	140.12	129.07	132.66	119.36	110.83	61.52	119.79	126.35	125.81	109.61	136.08	144.44	-	149.65	112.97	112.37	115.72	-
c.i.s	2.45	1.86	-3.28	3.93	0.47	0.42	0.21	-0.31	0.64	3.42	2.88	1.24	3..9	0.07	-	2.71	2.14	1.54	0.30	
$PdBr_2(L^2)$	146.23	109.22	144.35	127.78	130.83	117.90	111.22	61.15	118.69	123.98	123.98	108.51	133.52	143.88	-	150.90	110.39	110.39	115.60	-
c.i.s	-0.978	-3.07	0.95	2.64	-1.36	-1.04	0.60	-0.68	-0.45	1.05	1.15	0.14	0.63	0.14	-	-1.46	-0.44	-0.44	-0.18	-
(L^3)	149.86	113.71	144.47	125.96	135.98	119.40	114.13	61.89	129.24	126.41	125.22	109.69	131.71	144.77	-	144.35	112.58	104.53	115.79	-
$PdCl_2(L^3)_2{\cdot}2H_2O$	147.05	119.88	139.11	126.47	134.51	124.25	122.63	63.51	132.44	129.03	125.04	119.89	133.25	140.21	-	139.11	121.91	112.23	112.88	
c.i.s	-2.81	6.11	-5.36	0.51	-1.47	5.85	8.55	1.62	3.20	2.62	-0.73	1.02	1.54	-4.56	-	-5.24	9.33	7.70	-2.87	-
$PdBr_2(L^3)_2$	143.98	111.36	133.91	124.06	127.10	118.79	116.12	63.65	126.52	124.67	122.59	110.60	127.87	142.05	-	130.66	115.40	104.53	118.28	-
c.i.s	-5.88	-2.35	-10.76	-1.90	-8.88	-0.61	1.99	1.76	-0.72	1.74	-3.18	0.91	-3.84	-2.52	-	-13.69	-6.51	0.00	2.58	-
(L^4)	147.24	111.45	143.39	124.47	131.39	118.46	114.66	62.96	119.16	122.01	121.84	110.09	132.78	143.75	129.87	154.9 (OH)	125.98	117.72	115.74	126.39
$PdCl_2(L^4)_2$	147.15	112.96	140.33	124.29	132.49	119.32	114.31	56.02	119.99	122.93	122.00	112.37	134.66	139.21	129.22	147..81	124.06	116.70	116.22	126.02
c.i.s	-0.09	1.51	-3.06	-0.81	1.10	0.86	-0.35	6.94	0.38	0.92	0.16	2.28	1.88	-4.54	-0.15	-6.38	-1.92	-1.02	-0.48	-0.37
$PdBr_2(L^4)_2$	154.30	114.06	144.96	124.98	130.96	119.24	114.78	65.48	119.24	123.95	123.95	112.17	135.29	145.26	127.91	155.25	125.64	117.75	116.10	125.36
c.i.s	7.06	2.61	1.57	0.51	-0.43	0.78	0.12	2.52	-0.37	1.94	2.11	2.08	-2.51	1.51	-1.36	0.86	-0.34	0.03	0.36	-1.03









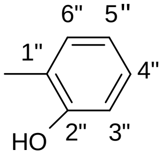


Table6: ^{13}C NMR for the ligands L^5 toL^8 and their Pd(II) complexes (in ppm) .

Compound/ complex	Quinazoline								Benzimidazole						R-Group					
	2	3	4	7	8	9	10	CH	2′	3′	4′	5′	6′	7′	1″	2″	3″	4″	5″	6″
(L^5)	147.11	111.84	143.56	124.62	131.52	118.02	114.70	68.15	118.55	121.99	121.83	110.70	132.90	143.89	130.52	127.78	115.35	159.1 (OH)	115.35	127.78
PdBr2(L^5)^2	143.77	112.82	141.94	125.49	131.82	122.24	122.11	73.77	122.24	123.48	124.34	112.48	133.75	143.77	131.82	129.08	118.32	149.55	118.82	129.08
c.i.s	2.66	-0.04	-1.62	0.87	0.30	-4.22	7.71	5.62	3.09	1.57	2.51	1.78	0.85	-0.13	1.30	1.30	2.97	-9.55	3.47	1.30
(L^6)	147.14	111.30	142.57	124.66	131.72	118.24	114.86	65.65	118.82	122.40	122.24	109.91	132.61	143.09	136.65	131.31	130.87	128.02	127.83	130.65
PdCl$_2$(L^6)2	146.00	112.35	138.69	122.62	129.05	121.90	119.83	56.01	121.90	123.11	123.11	112.35	132.66	140.16	134.40	129.05	126.32	124.50	124.50	126.32
c.i.s	-1.14	1.05	-3.88	-1.64	-2.67	3.66	4.97	-9.64	3.08	0.71	0.87	2.44	0.05	-3.83	-2.25	-2.26	-4.55	-3.52	-3.33	-3.83
PdBr$_2$(L^6)$_2$	148.80	110.00	136.20	121.9	131.80	119.00	115.20	64.00	119.00	121.60	121.60	108.80	134.20	139.90	135.20	131.00	126.20	122.40	122.40	126.20
c.i.s	1.66	-1.3	-6.37	-2.39	0.08	0.76	0.34	-1.65	0.18	-0.80	-0.64	-1.11	1.59	-4.09	-1.45	-0.31	-4.67	-5.62	-5.42	-3.95
(L^7)	143.94	111.97	139.40	124.75	132.82	118.40	114.94	67.12	118.79	122.32	122.19	110.43	133.59	142.86	131.73	128.83	127.83	146.85	127.93	128.83
PdCl$_2$(L^7)$_2$·2H$_2$O	140.15	112.36	138.66	124.52	132.67	121.89	119.81	56.03	121.89	123.13	122.61	112.36	134.40	138.66	134.40	129.05	126.35	146.83	126.35	129.05
c.i.s	-3.79	0.39	-0.74	-0.23	-0.15	3.49	4.87	-11.09	3.10	0.81	0.42	1.93	0.81	-4.22	2.67	0.22	-1.48	0.08	-1.48	0.22
PdBr$_2$(L^7)$_{1.5}$	144.00	112.00	137.62	127.54	134.23	118.73	115.35	67.31	118.73	125.58	125.22	112.00	134.88	144.00	130.30	129.06	128.11	146.00	128.11	129.06
c.i.s	0.06	0.03	-1.78	2.79	1.41	0.33	0.41	0.19	0.06	3.26	3.03	1.57	1.29	1.12	-1.43	0.23	0.28	-0.85	0.28	0.23
(L^8)	147.15	110.58	143.61	127.25	131.39	117.88	114.66	68.23	118.46	121.86	121.71	111.88	132.90	143.48	124.57	127.07	111.68	150.75	111.88	127.07
PdCl$_2$(L^8)	145.5	110.89	144.34	130.96	133.34	118.65	118.22	66.92	119.15	123.76	123.61	111.79	134.62	144.40	125.36	127.75	115.60	147.00	115.60	126.96
c.i.s	-1.66	0.30	0.73	3.71	1.95	0.77	3.56	-1.31	0.69	1.90	1.90	-0.09	1.70	11.92	0.79	0.68	3.92	-3.75	3.92	-0.11
PdBr$_2$(L^8)	145.5	110.30	143.5	130.66	131.94	117.74	115.45	66.53	117.93	123.68	122.33	110.93	133.40	144.29	124.59	127.50	114.85	146.14	114.85	126.74
c.i.s	-1.66	-0.28	-0.11	3.41	0.55	-0.14	0.79	-1.70	-0.53	1.82	0.62	-0.95	0.48	11.81	0.02	0.43	3.17	-4.61	2.97	-0.33