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Synthesis and Characterization of Palladium(II) Complexes with Substituted Dihydrobenzoimidazo Quinazoline 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^2, L^4 and L^5; X = Br, L = L^2; n = 1, X = Cl, L = L^1 and L^3} and $Pd_2X_4L_3$ [X = Br, L = L^1, L^3, L^4 and L^5] were prepared where L is 6-R-5,6-dihydrobenzoimidazo quinazoline (R-Diq; where R = ethyl: **L^1/** n or i-propyl: **L^2, L^3/** n or i-butyl: **L^4, L^5**) and characterized by elemental analyses, 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 all the complexes. Some of the complexes were investigated for anti-microbial activity.

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

1. Introduction

N-heterocycles like imidazoles, benzimidazoles and quinazolines have the ability to stabilize various oxidation states of metals belonging to the first and second row transition series.

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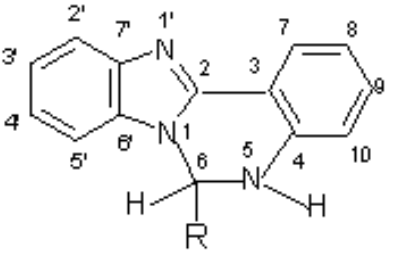
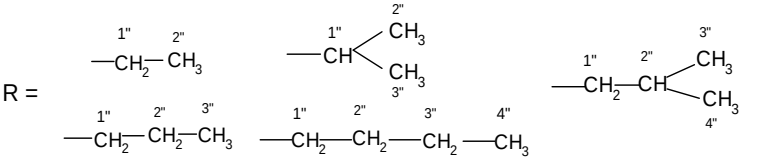
Quinazolines are an important class of N-heterocycles and are widely recognized for their medicinal applications. The quinazoline moiety is an important part of many natural alkaloids [1] and some natural substituted quinazolines exhibit intrinsic hypertensive, diuretic and uterotonic properties [2]. They also exhibit various biological activities like antiallergenic, antibacterial and antihelminthic [3]. Some of the compounds have been evaluated as cellular mitosis inhibitors [4], [5].These compounds are found to be useful in several areas like anticorrosion agents, as optical materials and as fluorescent tags in DNA sequencing [6-9]. Palladium(II) being a d^8 metal ion usually exhibits square planar geometry but reports of trigonal bipyramidal geometry are also available.

Complexes of divalent palladium find applications in catalysis [10], [11], biochemical reactions [12], environmental studies [13] and as anticancer drugs [14]. In view of the importance of quinazoline derivatives and palladium complexes, a series of such complexes with substituted quinazoline derivatives (**I**) have been synthesized and characterized.



I



R-Diq; R = ethyl: L^1/ n or i-propyl: L^2, L^3/ n or i-butyl: L^4, L^5

2. Experimental

All the reagents were of analar grade. The solvents used were purified according to standard procedure. Palladium chloride was obtained from Arora Matthey, Kolkata, India. Palladium bromide and N-heterocycles were prepared according to the published procedures [15] – [18].

Microanalyses were obtained from 240B Perkin – Elmer elemental analyzer. IR (nujol mull) spectra were recorded on Shimadzu FTIR 8400s spectrometer and far-IR spectra were recorded on a Bruker IFS 66 v/S instrument. Electronic spectra of complexes in DMF were recorded on Shimadzu UV 3101PC spectrophotometer. 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 and ESI-MS was recorded using Micromass Quattro II triple quadrupole mass spectrometer. NMR spectra of the compounds in DMSO-d_6 were recorded on a Bruker WH 270 MHz and Bruker AMX 400 MHz spectrometers (both equipped with Aspect 2000 computers). Molar conductivity measurements were made on a Systronic conductivity meter 304 - cell type CD-10.

2.1 Synthesis

2.1.1 6-R-5,6-dihydrobenzoimidazo[1,2-c]quinazoline derivatives (L^1, L^3 - L^5)

Synthesis and characterisation of L^2 was reported earlier [17]. 6-R-5,6-dihydrobenzimidazo[1,2-c]quinazoline derivatives (L^1, L^3 - L^5) were synthesized as follows. A mixture of 2-aminophenylbenz imidazole (0.05 mol) in 200 ml alcohol and the corresponding aldehyde (0.05 mol; L^1, propionaldehyde/ L^3, i-butyraldehyde/ L^4, n-valeraldehyde or L^5, i-valeraldehyde) was 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%.

2.1.2 $[PdX_2L_2]\cdot H_2O$ & $Pd_2X_4L_3$

Palladium halide (chloride and bromide) was reacted with quinazoline derivatives L^1 to L^5 in acetone in 1:1 mole ratio to produce complexes of the types $[PdX_2L_2]\cdot H_2O$ {n = 0, X = Cl, L = L^2, L^4, L^5, X = Br, L = L^2 and L^4; n = 1, X = Cl, L = L^1 and L^3} and $Pd_2X_4L_3$ [X = Br, L = L^1, L^3 and L^5]. These complexes were filtered, washed with acetone, water and dried in vacuum. Yield 65%.

3. Results and Discussion

The complexes were partially soluble in common organic solvents but completely soluble in DMF and DMSO in which they behaved as non-electrolytes. The analytical and physical data of the complexes are given in Table 1. The infrared spectra of the complexes exhibited peaks similar to those of the uncoordinated N-heterocycles L^1 to L^5 except for minor shifts implying the coordination of the ligands to palladium(II) ion [19], [20]. The spectra of I and V exhibited peaks at 3476 and 3452 cm^{-1} respectively assignable to υ_{O-H} of lattice water. Spectra of L^1 to L^5 revealed $\upsilon_{C=N}$ of benzimidazole and $\upsilon_{C=C}$ of benzimidazole and quinazoline moieties in the region 1616 – 1618 cm^{-1} and these complexes were shifted by 2 - 6 cm^{-1} on complexation. The spectra of these complexes I to X exhibited υ_{N-H} in-plane bending vibration around 1581 cm^{-1} and υ_{C-N} and δ_{NH} in the region 1331 – 1342 cm^{-1}. A peak due to CH out-of-plane deformation of quinazoline ring vibration was observed in the range 1157 – 1161 cm^{-1}. CH out-of-plane bending vibrations exhibited a peak in the range 850 - 858 cm^{-1}. Skeletal vibrational frequency of quinazoline moiety was observed in the region 655 – 670 cm^{-1}. The far-IR spectra of the complexes revealed the presence of Pd – X (Cl or Br) bond in the complexes. The spectra of the chloro complexes of L^1 – L^5 had a strong peak in the range 330 – 334 cm^{-1} assignable to the terminal υ_{Pd-Cl} [21] and bromo complexes had exhibited a forked peak in the region 249 – 282 cm^{-1} attributed to the terminal υ_{Pd-Br}.

Table 1. Physical and analytical data of the complexes

Complex	Colour	Molecular formula	D.Pt (°C)	Λ#	Analytical data* C	H	N
I	Pale yellow	$PdCl_2C_{32}H_{32}N_6O$	292	13	54.43 (55.38)	4.31 (4.65)	11.25 (12.11)
II	Dark yellow	$Pd_2Br_4C_{48}H_{45}N_9$	224	25	46.00 (45.03)	3.82 (3.54)	10.11 (9.85)
III	Yellow	$PdCl_2C_{34}H_{34}N_6$	278	28	57.05 (58.00)	3.73 (4.89)	11.64 (11.94)
IV	Dark yellow	$PdBr_2C_{34}H_{34}N_6$	218	26	51.04 (51.50)	4.20 (4.32)	10.67 (10.60)
V	Yellow	$PdCl_2C_{34}H_{36}N_6O$	304	21	56.66 (56.56)	4.74 (5.02)	11.80 (11.64)
VI	Dark yellow	$Pd_2Br_4C_{51}H_{51}N_9$	262	22	47.03 (46.32)	3.90 (3.88)	9.90 (9.53)
VII	Dark yellow	$PdCl_2C_{36}H_{38}N_6$	283	20	58.16 (59.07)	5.75 (5.23)	11.37 (11.48)
VIII	Pale yellow	$PdBr_2C_{36}H_{38}N_6$	228	16	52.88 (52.67)	4.23 (4.67)	10.61 (10.24)
IX	Yellow	$PdCl_2C_{36}H_{38}N_6$	294	26	59.01 (59.07)	4.92 (5.23)	11.92 (11.48)
X	Dark yellow	$Pd_2Br_4C_{54}H_{57}N_9$	228	20	48.48 (47.53)	4.45 (4.21)	9.64 (9.24)

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

The electronic spectra of the complexes I to X were recorded in DMF and compared with those of L^1 to L^5. The complexes displayed bands at 29,990 and 34,060 cm^{-1} assignable to π – π* and n – π* transitions respectively of the N-heterocycles. The band due to metal-to-ligand charge-transfer transition dπ → pπ* was observed in the region 27,000 to 27,700 cm^{-1} and d-d transition appeared as weak band in the range 20,200 to 22,300 cm^{-1} assignable to $^1B_{1g} \rightarrow {}^1A_{1g}$ transition which is characteristic of a palladium(II) square planar complex [22] – [25]. The electronic and far-IR spectral data are compiled in Table 2.

The ^1H and ^{13}C NMR spectroscopic assignments of the complexes of L^1 – L^5 were made based on the 2D spectral studies and reported literature for similar compounds [26], [27]. The ^1H and ^{13}C NMR

spectra exhibited both positive and negative coordination induced shifts (c.i.s.) attributed to ligand–to–metal σ–donation and metal-to-ligand π–back donation [28].

Table 2. Far-IR and electronic spectral data* of the complexes (cm^{-1})

Complex	$\upsilon_{Pd-X(t)}$ X = Cl / Br	Ligand transitions	MLCT	d-d transition
		n → π* & π → π*	dπ → pπ*	$^1B_{1g} \rightarrow {}^1A_{1g}$
I	334	33990(18294), 32895(19072)	27100(1036)	22104(155)
II	249,264	34060(18858), 33025(21395)	27640(11606)	20358(134)
III	333	34037(16383), 32984(17837)	27472(9149)	22026(328)
IV	271,282	33921(10516), 32906(10892)	27144(4366)	22222(342)
V	331	33990(21908), 32916(23496)	26998(3067)	22056(148)
VI	244,261	33990(18242), 33003(21899)	27579(1819)	20284(216)
VII	332	33967(20844), 29916(27100)	27100(2695)	22017(83)
VIII	259,274	33990(20274), 32982(21888)	27397(2018)	20973(233)
IX	330	33967(9934), 32895(10415)	27129(6126)	22272(90)
X	249,262	34014(11375), 33025(12524)	27670(5937)	20286(216)

*: spectra recorded in DMF; values in paranthesis are molar extinction coefficients

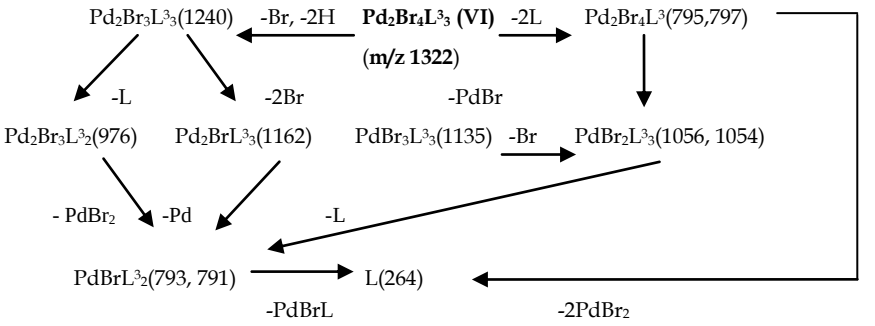
The proton NMR spectral data of the complexes of L^1 to L^5 were comparable with those of the uncoordinated N-heterocycles (Table 3). The spectra of the ligands exhibited a singlet around 7 δ due to the NH proton of quinazoline moiety while in the spectra of the complexes it showed a downfield shift by 0.22 to

3.74 δ. CH proton resonance which was observed as a singlet around 6δ in the spectra of the heterocycles exhibited a shift by about 0.38 on complexation. In complexes I to X protons resonances of the quinazoline moiety H – 7, 8, 9, and 10 appeared in the region 8.68 – 6.77 δ with positive and negative c.i.s. of -0.02 – 1.17 δ. The signals of benzimidazole ring protons H – 2′, 3′, 4′ and 5′ appeared as multiplets between 8.04 and 7.46 δ and were shifted by about -0.27 to 0.64 δ in the complexes. The alkyl proton peaks of the ligands were seen in the upfield region between 1.86 and 0.75 δ as a triplet for the CH_3 group and as multiplets for the CH_2 and CH groups with c.i.s. values in the range -0.78 – 0.26 δ.

The ^{13}C NMR spectra of L^1 – L^5 and those of palladium(II) complexes exhibit similar patterns barring minor shifts in the positions of the signals on complexation. The resonance signal of C-2 for the ligands was observed to be shifted to the downfield region of 147.16 – 143.95 δ as it is bonded to two nitrogen atoms and carbon atom and hence most deshielded. Negative shift in the range -C-6′ and C-7′ which are also bonded to one nitrogen appeared in the downfield region 134.80 – 131.70 δ and 144.79 – 140.32 δ respectively. Of the two, the resonance of C-7′ was shifted more downfield by ~ 11 δ as compared to C-6′ as it is bonded to tertiary nitrogen. The quinazoline carbons C - 3, 7, 8, 9 and 10 exhibited resonance signals in the range δ 133.59 - 110.36 and were shifted upfield by 3.05 to 7.24 δ on complexation. The benzimidazole carbons 2′, 3′, 4′ and 5′ showed signals between 127.79 - 104.32 δ and these exhibited positive and negative shifts in the range -5.15 – 5.07 δ on complexation. The resonance signals of the substituted alkyl carbons appeared in the upfield region 43.31 – 8.56 δ with c.i.s. values of -12.35 to 4.50 δ.

Thermogravimetric analysis of I and V revealed that both the complexes lose a water molecule below 100°C indicating the presence of lattice water. The chloride ions were lost below 330°C. The loss of heterocycles was observed above 430°C for I and above 336 °C for II.

The electrospray ionization mass spectrum was recorded for complex VI. It exhibited a peak at m/z 1322 supporting dimeric nature of the complex. The spectrum also exhibited twin peaks separated by two mass units at 1058 and 1060 for $Pd_2Br_4L^3_2$, at 1054 and 1056 for $PdBr_2L^3_3$, at 795 and 797 for $Pd_2Br_4L^3$ and 791 and 793 for $PdBr_2L^3_2$ due to the isotopes of bromine, ^{79}Br and ^{81}Br of natural abundances of 50.5 and 49.5 respectively. Decomposition pattern of $Pd_2Br_4L^3_3$ (VI) is depicted in Scheme 1.

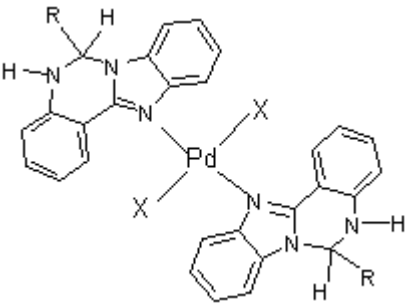


Scheme 1: Decomposition pattern of $Pd_2Br_4L^3_3$ (VI)

4. Stereochemistry

Coordination of the N-heterocycles to the metal ion is indicated by the analytical data, molar conductance, IR and ^1H and ^{13}C NMR spectral results. The electronic spectral results imply the presence of a square planar geometry around the palladium(II) ion. The thermogram of the chloro complexes of L^1 and L^3 suggest the presence of lattice water. The far-IR spectra reveal the presence of terminal halides for all the complexes. FAB-MS of the complex $[Pd_2Br_4(L^3)_3]$ supports binuclear structure for the complex. The N-heterocycles behave as monodentate ligands coordinating through the tertiary nitrogen of the benzimidazole moiety whereas in bromo complexes of L^1, L^3 and L^5, they act as both monodentate and bridging bidentate coordinating through the tertiary nitrogen of the benzimidazole moiety and the nitrogen of the quinazoline moiety. Based on these studies a monomeric structure is proposed for the chloro complexes of L^1 to L^5 and bromo complexes of L^2 and

L^4 (**II**) and a dimeric structure is assigned for the bromo complexes of L^1, L^3 and L^5 **(III).**

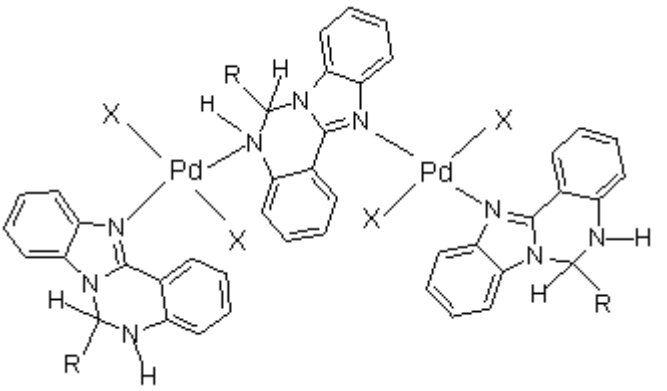


PdX_2L_2

X = Cl, R = ethyl, n-propyl, i-propyl, n-butyl or i-butyl

X = Br, R = n-propyl or n-butyl

II



$Pd_2X_4L_3$, X = Br, R = ethyl, i-propyl or i-butyl

III

5. Biological Activity

Two of the quinazoline derivatives L^1 and L^4 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 [29-32]. Septran and ampicillin was 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* (Table 4). The Pd(II) complexes were found to be effective against the microbes at 100 ppm concentration. It was observed that the Pd(II) complexes exhibit 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 ligand L^1 and the chloro complex of L^4 were found to be ineffective against the microbe *E.coli* and the palladium salt $PdCl_2$ was found to be ineffective against the microbe *Bacillus subtilis*. Both the ligands and their complexes were effective against *Yeast* with the complexes showing greater percentage inhibition.

Table 4: Antimicrobial activity of the quinazoline derivatives and the complexes.*

Compound‡	*Bacillus subtilis*	*E.coli*	*Yeast*	Pd complex†	*Bacillus subtilis*	*E.coli*	*Yeast*
L^1	46	nd	40	I	14	23	63
L^4	57	50	50	VII	50	nd	61
Standard	76	76	67	$PdCl_2$	nd	75	69

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

6. Conclusion

Synthesis of chloro and bromo complexes of palladium II with dihydrobenzoimidazo quinazoline derivatives L^1 – L^5 were carried out and characterised by various physicochemical techniques. Based on these studies monomeric/dimeric structures with square

planar geometry around the palladium(II) ion have been proposed. Two of the heterocycles L^1 and L^4 and their chloro complexes with palladium(II) were tested for antimicrobial activity and found to be moderately active.

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