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SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF COORDINATION COMPOUNDS OF PALLADIUM (II) WITH PURINE BASES

Chemistry

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ABSTRACT

A new series of mixed ligand coordination compound of Palladium having square planner stereochemistry, around the metal ion with the general formula $[PdL_2Cl_2]$ where L= Adenine, Guanine have been isolated in the solid state by the interaction of with the aforesaid ligands. The synthesized coordination compound has been characterized by elemental analysis, molar conductance, magnetic measurements, electron spin resonance, infra red spectral measurements and cyclic voltammogram, Biochemical properties (DPPH Scavenging Activity, ABTS Scavening Activity, α –glucosidase Activity). A square planner structure has been proposed for square planner complex. It is observed that, the synthesized compound is grey and green in colour. The complex has anti tumor activity.

KEYWORDS

Coordination chemistry, Adenine, Guanine , Palladium(II), Anti tumor activity

INTRODUCTION

Considerable attention has focused on Adenine, Guanine palladium complex and their rearrangement mechanisms because they are postulated intermediates for certain homogeneously catalyzed reactions. Coordination of a reactive organic moiety to the transition metal often allows a configuration to be assumed which leads to stereoselectivity in the reaction products .Presumable, studies of these complexes will lead to a greater understanding of the factors which influence these stereo selective reactions. The substitution reaction of the palladium (II) complex has been reviewed in the past. It is therefore thought worthwhile to synthesized and characterize d^8 complexes are Palladium with Adenine and Guanine. They can be used in two ways: as unique stoichiometric oxidizing agents; and as precursors of Pd(0) complexes. $PdCl_2$ is stable, but its solubility in water and organic solvents is low. The nitrogen containing biological compound which form nucleosides, consisting the basic building blocks of nucleic acids are called nucleobases or nitrogenous bases. There are five nuleobases-

Adenine(A), Cytosine(C), Guanine(G), Thymine (T), and Uracil (U). These are called primary or caronical. They are fundamental unit of the genetic code with the bases A,G,C and T found in DNA where as A,G,C and U found in RNA. The synthesized coordination compound has been characterized by elemental analysis, molar conductance, magnetic measurements, electronic spectra, infra red spectral measurements, cyclic voltammogram, Biochemical properties (DPPH Scavenging Activity, ABTS Scavening Activity, α –glucosidase Activity).

2. Experimental methods

2.1 Materials and Methods

Adenine and Guanine were procured from Aldrich Chemical Company , U.S.A. and used as such.PdCl2 obtained from TOKYO KASEI Organic Chemical, Japan and B.D.H England. Distilled water used in all the operations.

2.1.1 Preparation of the coordination compound

An 1:2 molar ratio of alcoholic solution of Cytosine was added to a filtered acidic solution of palladium chloride ($PdCl_2$) in (0.1 N HCl) with shaking. The resulting solution was heated for 4 hours with continuously shaking at 80 ^{0}C over a water bath. A colored precipitated was obtained. The precipitate was in c e ntrifuge and wash several times with distilled water and finally with ethanol. Precipipate were dried in vacuum desiccators over silica gel at room temperature. Here we followed the same as other ligands.

The General reaction for the preparation of coordination compound of palladium is as follows:

$$[Pd(Cl)_2] + 2L \xrightarrow[H_2O]{CH_3OH} [Pd(L_2)(Cl)_2]$$

where L = Adenine, Guanine

3. Result and Discussion

3.1 Characterization of Palladium (II) complexes:

1. Elemental and ICP (Induced Coupled Plasma) Analysis of Palladium Complexes

The elemental and ICP analysis were done at CDRI, Lucknow and Indore respectively.

Table.1 represents the percentage composition of C, H, N and Pd in the complexes.

2. Molar conductance of Palladium(II) complexes

The molar conductance of palladium (II) complexes was studies at 3×10^{-3}M concentration. The values of conductivity are summarized in Table 1. Complex 1-2 was dissolved in DMF. The molar conductance data varies from 9.34-37.9 $\mu s^{-1}cm^2mol^{-1}$ indicating that the complexes were found non-electrolytic nature. The molar conductance data revealed that metal to ligand molar ration is 1:2 for complexes. [1].

Table .1 Percentage composition of complexes and Molar conductance

S. No.	Complex	Empirical Formula	Color	Formula Weight	Yield (%)	Conductance ($\mu s^{-1}cm^2mol^{-1}$) 3×10^{-3}	(Calculated Value %) Observed Value %			
							C	H	N	Pd
1	$[Pd(L_1)_2Cl_2]$	$C_{10}H_{10}N_{10}Cl_2Pd$	Grey	447.5794	48.33	14.60	(26.83) 28.32	(2.25) 3.01	(29.58) 31.29	(23.78) 24.59
2	$[Pd(L_2)_2Cl_2]$	$C_{10}H_{10}N_{10}O_2Cl_2Pd$	Green	479.5782	65.66	11.81	(25.04) 23.14	(2.1) 1.7	(29.21) 27.56	(22.19) 19.58

3. Magnetic Suseptbility of Palladium(II) complexes

Magnetic susceptibilities of the complexes were measured by the modified Gouy method at room temperature using Magnetic Susceptibility Sherwood Balance. The magnetic moment values of the complex are zero. Hence, they are diamagnetic. The square planar geometry of the complex is evident from their diamagnetic nature[2].

4. Electronic Spectra of Ligands and Palladium(II) complexes

The absorption spectra of palladium (II) chloride and their complexes were recorded in methanol/ 0.1 M HCl /DMF (according to their solubility) wavelength ranges from 1100 to 200 nm. The absorption band of Pd (II) in UV-Vis spectra should exhibit two d-d transition band $^1A_2g \rightarrow A'_2g$ (21,491) and $^1B_1g \rightarrow B'_1$ (33,095). In the synthesized complexes, absorption spectrum of $[Pd(Cytosine)_2Cl_2]$, $[Pd(Thiamine)_2Cl_2]$, shows only $^1B_1g \rightarrow B'_1$, d-d band because $1A_2g \rightarrow A'_2g$ band obscured due to the charge transfer overlapping [3,4].

The electronic spectral bands of the complexes and this spectra were shown in table.2 and fig.1-2 respectively.

Table. 2 Band Assignments of UV-Vis Spectra and Magnetic Susceptibility

S. No.	Compounds	Reported Band (Transition)	Experimented Band (Transition)	Wavelength Found (nm)	Wavenumber Found (cm^{-1})	Magnetic Susceptibility (BM)
1	$[Pd(L_1)_2Cl_2]$	$^1A_{2g} \rightarrow A_2^{'}$ $^1B_{1g} \rightarrow B'_1$	$^{**1}B_{1g} \rightarrow B_1^{'}$	303.85	32910.98	**0.86**
2	$[Pd(L_2)_2Cl_2]$	$^1A_{2g} \rightarrow A_2^{'}$ $^1B_{1g} \rightarrow B'_1$	$^{**1}B_{1g}$ $B_1^{'}$	308.69	32394.96	**0.89**

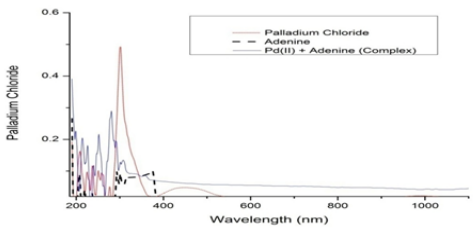


Fig. 1 Electronic Spectra of $[Pd(Adenine)_2Cl_2]$

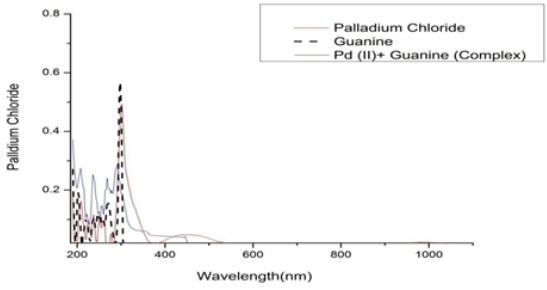


Fig.2 Electronic Spectra of $[Pd(Guanine)_2Cl_2]$

Infrared Spectra of Ligands and Palladium(II) complexes

The Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. In the IR spectra of the synthesized complex of $[Pd(Adenine)_2Cl_2]$ and $[Pd(Guanine)_2Cl_2]$ studied here the IR frequency of nitrogen of ring has been changed, there by suggesting that the nitrogen has been participate in the coordination.

The FTIR spectra of adenine and this complex is given in **Fig. 3** and **4.** Experimented frequencies are listed in **Table. 3.** The frequencies of stretching and scissoring modes are assigned by comparison of the FTIR spectra of free ligand and its palladium(II) complex. The five -CH bending modes were resolved properly in free ligands. The two frequency of ring -NH bending was found intact as observed in free ligand after complexation 1451 cm^{-1} was obscured by peak broading and 870 cm^{-1} was sharp. The $-NH_2$ stretching, scisering and rocking modes frequency was found at 1672,1603, 1507,1251 and 1023 cm^{-1} first three frequencies was belong to scisering mode while next two stretching and rocking respectively in free ligand. After the complexation the frequency of $-NH_2$ get obscured broaden because of binding of palladium(II) to $-NH_2$ group of ligand. **[5,7].**

The FTIR spectra of Guanine and this complex is given in **Fig.5** and **6.** Experimented frequencies are listed in Table **4.** The frequencies of stretching and bending modes are assigned by comparison of the FTIR spectra of free ligand and its palladium(II) complex. The -CH bending modes were resolved properly in free ligands. The two frequency of ring -NH bending was found intact as observed in free ligand after complexation 879 cm^{-1} was obscured by peak broading and 950 cm^{-1} was sharp. The $-NH_2$ stretching, bending and rocking modes frequency was found at 1698,1213 and 1044 cm^{-1} respectively in free ligand. After the complexation the frequency of $-NH_2$ get disappear broaden because of bending of palladium(II) to $-NH_2$ group of ligand **[6,7].**

The FTIR spectral bands and the fig. of the complexes (table 3,4) were assigned according to the literature.

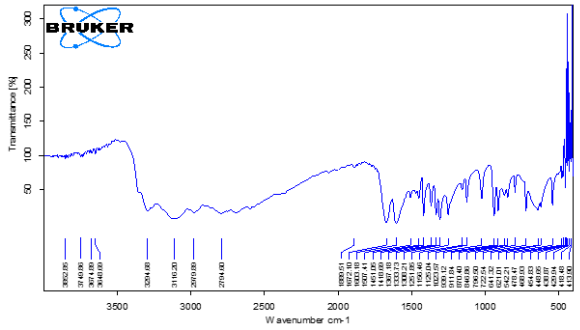


Fig .3 IR Spectra of Adenine

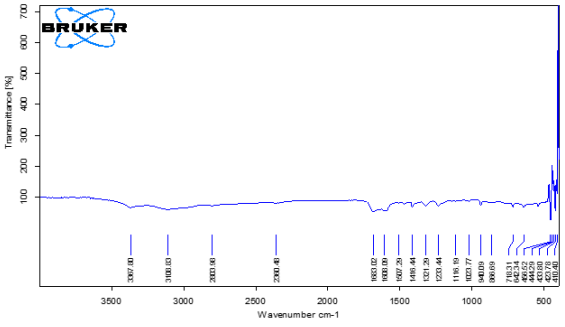


Fig. 4. IR Spectra of $[Pd(Adenine)_2Cl_2]$

Table 3. Group assignment of IR Spectra of Adenine and $[Pd(Adenine)_2Cl_2]$

S. No.	IR frequency of reported Adenine (cm^{-1}) (Akiko. Hirakawa et al.(1985))	IR frequency of Adenine(cm^{-1}) (Experimented)	IR frequency of [Pd (Adenine)$_2$ Cl$_2$] (cm^{-1})	Band Assignments
1	1673	1672	-	NH_2 scis.
2	1637.6	-	-	NH_2 scis 1
3	1604.0	1603	1608	NH_2 scis 2
4	1507.8	1507	1507	NH_2 scis 3
5	1451.4	1451	-	N (9) –H bend.
6	1421.1	1418	1416	ν_5
7	1368.0	1367	-	C (2) –H bend.
8	1334.7	1333	-	ν_6
9	1308.7	1308	-	ν_7
10	1252.8	1251	-	C (6) –NH_2 str.
11	1234.0	-	1233	ν_8
12	1156.8	1156	-	C (8) –H bend.
13	1125.9	1125	-	ν_9
14	1024.7	1023	1023	NH_2 rock.
15	951	-	-	ν_{14}
16	940.3	939	940	C (8) –H bend.
17	913.3	911	-	ν_{11}
18	872.1	870	866	N(9)-H bend.
19	844	846	-	C (2) –H bend.
20	797.1	796	-	ν_{16}
21	723.3	722	718	ν_{10} ring br.
22	684.2	-	-	ν_{19}
23	660	-	-	NH_2 wag.
24	640.8	641	642	ν_{20}
25	621.6	621	-	ν_{12}
26	543.0	542	-	ν_{13}
27	529.9	-	-	ν_{18}

28	380	-	-	NH_2 tor.
29	337.1	-	-	C (6) –NH_2 bend.
30	249.3	-	-	v_{21}

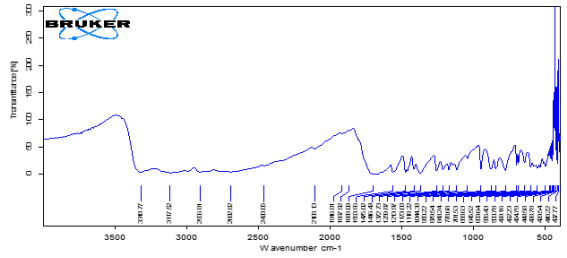


Fig .5 IR Spectra of Guanine

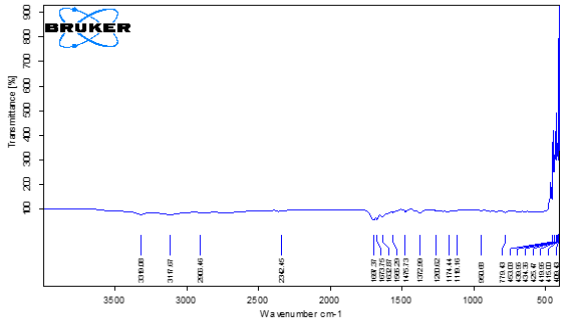


Fig.6 IR Spectra of [Pd(Guanine)$_2$Cl$_2$]

Table 4. Group assignment of IR Spectra of Guanine and [Pd(Guanine)$_2$Cl$_2$]

S. No.	IR Spectra of Guanine (Reported) [MOHAMD MATHLOLJTHI, ANNE MARIE SEUVRE+, 146 (1986) 15-27]	IR Spectra of Guanine (cm^{-1}) (Experimented)	IR Spectra of [Pd (Guanine)$_2$ Cl$_2$] (cm^{-1})	Band Assignment
1	1700	1698	-	ϑ (C = O), δ (NH_2)
2	1676	-	1673	ϑ (C = O)
3	1566	1563	1565	ϑ (C-2=N-3)
4	1554	-	-	ϑ (C = C)
5	1480	1475	1475	ϑ (N-7=C-8) and ϑ (C-8-N-9)
6	1465	-	-	δ (C-N-H)
7	1420	1416	-	δ (N-7 =C-8-H),
8	1375	1372	1372	-------
9	1358	-	-	δ (C-8-N-H), δ (C-8-H), ϑ (C-8-N)
10	1264	1259	1260	ϑ(C-5-N-7) and (C-4-N-9)
11	1216	1213	-	ϑ(C-2-NH_2)
12	1175	1173	1174	δ (C-8-H) in plane
13	1150	-	-	
14	1120	1118	1119	δ (C –N=C)
15	1043	1044	-	r (NH_2)
16	950	950	950	δ (N-9-H) out-of-plane
17	880	879	-	δ (N-9-H) out-of-plane
18	852	848	-	ϑ (C-C)
19	790	-	-	δ (N-1-H).
20	780	778	779	
21	727	-	-	
22	704	701	-	δ (ring)
23	=690	-	-	
24	648	645	-	Breathing

Electrochemical behavior by cyclic voltammeter of Ligands and Palladium(II) complexes

The cyclic voltammogram (CV) of complexes 20 mM TBAP (acetonitrile) adenine, guanine, and complexes [Pd(adenine)$_2$Cl$_2$], [Pd(guanine)$_2$Cl$_2$], in 0.1 M KCl (water) in electrolyte is shown . The complexes of palladium (II) (Guanine, Adenine,) exhibits a completely irreversible reduction at $E_{1/2}$ = -115 mV respectively . Palladium (II) complex of adenine doesn't show $E_{1/2}$ value. No return wave was deciated at 300 mV/s in palladium adenine complexes. The electrochemical data of ligand and their respective palladium(II) complexes are summaried in **Table. 11** and the voltamogram of ligands and their palladium(II)complexes are given from **Fig. 34-42**.The voltammogram of Guanine shows two reduction peak Epc in cathodic direction which are assigned at Epc = -121,34.7 mV. The oxidation peak at -109 mV is due to irreversible oxidation of Guanine . The **Fig. 35** voltammogram of [Pd(Adenine)$_2$Cl$_2$] shows one reduction peak Epc in cathodic direction which are assigned at Epc = -219mV. The oxidation peak at -201 mV is due to irreversible oxidation of [Pd(Adenine)$_2$Cl$_2$] . The **Fig. 37** voltammogram of [Pd(Guanine)$_2$Cl$_2$] shows one reduction peak Epc in catshodic direction which are assigned at Epc = - 412 mV. The oxidation peak at -137 mV is due to irreversible oxidation of [Pd(Guanine)$_2$Cl$_2$].

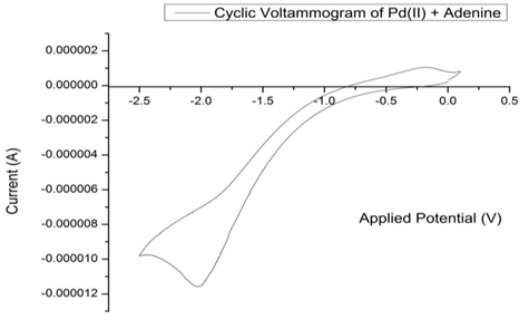


Fig .7. Cyclic Voltammogram of [Pd(Adenine)$_2$Cl$_2$]

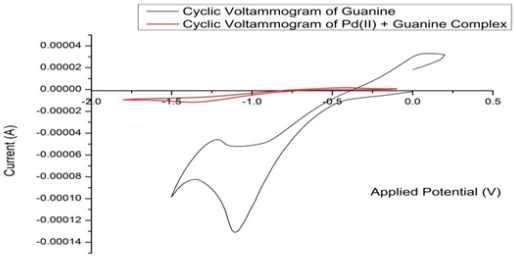


Fig . 8. Cyclic Voltammogram of Guanine and [Pd(Guanine)$_2$Cl$_2$]

Table no. 5 CV Parameters

S.No	Metal, Ligand, Complexes	Epc (mV)	Epa (mV)	Ep(mV)	E1/2 (mV)
1	Guanine	-121 34.7	-109	12	-115
2	[Pd(Adenine) 2Cl2]	-219	-201	-18	-210
3	[Pd(Guanine) 2Cl2]	-412	-137	275	-274.5

Biochemical properties of Palladium(II) complexes

In the present work we have also evaluated the palladium (II) complexes for DPPH Scavenging Activity, ABTS Scavening Activity and α- glucosidase does not show any results inhibitory action [8,9].

CONCLUSION

The mixed ligand complex [Pd(L$_2$)Cl$_2$] where (L = Cytosine, Thymine), have been prepared by the interaction of parent compound [PdCl$_2$] with ligand. The complex is characterized by elemental analysis, magnetic measurement and infrared spectral studies. The molecular orbital approach was used to explain the structure of square –planar complexes of the d^8 elements.

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