Synthesis and Characterization of Palladium (II) Complexes With Some Pyridine Derivatives

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تحضير ودراسة معقدات البلاديوم (II) مع بعض مشتقات البريدين

الخلاصة

تضمن هذا البحث تحضير معقدات جديدة للبلاديوم (II) مع مشتقات البريدين ذات الصيغة العامة:

trans- $[PdCl_2L^1_2]$, *trans* - $[PdCl_2L^2_2]$, $[PdL^2_4](BF_4)_2$ حيث:

L^1 = 2-picoline , 3-picoline , 4-picoline

L^2 =2-aminopyridine , 3-aminopyridine , 4-aminopyridine

$[PdL^1_4](BF_4)_2$ حيث:

L^1 = 2-picoline , 3-picoline

شخصت المعقدات المحضرة بالطرائق الطيفية [الاشعة تحت الحمراء، الاشعة المرئية – فوق البنفسجية ، مطيافية التذرية] وبالتحليل الكمي الدقيق للعناصر C.H.N والتوصيلية المولارية. من النتائج المحصول عليها فأن الشكل الفراغي المقترح لجميع المعقدات هو المربع المستوي .

ABSTRACT

Complexes of palladium (II) with pyridine derivatives in general formula: *trans*- $[PdCl_2L^1_2]$, (where: L^1 = 2- picoline, 3- picoline, 4- picoline); [pd L^1_4]$(BF_4)_2$, (Where: L^1=3-picoline, 4-picoline); *trans*- $[PdCl_2L^2_2]$ and [pd L^2_4] $(BF_4)_2$, (Where: L^2 = 2-aminopyridine, 3 - aminopyridine, 4 -aminopyridine) were prepared.

All componnds have been characterised by spectroscopic methods [I.R, U.V-Vis, Atomic Absorption], Microanalysis (C. H .N) a long with conductivity measurements.

From the above data the proposed molecular structure for all prepared complexes are square planar geometries about pd (II).

Introduction

A large number of pyridine derivatives and their complexes have been synthesis and developed such (bipy), (phen) [1,2]. The complexes of some transition metals with pyridine derivatives were reported for having biological activity and used as drugs in the medical applications [3]. Recently, the square planar complexes of Pd (II) with ligands contain nitrogen donor atoms were prepared such as complex of pd (II) with phosphine and DMF which are uses as catalyst for reduction co_2 to co [4-10]. Great attention was given to synthesis the complex [pd (en) Cl (py)]$^+$ which has a capability of balking the division of cancer tumours [11]. This paper reports the synthesis and characterisation of some complexes of pd (II) with 2-picoline, 3-picoline, 4-picoline, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine and the geometry structure was determined for this complexes.

Experimental Methods

Reagents were purchased from fluka & Redial-Dehengc co.I.R spectra were recorded as KBr or CsI discs using perkin-Elmer 1330 Infrared Spectrophotometer and Fourier Transform Infrared Spectrophotometer Shimadzu 24FT-I.R8300. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3} M solutions in DMF at 25ºC using shimadzu-U.V-160 A Ultra violet Visible - Spectrophotometer with 1.000±0.001 cm matched quartz cell. Elemental microanlysis (C.H.N) were performed by using perkin–Elmer 24B Elemental Analysis. While metal contents of the complexes were determined by Atomic Absorption (A.A) Technique using Japan A.A-670 Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25ºC for 10^{-3} M solutions of the samples in DMF using pw9527 Digital conductivity meter (Philips).
Melting points were recorded by using Stuart melting point apparatus

Synthesis of *trans*-$[PdCl_2L'_2]$:

In (50) ml round bottom flask (0.2g, 1.13 mmol) of $PdCl_2$ was dissolved in (5) ml methanol. A solution (0.132 g, 62.26 mmol) of NaCl in (2) ml distilled water was added to the above solution .The mixture was allowed to reflux until the reddish brown solution formed, added to it (0.22 ml, 2.26 mmol) from the ligand L^1 (where L^1=2-picoline, 3-picoline.4-picoline) in (1) ml methanol. The reaction mixture was allowed to reflux for (2) hrs, the yellow precipitate formed which was filtered and washed with (4) ml methanol and (5) ml ether and dried to give the weight of product complex and yield % (Table-1).

Synthesis of $[PdL'_4](BF_4)_2$:

In (50) ml round bottom flask (0.2 g, 0.55 mmol) of *trans*-$[PdCl_2L'_2]$ (where: L^1= 3-picoline, 4-picoline) was dissolved in (5) ml methanol, solution of

(0.26 ml, 2.7 mmol) from ligand L^1 (L^1=3-picoline, 4-picoline) in (2) ml methanol was added to the above solution .The reaction was allowed to reflux until the solid material solved and yellow colour solution formed. The mixture allowed to cool at room temperature, filtered and added to it (0.12g, 1.1mmol) $NaBF_4$, the mixture allowed to reflux (30) min. The solution was concentrated to (3) ml by distillation under reduced pressure (vacuum), cooling at room temperature and added to it (5) ml methanol, (7) ml ether, the yellow precipitate formed, which was cooled it to (- 5ºC) for (1) hr, filtered and washed with (4) ml methanol, (8) ml ether to give the weight of product complex and yield %(Table-1).

Synthesis of *trans* -$[PdCl_2L^2_2]$:

The method used to prepare *trans*-$[PdCl_2L^2_2]$ (where: L^2 =2-aminopyridine, 3- aminopyridine, 4-aminopyridine) was analogous to the procedure given for the complex *trans*-$[PdCl_2L^1_2]$ but with (0.22 g, 2.34 mmol) of the ligand L^2 instead of 2-picoline, 3-picoline, 4-picoline. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave yellow precipitate, which was weighted to give the yield % of the product complex (Table-1).

Synthesis of $[PdL^2_4](BF_4)_2$:

A similar procedure to that described for preparation complexes $[PdL^1_4](BF_4)_2$ (where:L^1=3-picoline,4-picoline) was used to prepare the complexes $[PdL^2_4](BF_4)_2$ (where L^2=2-aminopyridine , 3-aminopyridine, 4-aminopyridine) but with (0.2g, 0.55 mmol) from the complex *tarns*-$[PdCl_2L^2_2]$ inplace of *trans*-[$PdCl_2L^1_2$] and used (0.26g,2.8mmol) from the ligand L^2 inplace of the ligand L^1 to give yellow precipitate which was filtered and washed with (4)ml methanol ,(6)ml ether and dried to give the weight of product complex and yield % (Table-1) .

Results and Discussion

The prepared complexes are stable in solution (Table-3), the analytical and physical data (Table-1) and spectral data (Table-2 and 3) are computable with the suggested structure (Fig.1). All complexes dissolve in DMF solvent.

I.R spectra:

The I.R spectra for all prepared complexes gave different spectra when it is comparision with I.R spectra of free ligand L^1, L^2 (Table 2). In general the I.R spectra of all complexes revealed two bands, the first at the range (1600-1628)cm^{-1} and the second at the range (1480-1510) cm^{-1} due to stretching frequancy of aromatic ring groups υ(C==N), υ (C==C) respectively, which are shifted to high frequency when it comparison with spectra of free ligands [12], these shifting of two bands indicate the coordination between nitrogen atom of

the ring and metal ion pd(II) [13,14]. The I.R spectra of complexes $[PdCl_2L^1{}_2]$ (Fig.2) and $[PdCl_2L^2{}_2]$ exhibit two new bands, the first at the range (480-550) cm^{-1}, the second at the range (334-350) cm^{-1} assigned to the stretching frequency of trans-υ (Pd---N) and trans-υ (Pd---Cl) respectively [15,16]. The I.R spectra of the complexes $[PdL^1{}_4](BF_4)_2$ and $[PdL^2{}_4](BF_4)$ (Fig.3) show two new bands at the range (1038-1070) cm^{-1} due to stretching frequency of BF_4^- group [17], and a band at the range (513-550) cm^{-1} due to stretching frequency υ (Pd---N) [4,16]. Moreover the absence of a band at range (334 -350) cm^{-1} which due to υ (Pd---Cl) in the I.R spectra of the complexes $[Pd\ L^1{}_4](BF_4)_2$ and $[PdL^2{}_4]\ (BF_4)_2$ indicate the uncoordinated of Cl with the Pd(II) in these complexes.

Electronic spectra:

The electronic spectral data of the free ligands L^1 and L^2 and their complexes are summarized in table-3. The u.v-vis spectra of the free ligand in DMF solvent appeared absorption peak at (275) nm due to overlap of electronic transition ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi^*$) [18]. The electronic spectra of the complexes in general formula $[PdCl_2L^1{}_2]$ (Fig.4), $[PdL^1{}_4](BF_4)_2$ and $[PdL^2{}_4](BF_4)_2$ displayed three absorption peaks, the first peak at the range (275-290) nm assigned to ligand field , which were shifted to high frequency when it comparison with spectra of the free ligands L^1 and L^2 [19] , the second peak at the range (301-360)nm and the third peak at the range(391-783)nm are attributed to (d-d) electronic transition type ($^1A_1g \longrightarrow {}^1B_1g$) , ($^1A_1g \longrightarrow {}^1A_2g$) respectively[20,21], while the electronic spectra of complexes in general formula $[PdCl_2L^2{}_2]$ show two peaks, the first peak at the range(278-291)nm and the second peak at the range (305-365) nm, are attributed to the ligand field [19] and (d-d) electronic transition type($^1A_1g \longrightarrow {}^1B_1g$) [21] respectively.

The peaks in the electronic spectra of all complexes which assigned to (d-d) electronic transition ($^1A_1g \longrightarrow {}^1B_1g$), ($^1A_1g \longrightarrow {}^1A_2g$) give a good evidence for square planar geometry about pd(II) [22,23].

Molar Conductance:

The molar conductance values of the complexes in DMF solvent in 10^{-3} M at 298º K (Table-3) indicted that the complexes *trans*- $[PdCl_2L^1{}_2]$ and *trans*-$[PdCl_2L^2{}_2]$ are neutral, while the complexes $[PdL^1{}_4](BF_4)_2$, $[PdL^2{}_4](BF_4)_2$ are electrolyte with 2:1 [24,25].

Atomic Absorption:

The atomic absorption measurements (Table-1) for all complexes gave approximated values for theoretical values.

In conclusion, our investigation this suggest that the ligands L^1 and L^2 coordinate with pd (II) forming square planar geometry (Fig-1).

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Table 2: I.R spectral data of the ligands and its complexes (cm^{-1})

Compounds	u **(C---H) Ar.,AI.**	**Ring vibration** u **(C----N),** u **(C----C)**	d **inplane (C----H)**	u **(Pd---N)**
2-pic	**3070 ,2933**	**1596 ,1470**	**1052**	**------**
***trans*-[$PdCl_2$(2-pic)$_2$]**	**3050 ,2945**	**1602 ,1490**	**1100**	**480**
3-pic	**3050 ,2941**	**1590 ,1481**	**1031**	**-------**
***trans*-[$PdCl_2$(3-pic)$_2$]**	**3052 ,2951**	**1600 ,1480**	**1100**	**520**
[Pd(3-pic)$_4$](BF_4)$_2$	**3050 ,2928**	**1600 ,1490**	**1170**	**520**
4-pic	**3075 ,2930**	**1603 ,1493**	**1040**	**------**
***trans*-[$PdCl_2$(4-pic)$_2$]**	**3070 ,2924**	**1618 ,1502**	**1070**	**507**
[Pd(4-pic)$_4$](BF_4)$_2$	**3070 ,2923**	**1622 ,1510**	**1100**	**513**
Compounds	u **(N---H) as.,s.**	**Ring vidration** u **(C----N),** u **(C----C)**	d **inplane (N---H)**	u **(Pd---N)**
2-ampy	**3455 ,3335**	**1600 ,1492**	**1625**	**-------**
***trans*-[$PdCl_2$(2-ampy)$_2$]**	**3460 ,3340**	**1605 ,1510**	**1550**	**490**
[Pd(2-ampy)$_4$](BF_4)$_2$	**3451 ,3395**	**1632 ,1499**	**1600**	**527**
3-ampy	**3350 ,3205**	**1590 ,1481**	**1620**	**-------**
***trans*-[$PdCl_2$(3-ampy)$_2$]**	**3410 ,3205**	**1620 ,1485**	**1580**	**550**
[Pd(3-ampy)$_4$](BF_4)$_2$	**3400 ,3300**	**1628 ,1505**	**1555**	**550**
4-ampy	**3444 ,3330**	**1602 ,1493**	**1630**	**---------**
***trans*[$PdCl_2$(4-ampy)$_2$]**	**3442 ,3223**	**1620 ,1510**	**1556**	**520**
[Pd(4-ampy)$_4$](BF_4)$_2$	**3440 ,3320**	**1620 ,1500**	**1585**	**540**

Ar =Aromatic AI =Aliphatic as. =Asymetric s. =symertric p**ic=picoline**

Table 3: Electronic spectral data and conductance measurments of the ligands and its complexes in DMF solvent.

Compounds	l (nm)	u^{-} (cm^{-1})	ε max M^{-1}.cm^{-1}	M.C.* Ohm^{-1}.cm^{2}.mol^{-1}
2-pic	275	36363	2411	-----
trans-[$PdCl_2(2\text{-pic})_2$]	281 314 391	35587 31874 25575	1660 982 331	18.9
3-pic	275	36363	1975	
trans-[$PdCl_2(3\text{-pic})_2$]	284 317 394	35211 31545 25380	2197 1130 932	20
[$Pd(3\text{-pic})_4$](BF_4)$_2$	278 330 725	35971 30303 13793	1353 250 2	133
4-pic	275	36363	2354	
trans-[$PdCl_2(4\text{-pic})_2$]	278 310 392	35971 32258 25510	1233 300 324	17
[$pd(4\text{-pic})_4$](BF_4)$_2$	279 360 752	33670 27777 13297	1810 790 35	143
2-ampy	275	36363	2043	
trans-[$PdCl_2(2\text{-ampy})_2$]	278 305	35971 32786	1679 1032	15.5
[$Pd(2\text{-ampy})_4$](BF_4)$_2$	279 325 735	33670 30769 13605	1580 750 28	150
3-ampy	275	36363	1553	
trans--[$PdCl_2(3\text{-ampy})_2$]	278 317	35971 31545	923 1186	11.6
[$Pd(3\text{-ampy})_4$](BF_4)$_2$	275 301 702	36363 33222 14245	1631 2466 7	160
4-ampy	275	36363	2340	
trans-[$PdCl_2(4\text{-ampy})_2$]	291 365	34364 27397	936 279	21.7
[$Pd(4\text{-ampy})_4$](BF_4)$_4$	290 360 783	34482 27777 12771	2356 750 71	135

*** M.C = Molar conductance**

Table 1: Analytical and physical data of the complexes:

Complexes *	colour	M.Wt	Dec.^{o} c	Yield%	Fou
					C
***trans* –[$PdCl_2(2\text{-pic})_2$)]**	Pale yellow	363.57	325	93	39.4 (39.6)
***trans*-[$PdCl_2(3\text{-pic})_2$]**	Greensh yellow	363.57	320	97	38.4 (39.6)
[$Pd(3\text{-pic})_4$](BF_4)$_2$	Yellow	652.52	265	84	44.0 (44.1)
***trans*-[$PdCl_2(4\text{-pic})_2$]**	Pale yellow	363.57	330	97	39.4 (39.6)
[$Pd(4\text{-pic})_4$](BF_4)$_2$	Pale yellow	652.52	265	81	43.87 (44.1)
***trans*-[$pdCl_2(2\text{-ampy})_2$)]**	Pale-yellow	365.55	336	85	30.9 (32.8)
[$Pd(2\text{-ampy})_4$](BF_4)$_2$	Dark yellow	656.48	280	72	32.4 (36.5)
***trans*-[$PdCl_2(3\text{-ampy})_2$]**	Greensh yellow	365.55	335	93	33.02 (32.8)
[$Pd(3\text{-ampy})_4$](BF_4)$_2$	Dark yellow	656.48	270	75	35.4 (36.5)
***trans*-[$PdCl_2(4\text{-ampy})_2$]**	Pale yellow	365.55	340	93	32.6 (32.8)
[$Pd(4\text{-ampy})_4$](BF_4)$_2$	Dark yellow	656.48	275	87	35.8 (36.5)

- pic = picoline ampy = aminopyridine

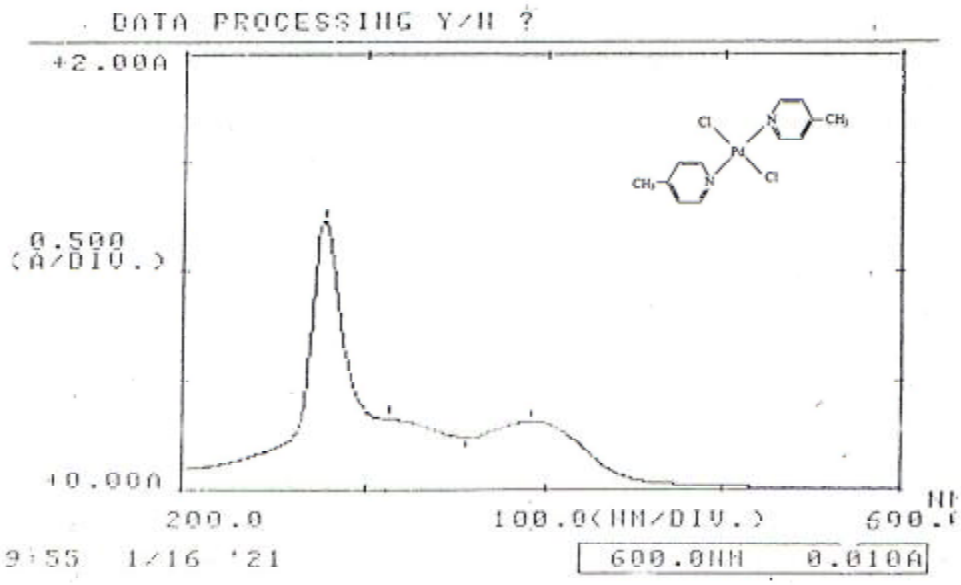

Fig. (4) Electronic spectrum of complex *trans* –[$PdCl_2$(4-Pic)$_2$]

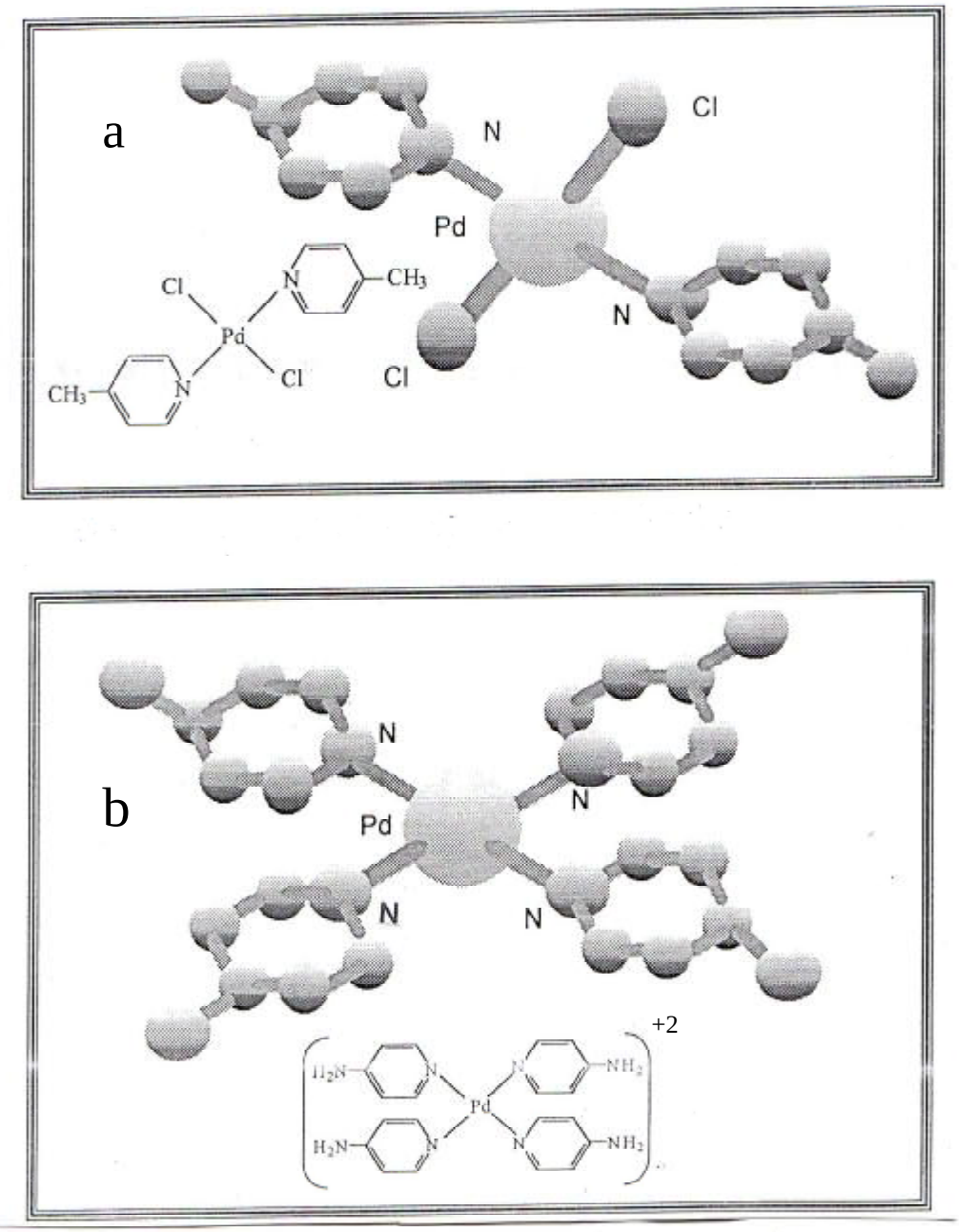

Fig 1: The suggested structure for the complexes
a - *trans*-[Pd Cl_2 $(4\text{-pic})_2$]
b - $[Pd(4\text{-ampy})_4]^{+2}$
pic = picoline
ampy = aminopyridine

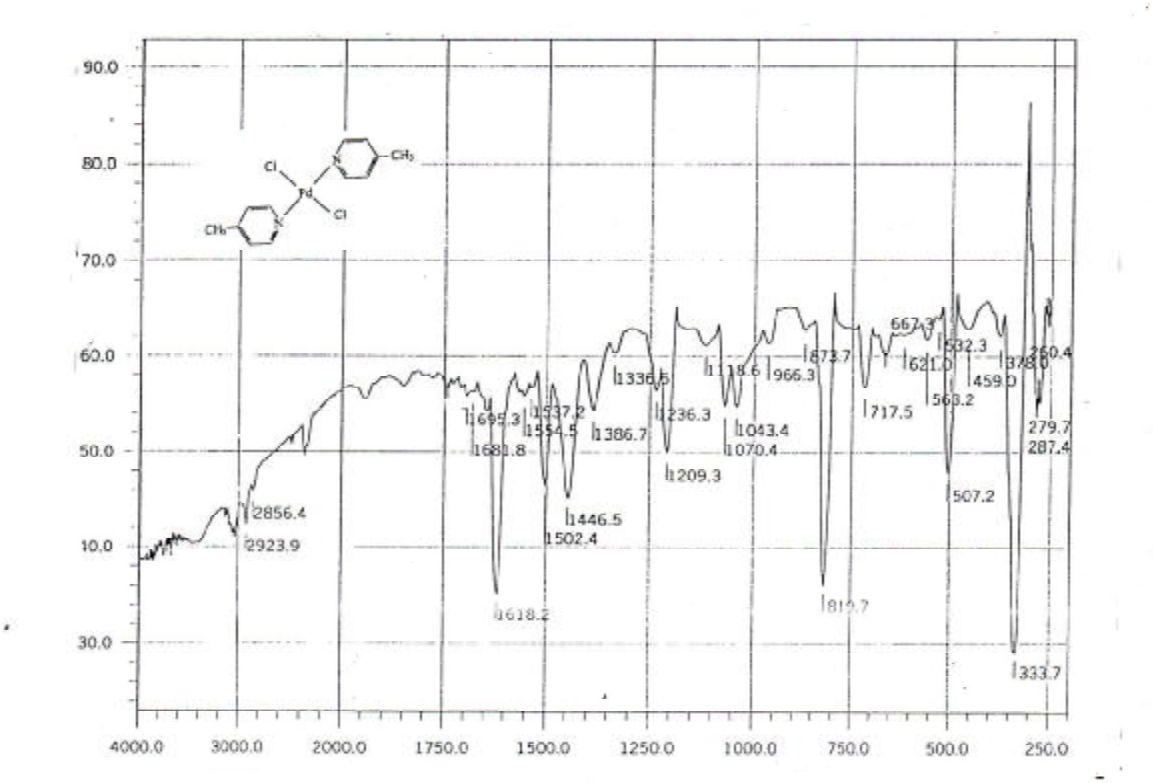

Fig 2: I.R spectrum of *trans* – $[PdCl_2(4\text{-}Pic)_2]$

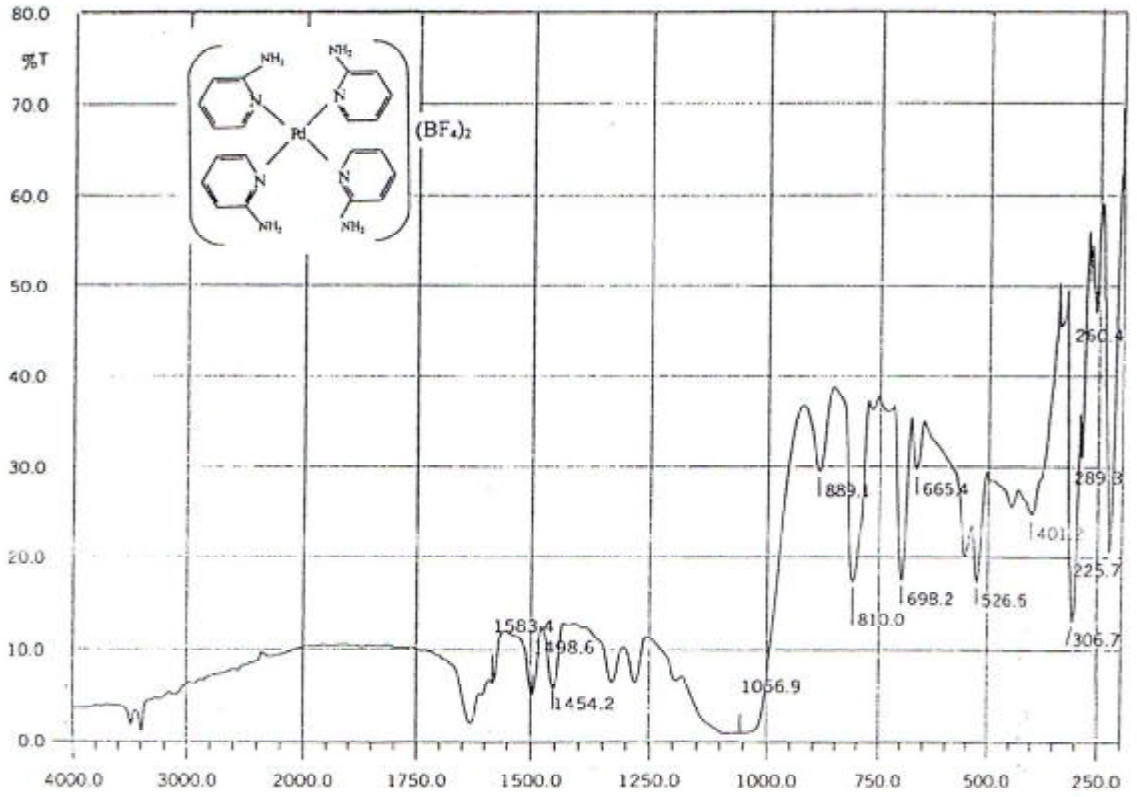

Fig 3: I.R spectrum of complex $[Pd(2\text{-}ampy)_4]^{+2}$