Synthesis, Spectral Characterization and X – Ray Diffraction studies of some Pd(II) Complexes with Schiff bases

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ABSTRACT

The synthesis, spectroscopic and X – Ray Diffraction studies of some Pd(II) complexes with bidentate Schiff bases are reported here. These Schiff bases were derived by condensing aldehydes like 2-hydroxy-1-naphthaldehyde, 5-chloro salicyladehyde with amines like 4-nitro aniline, 4-methyl aniline and 4-methoxy aniline. The complexes were characterized on the basis of elemental analysis, molar conductivity, spectral (IR, ^{1}H and electronic) as well as thermal analysis. All the Pd (II) complexes exhibit square planar geometry with 1:2 (metal : ligand) stoichiometry. The X- ray diffraction studies suggest monoclinic crystal system for these complexes.

*Keywords***:** Pd(II) complexes; Schiff bases; Structural analysis; X- ray diffraction studies

1. INTRODUCTION

Progress in the field of Coordination chemistry has received considerable significance because of its importance in chemical industry and life itself.

Schiff bases contain azomethine (>C=N) group as functional group and hence act as an effective ligand.

Transition metal complexes of Schiff bases have witnessed a great deal of interest in the recent years because of their chemical, pharmacological[1,2] and analytical applications[3]. In addition the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation[4], reduction[5], hydrolysis and possess antibacterial activity[6].

In this paper, the synthesis, characterization and crystal lattice parameters of some Pd (II) complexes with bidentate Schiff base ligands are reported.

2. MATERIALS AND METHODS

2. 1. Chemicals

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) and used without further purification. Distilled solvents were used throughout the experiments.

2. 2. Synthesis of Schiff bases

The Schiff base was synthesized by condensing ethanolic solution of 0.01 mol of aldehyde with 0.01 mol of amine in 1:1 stoichiometric ratio and refluxed for 3-4 hours. The solution was then reduced to ¼th of its original volume and poured in ice cold water. The solid precipitated was filtered off, washed with methanol and then recrystallized from ethanol. The purity of ligands was checked by thin layer chromatography and elemental analysis. The yield of the ligands was about 80-95 %.

L^1H = 2-hydroxy -1-naphthaldehyde (1.722 g) and 4-nitro aniline (1.382 g).

L^2H = 2-hydroxy -1-naphthaldehyde (1.722 g) and 4-methyl aniline (1.072 g).

L^3H = 5- chloro salicyladehyde (1.567 g) and 4-methoxy aniline (1.230 g).

2. 3. Synthesis of the Pd complexes

All the complexes were prepared by adding stoichiometric amount of ligands to metal chlorides in a 2:1 mole. To an ethanolic solution of 0.002 mol of ligand, ethanolic solution of $PdCl_2$ (0.001 mol) was added. The reaction mixture was refluxed for about 4-5 hours and the pH adjusted to optimum level. The complexes which precipitated were filtered off, washed with cold methanol and recrystallized from ethanol. The products were finally dried in vacuum over fused Calcium Chloride.

2. 4. Experimental Analysis

Metal content was determined in the laboratory by the reported methods[7]. C, H and N analyses were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400 cm^{-1} region using a FTIR spectrum One supplied by Perkin Elmer instrument. The electronic Spectra were recorded in DMSO solution using a UV-visible 2100 Spectrophotometer supplied by M/s Perkin Elmer lambda 25. The ^{1}H NMR spectra were recorded in DMSO using a Bruker Advance 300 MHz spectrometer. TGA analysis was carried out using a Pyris Diamond TGA supplied by Perkin Elmer instruments. The X–ray analysis was carried out at TIFR Mumbai.

3. RESULTS AND DISCUSSION

All the metal complexes are crystalline solids and decompose at high temperature. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The elemental analysis show 1:2 (metal : ligand) stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1. The molar conductivities of 1 x 10^{-3} S cm^2 mol^{-1} solutions of the complexes in DMSO indicate their non-electrolytic nature[8].

Table 1. Physical and Analytical Data of the Ligand and Metal Complexes.

Ligand/Complex	Mol. Wt. (Colour)	M. P. (ºC)	Λ_M (S cm^2 mole^{-1})	Elemental Analysis % Found % (Calculated)				
				C	H	N	Cl	M
$C_{17}H_{12}O_3N_2$ L^1H	292.00 (Orange red)	225	--	69.82 (69.86)	3.89 (4.10)	9.23 (9.58)	--	--
$Pd(C_{34}H_{22}O_6N_4)$ $Pd(L^1)_2$	688.42 (Yellow)	>300	16.10	58.42 (59.26)	3.52 (3.19)	8.20 (8.13)	--	15.22 (15.45)
$C_{18}H_{15}ON$ L^2H	261.00 (Yellow)	130	--	82.66 (82.75)	5.47 (5.74)	5.23 (5.36)	-- --	-- --
$Pd(C_{36}H_{28}O_2N_2)$ $Pd(L^2)_2$	626.42 (Green)	240	16.90	68.72 (68.96)	4.52 (4.47)	4.20 (4.47)	-- --	16.77 (16.98)
$C_{14}H_{12}O_2NCl$ L^3H	261.5 (Green Yellow)	137	--	62.45 (64.24)	4.47 (4.59)	5.23 (5.35)	13.36 (13.57)	-- --
$Pd(C_{28}H_{22}O_4N_2Cl_2)$ $Pd(L^3)_2$	627.42 (Brown)	255	18.30	53.42 (53.55)	3.52 (3.50)	4.20 (4.46)	11.21 (11.36)	16.60 (16.96)

3. 1. IR Spectra

The infrared spectra of the free ligands were compared with those of their Pd(II) complexes to determine the bonding mode of the ligands to the metal in the complexes. The spectra of the ligands shows strong and broad absorption band in the region 3450-3050 cm^{-1}, which is assigned to hydrogen bonded $\upsilon_{(0-H)}$ stretching vibration[9]. This band is missing in the complexes indicating the absence of water molecule which is further confirmed by TGA analysis. The phenolic oxygen, after the loss of OH proton gets coordinated to the metal is further supported by the shift in the stretching frequency of the $\upsilon_{(C-O)}$ to lower wave numbers by 20-30 cm^{-1} from its position in the free ligands1[10,11].

The coordination of azomethine nitrogen is confirmed by the presence of bands in the 1625-1600cm^{-1} region in the ligand which underwent a shift to a lower frequency after complexation[12]. All complexes show extra bands in the 580-520 cm^{-1} and 485-470 cm^{-1} region assigned to $\upsilon_{(M-N)}$ and $\upsilon_{(M-O)}$ stretching vibrations. This data is in good agreement with literature value[13,14].

Thus these Schiff bases behave as bidentate ligand coordinating through the deprotonated phenolic oxygen and azomethine nitrogen. Selected IR bands for the ligands and their metal complexes along with their tentative assignment are given in Table 2.
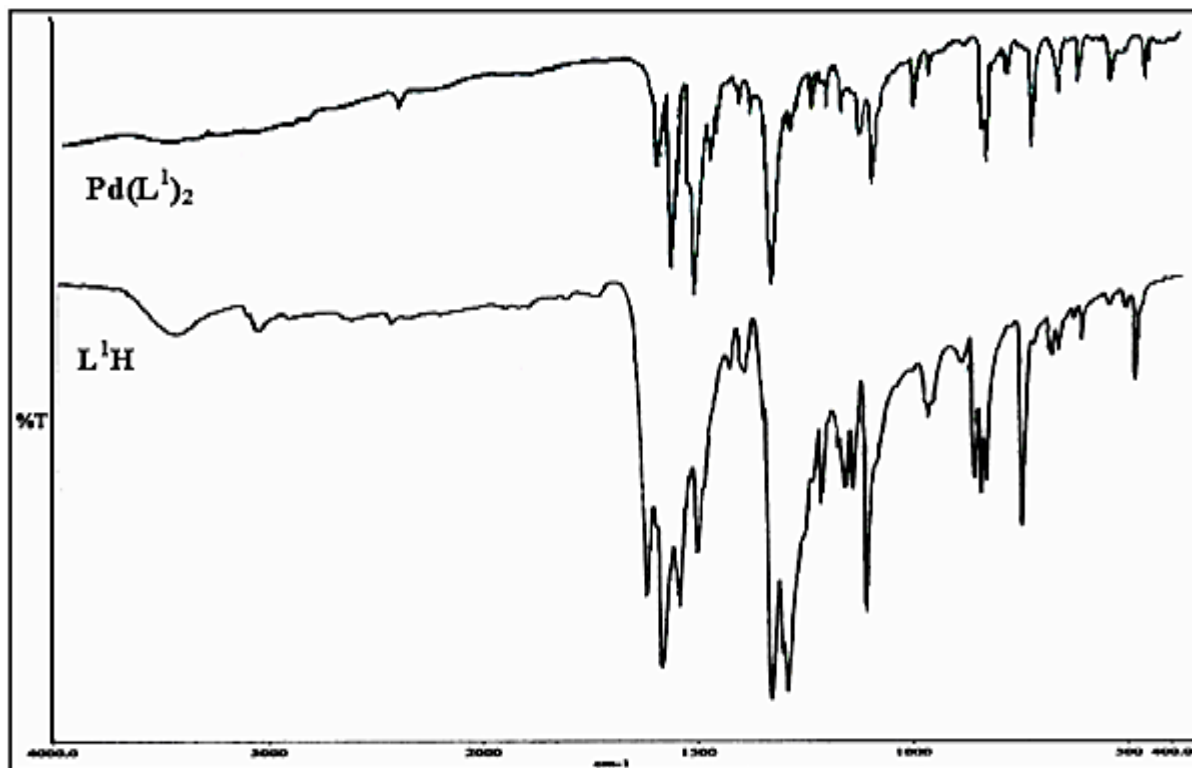
Figure 1. Infrared absorption Spectra of L^1H and $Pd(L^1)_2$.

3. 2. ^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands and Pd(II) complexes were recorded in DMSO solvent and the assignments are detailed in Table 2.

Table 2. IR Spectral data (cm^{-1}) and ^{1}H NMR spectra of Ligand and Metal Complexes.

Ligand/complexes	IR Spectral data (cm^{-1})					^{1}H NMR Chemical Shift (δ ppm)		
	$\upsilon_{(0-H)}$	$\upsilon_{(C=N)}$	$\upsilon_{(C-O)}$	$\upsilon_{(M-N)}$	$\upsilon_{(M-O)}$	Aromatic	CH=N	OH
L^1H	3434	1621	1398	----	----	6.95 – 8.50	9.64	14.21
$Pd(L^1)_2$	----	1602	1278	517	485	6.60 – 8.83	10.20	---
L^2H	3050	1620	1290	----	----	6.52 – 8.40	8.95	14.11
$Pd(L^2)_2$	----	1600	1259	580	470	6.46 – 8.73	9.40	---
L^3H	3436	1624	1485	----	----	7.00 – 8.60	9.20	14.70
$Pd(L^3)_2$	----	1609	1464	544	472	6.70 – 8.62	9.46	---

The OH protons that appeared in the region 14.11-14.70 ppm disappeared in the complexes confirming the deprotonation of the hydroxyl proton due to coordination of oxygen to the central metal atom[15]. The signals of azomethine appeared to be deshielded as they showed a downfield shift compared to the respective ligands indicating coordination through azomethine nitrogen atom[16]. The multiplets in the region 6.46-8.83 ppm were assigned to aromatic ring protons.

3. 3. Electronic Spectra

The electronic spectrum of Pd(II) complex display bands at 22600-23419 cm^{-1}, 27777-28500 cm^{-1} and 29411-30300 cm^{-1} which may be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions respectively[17]. These transitions correspond to the three d-d spin forbidden transitions from the lower lying d levels to the empty d_{x2-y2} orbitals, the ground state $^1A_{1g}$ and excited states corresponding to the transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. It is in fairly good agreement with the transitions suggested for Pd(II) complexes having square planar environment of ligands[18,19]. This is further supported by diamagnetic behaviour of Pd(II) from the magnetic susceptibility measurements.

3. 4. Thermal analysis

The thermal decompositions of the complexes were studied using the TGA technique in air within the range 30-1000°C at 10 °C/min. The thermograms of Pd(L^1)$_2$, Pd(L^2)$_2$ and Pd(L^3)$_2$ do not show any significant loss between R.T to 120 °C indicating absence of water molecules as it is thermally stable upto 200 °C. It was observed that for all the complexes decomposition begins around 250-300 °C and are completely decomposed around 550-650 ºC. After decomposition metal oxide remain as a residue[20-24]. The percentage loss at decomposition temperature was in agreement with the calculated values.

3. 5. XRD Analysis

In X-ray diffractogram of the complexes, major refluxes were recorded in the range 5° to 60° 2θ value. The major refluxes were measured and corresponding *d*-values were obtained using Bragg's equation. The independent indexing of major refluxes was carried out using least square method. The miller indices *h, k, l* were calculated and refined by using Back − cal program on computer. The complexes were successfully indexed to monoclinic system with Z = 16 for all the complexes[21]. The lattice parameters are summarized in Table 3. The correctness of *d*–values was confirmed by comparing the observed density with that calculated from the X–ray diffractogram.

Table 3. Crystal Lattice Parameters of Metal Complexes.

Complex	a(Aº)	b(Aº)	c(Aº)	αº	βº	γº	D_{obs} (g/cm^3)	D_{cal} (g/cm^3)	Vol. (A^3)
[Pd(L^1)$_2$]	13.4778 ± 0.013	13.9495 ± 0.0242	16.8129 ±0.0235	90	87.32	90	1.4205	1.3985	3009.77

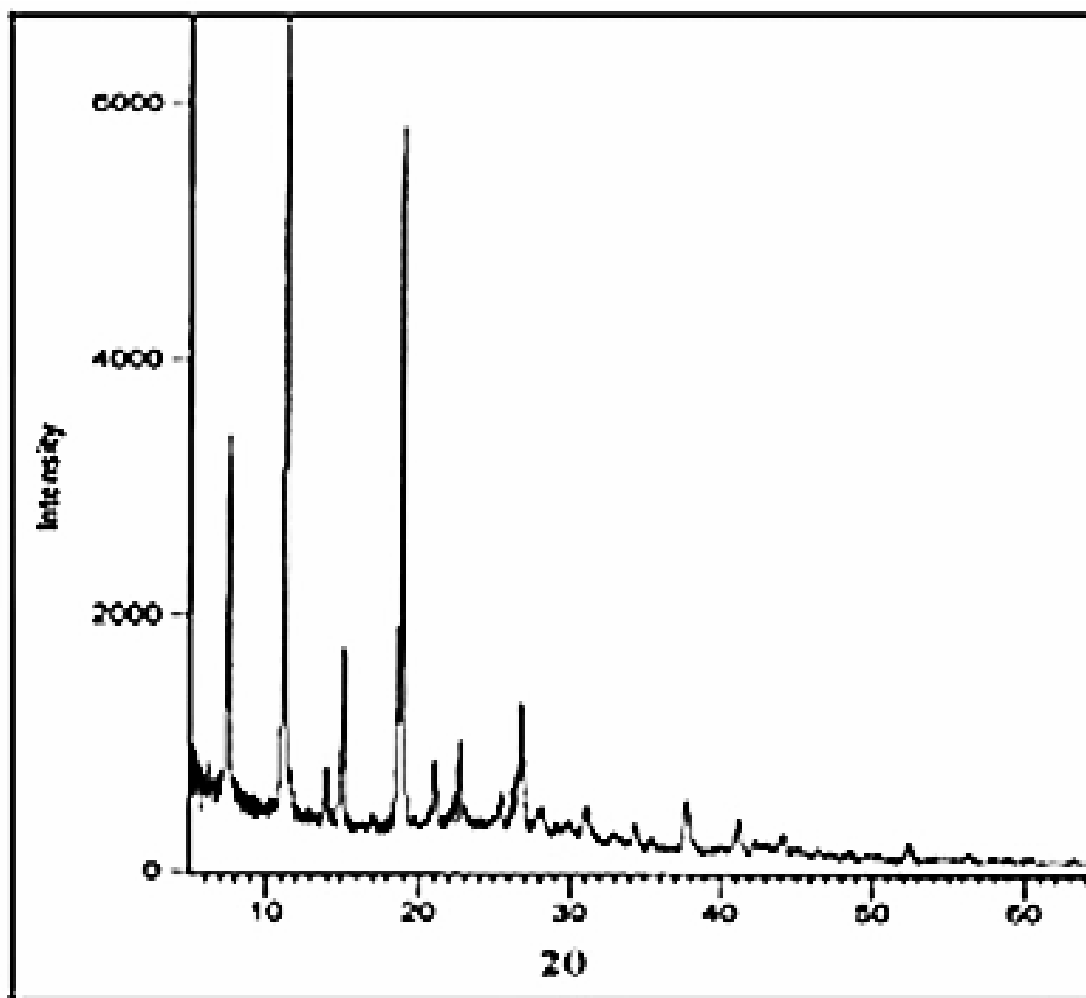| $[Pd(L^2)_2]$	14.8131 ± 0.0200	18.6662 ± 0.0185	21.4753 ± 0.0524	90	86.83	90	1.7224	1.5180	2753.02
$[Pd(L^3)_2]$	21.6319 ±0.0331	20.5460 ±0.1070	36.1623 ±0.2845	90	72.21	90	1.7861	1.7802	15882.09

Figure. 2. X – Ray Diffractogram of $Pd(L^1)_2$.

4. CONCLUSIONS

The Schiff base and their Pd(II) complexes were characterized by elemental analysis, conductance measurements, IR, ^1H NMR, uv-vis spectra, thermal and XRD studies. On the basis of above data these Schiff bases appear to behave as bidentate ligand coordinating through the deprotonated phenolic oxygen and azomethine nitrogen in Pd(II) complexes and exhibit square planar structure.

The proposed structures are:
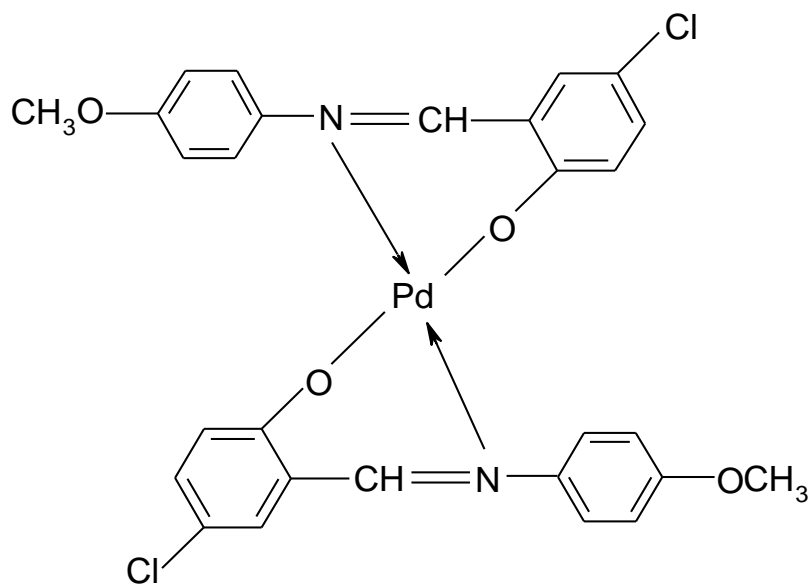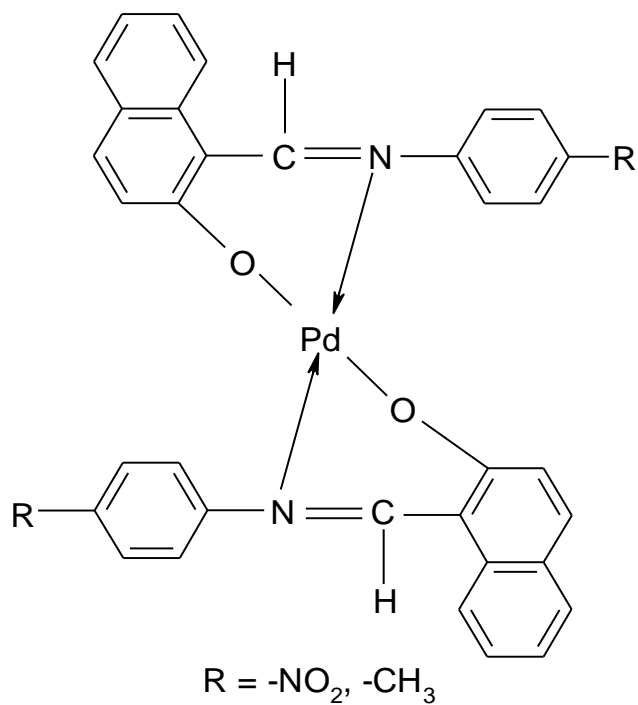
R = -NO₂, -CH₃

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