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Synthesis and Characterization of Pd (II) Schiff Base Metal Complexes

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ABSTRACT

Pd (II) complexes were synthesized from Schiff base bis(2-hydroxynaphthalidene)-1,4-phenyldiamine and N,N'-bis(2-hydroxynaphthalidene)benzidine using metal: ligand in (1:2) mole ratio. The structures of the ligands and their metal complexes were elucidated by analytical and spectroscopic techniques viz. elemental analysis, I.R., mass, ¹HNMR and TGA. These Schiff bases are bidentate ligands gave square planar complex with Pd (II).

Keywords: 2-Hydroxy-1-naphthaldehyde, *p*-phenylenediamine, Benzidine, Pd (II) complexes, Square planar geometry, Bidentate ligands

INTRODUCTION

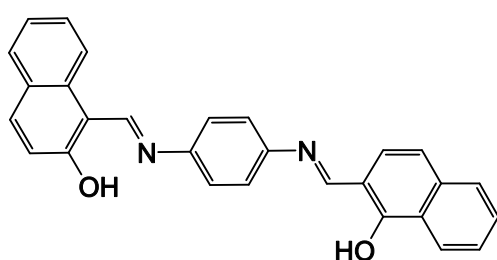
The extensive research is going on in the synthesis of Schiff bases of 2-hydroxy-1-naphthaldehyde and their metal complexes due to their wide range of applications in medicine, catalyst, biology and in technology up gradation [1-3]. The metal complexes of Schiff bases were used as catalysts in organic reactions and also showed biological activities [4, 5]. Palladium complexes has been investigated for its anti-HIV, antifungal and antitumor activities [6]. The Schiff base complexes showed antimicrobial activity, and hence are used in formulation of drugs [7, 8]. In this paper we described the synthesis and characterization of Schiff bases and their Pd (II) complexes. Extensive work have been carried out involving synthesis of Schiff bases containing O, N and S as donor atoms and their metal complexes [9]. Bidentate Schiff bases were used for the synthesis of various complexes and were characterized [10, 11]. Tetradentate Pd (II) complexes of Schiff bases were also derived from aldehydes and amine which showed antibacterial activity against Gram +ve and Gram -ve bacteria [12]. Unsymmetrical tetradentate Schiff bases and their Pd (II), Pt (IV) complexes were characterized and tested in vitro against 10 human pathogenic bacteria [13]. The Pd (II) complexes of Schiff bases e.g. 2,6-diacetylpyridine bis(thiosemicarbazone) have been synthesized and calculation of ligand field parameters were done by using various energy level diagrams and were tested against plant pathogenic fungi and bacteria [14].

MATERIALS AND METHODS

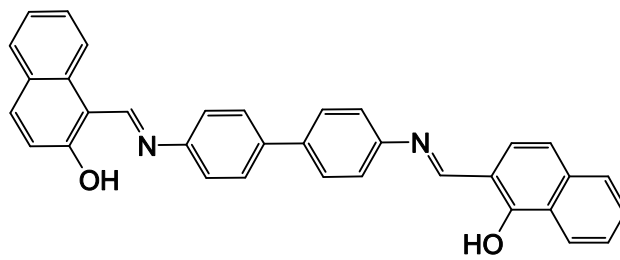
All reagents used were of analytical reagent type and were used without further purification. Analytical grade solvents were used without further purification. 2-Hydroxy-1-naphthaldehyde, benzene-1,4-diamine, benzidine, tetrakis(triphenylphosphine)palladium (0) were purchased from Sigma Aldrich, Merck and Spectrochem chemicals. Melting points were determined on a Gallenkamp melting point apparatus. The ^1H (300 MHz) and ^{13}C (75MHz) NMR spectra were recorded on a Bruker Avance II 500 MHz Spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS), and multiplicities are given as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. UV-visible spectra were recorded on Shimadzu 2450 UV-visible spectrophotometer. TGA analysis was done on Shimadzu DTG 60 analyzer. ICP-Atomic Emission spectroscopy analysis was performed on inductively coupled plasma ARCOS, Germany Atomic Emission spectrometer at IIT, Powai, Bombay. Mass spectra were recorded on a Shimadzu LC-MS:EI QP 2010A mass spectrometer with an ionization potential of 70eV. Elemental analyses were performed on Quest flash 1112 Series EA Analyzer at SAIF, Punjab University, Chandigarh. Molar conductivity of complexes was recorded using 1×10^{-3} M solutions in DMSO on Toshniwal TSM 15 conductivity metre. Reactions were monitored by thin layer chromatography (TLC), carried out on 0.2 mm silica gel 60 F₂₅₄ Merck plates using UV light (254 and 366 nm) for detection.

Synthesis of bis(2-hydroxynaphthalidene)-1,4-phenyldiamine (**L**₁)

2-Hydroxy-1-naphthaldehyde (3.44 g, 0.02 mol) was dissolved in ethanol (100 mL) and stirred at room temperature. To this stirring solution of *p*-phenylenediamine (1.08 g, 0.01 mol) in ethanol (50 mL) was added. Reaction mixture was refluxed for about 3 hrs. The red colored solid product separated was filtered and washed with anhydrous ethanol followed by acetone. It was recrystallized from chloroform. Yield: 87%, 3.65 g M.P. 309°C Lit 310°C [23, 24].



L₁ Schiff's Base C₂₈H₂₀N₂O₂



L₂ Schiff's Base C₃₄H₂₄N₂O₂

Synthesis of Schiff base N, N'- bis(2-hydroxynaphthalidene)benzidine (**L**₂)

Similar procedure was used for synthesis of N,N'- bis(2-hydroxynaphthalidene)benzidine (**L**₂) using benzidine (1.84g, 0.01 mol) and orange red product separated was recrystallized from xylene. Yield: 85%, 4.2 g, M.P. 326°C Lit 326° [25]

Synthesis of Pd (II) complex (C₁₀₀H₇₈N₂O₂P₄Pd₂)

Tetrakis(triphenylphosphine)palladium (2.312g, 0.02 mol) was dissolved in hot ethanol(50 mL) and slowly added to bis(2-hydroxynaphthalidene)-1,4-phenyldiamine (0.416g, 0.01 mol) in hot chloroform (50 mL). Reaction mixture was refluxed at 60°C for overnight. The dark brown crystalline product obtained after filtration was washed with chloroform and then with diethyl ether. Yield: 75%, 1.26 g.

Synthesis of Pd (II) complex (C₁₀₆H₈₂N₂O₂P₄Pd₂)

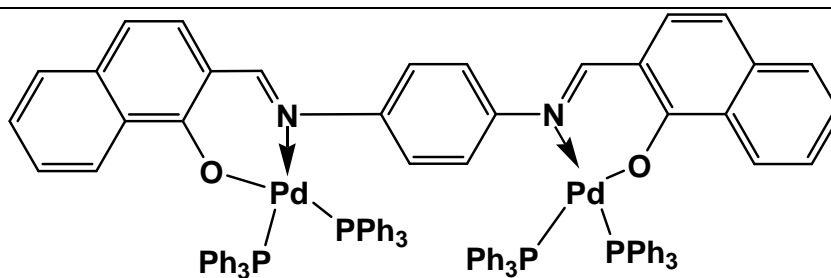
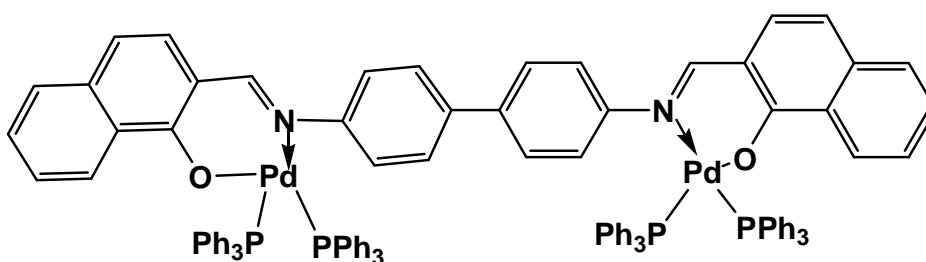
Tetrakis(triphenylphosphine)palladium (2.312g, 0.02 mol) was dissolved in hot ethanol (50 mL) and slowly added to Schiff base N,N'- bis(2-hydroxynaphthalidene)benzidine (0.492g, 0.01 mol) in hot chloroform (50 mL). Reaction mixture was refluxed at 60°C for overnight. The dark brown crystalline product obtained after filtration was washed with chloroform and then with diethyl ether. Yield: 71%, 1.25 g.

Table 1: Physical and Analytical Data of Schiff base and Pd (II) complexes

Sr. No.	Ligand/Metal Complex	Mol. Weight		% Yield	Colour	M.P. (°C)	Elemental Analysis Found (% Calculated)			
		Theoretical	Observed				C	H	N	M
1	C ₂₈ H ₂₀ N ₂ O ₂ (L ₁)	416.47	417.6	87	Red	310	79.62 (80.75)	4.76 (4.84)	6.14 (6.73)	-
2	C ₃₄ H ₂₄ N ₂ O ₂ (L ₂)	492.57	493.6	85	Orange Red	326	83.54 (82.91)	5.83 (4.91)	5.19 (5.69)	-
3	C ₁₀₀ H ₇₈ N ₂ O ₂ P ₄ Pd ₂	1674.44	-	75	Dark brown	>300°C	71.6 (71.64)	4.59 (4.69)	1.53 (1.67)	10.06 (12.70)
4	C ₁₀₆ H ₈₂ N ₂ O ₂ P ₄ Pd ₂	1752.53	-	71	Dark brown	>300°C	72.43 (72.65)	4.6 (4.72)	1.54 (1.60)	6.68 (6.07)

Table 2 I.R. and U.V.-visible Spectroscopic Data of Schiff base and Pd (II) complexes

Sr. No.	Ligand/Metal Complex	IR Spectral Data cm ⁻¹						¹ HNMR spectral data
		V _(OH)	V _(C=N)	V _(Ph-C-O)	V _(Pd-N)	V _(Pd-O)	V _(PPh₃)	
1	C ₂₈ H ₂₀ N ₂ O ₂ (L ₁)	3051	1622	1330	-	-	-	7.2-7.8 δ (16 H, m, Ar-H), 8.2 δ (CH=N) 9.4 δ (1H, s, NH)
2	C ₃₄ H ₂₄ N ₂ O ₂ (L ₂)	3039	1622	1311	-	-	-	7.0-7.95 δ (20 H, m, Ar-H), 8.54 δ CH=N) 9.73 δ (1H, s, NH)
3	C ₁₀₀ H ₇₈ N ₂ O ₂ P ₄ Pd ₂	-	1612	1394	501	453	698	-
4	C ₁₀₆ H ₈₂ N ₂ O ₂ P ₄ Pd ₂	-	1605	1395	536	450	693	-

Expected structure of C₁₀₀H₇₈N₂O₂P₄Pd₂ complex with Schiff's Base (L₁)Expected structure of C₁₀₆H₈₂N₂O₂P₄Pd₂ complex with Schiff Base (L₂)

RESULTS AND DISCUSSION

2-Hydroxy-1-naphthaldehyde and benzene-1,4-diamine (0.01 mol), benzidine. (0.01 mol) in ethanol was reacted at reflux temperature. The solid obtained during reaction was filtered and recrystallized from ethanol and further were characterized by analytical and spectroscopic techniques. Tetrakis(triphenylphosphine)palladium (0.02 mol) was reacted with Schiff bases (L₁ and L₂) (0.01 mol) in ethanol at reflux temperature afforded dark brown colour

complex of Pd (II), was washed with dry ethanol and acetone. Both Pd (II) metal complexes were characterized by elemental analysis, I.R., and TGA and electronic spectra.

Molar conductance measurements:

The lower value of molar conductance ($2.2- 3.7 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$) for DMSO solutions of the prepared complexes indicated the non-electrolytic nature [15].

IR Spectra:

IR spectral data of ligands L_1 and L_2 showed medium intensity at 3051 cm^{-1} and 3039 cm^{-1} due to the phenolic OH. The lower frequency indicates the presence of intramolecular hydrogen bonding [16]. This bond was absent in Pd (II) complexes indicating the formation of new bond between metal and oxygen [17]. The up field shift in stretching frequency by $60-65 \text{ cm}^{-1}$ supported phenolic C-O bonding [18, 19]. The stretching frequency at 1330 and 1311 cm^{-1} in ligands is due to C-O bond which was shifted to higher frequency in complexes.

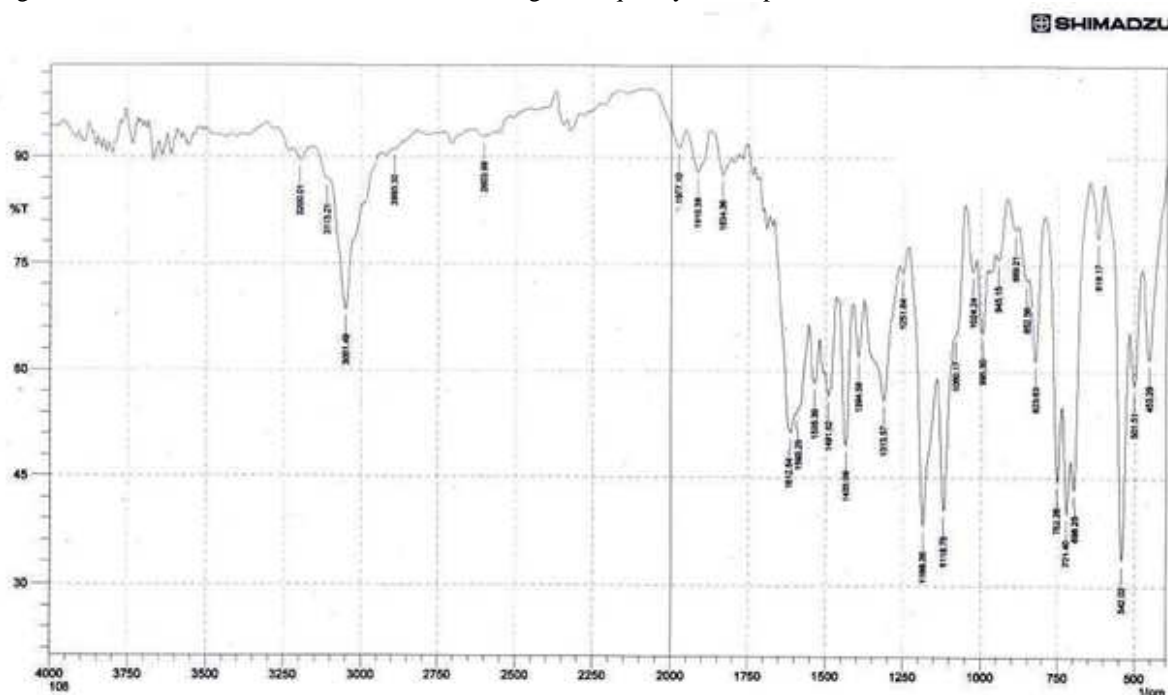


Fig.1: IR spectrum of Pd (II) complex with Schiff's base (L_1)

The IR Spectra of ligand showed band at 1622 cm^{-1} which was due to C=N confirms the formation of Schiff base. This stretching frequency at 1622 cm^{-1} C=N bond in the ligand is shifted to 1612 cm^{-1} and 1605 cm^{-1} in complexes, indicating coordination of azomethine group through nitrogen atom with metal ion [20-22]. The low stretching frequency to 501 cm^{-1} and 536 cm^{-1} indicates the formation of new Pd-N bond. Similarly the low stretching frequency at 453 cm^{-1} and 450 cm^{-1} indicates the formation of new Pd-O bond.

^1H NMR spectra of Schiff bases:

The ^1H NMR spectra of Schiff base (L_1 and L_2) were recorded in CDCl_3 showed peak at $\delta 7.00-8.00$ ppm were corresponded to aromatic protons. The doublet at 9.4 ppm indicates the associated hydrogen belongs to NH rather than OH group, which supports keto-enol tautomerism and found in accordance with literature data [23 24, 25].

Mass spectra of Schiff bases:

The mass spectra of Schiff's bases were recorded and were agreed with their stoichiometry. The molecular ion peak was observed at 417.6 and 493.6 for having Schiff base molecular formula $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_2$ and $\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_2$ respectively.

Thermogravimetric Analysis:

Figure 3 and 4 represents the TGA-DTA curve of the synthesized Pd (II) complex. The TGA-DTA curves showed the weight loss in two steps.

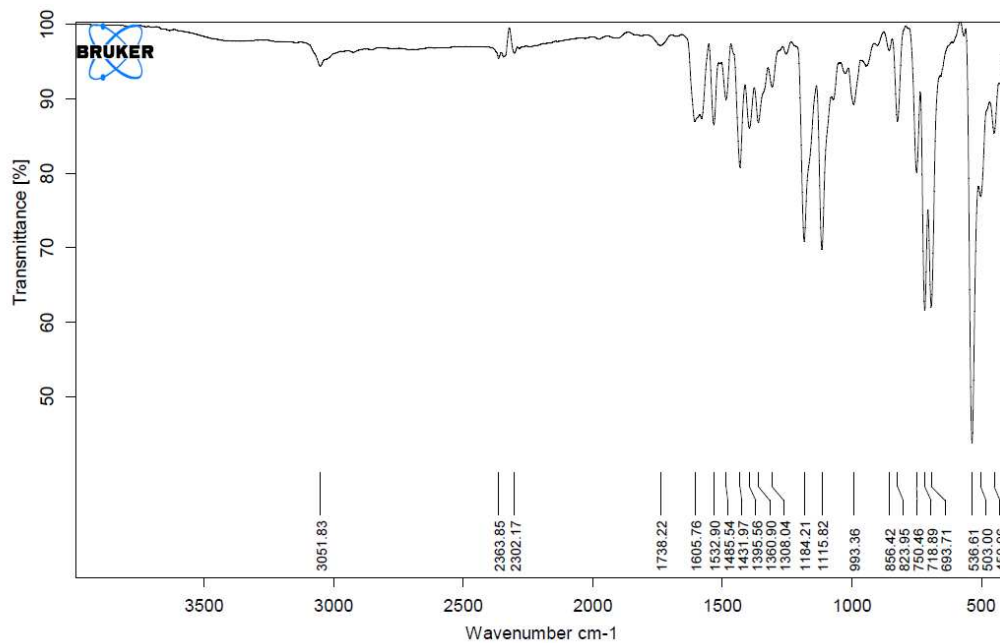


Fig.2: IR spectrum of Pd (II) complex with Schiff's base (L_2)

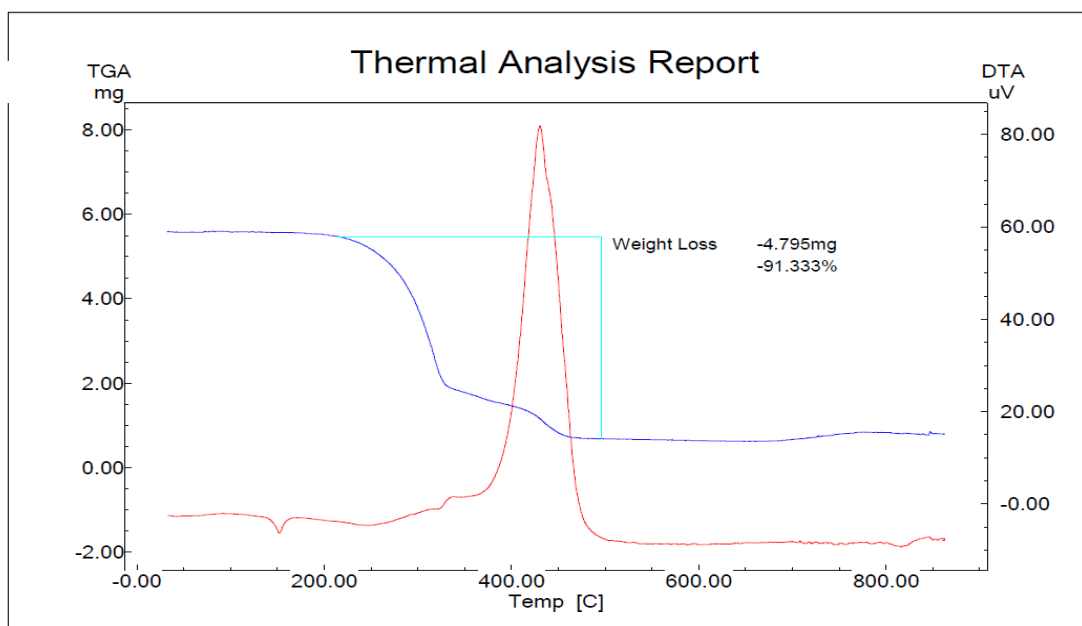


Fig.3: TGA thermogram of Pd (II) complex of $L_1(C_{100}H_{78}N_2O_2P_4Pd_2)$ & $L_2(C_{106}H_{82}N_2O_2P_4Pd_2)$

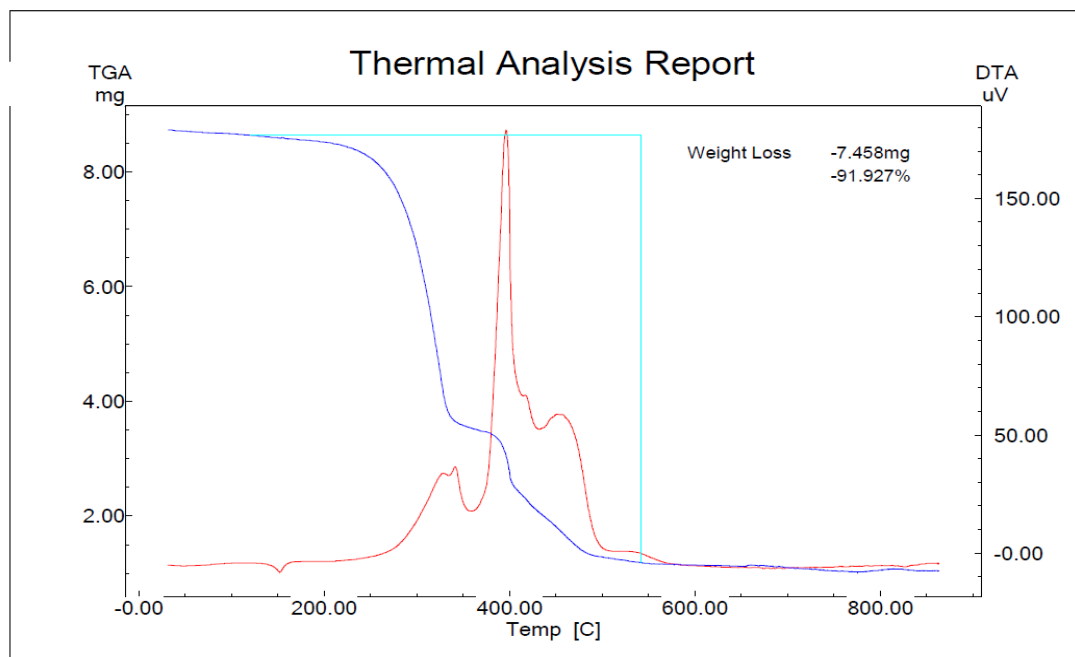


Fig. 4: TGA thermogram of Pd (II) complex ($C_{106}H_{82}N_2O_2Pd_2$)

The first weight loss was due to the loss of adsorbed water which was at about 200 to 300°C and the second exothermic loss due to decomposition of Pd-phosphine complex. The process accounts for one third of the total weight loss in the whole decomposition process from 200 to 600 °C according to the TGA result, with the major loss occurring between 200 to 450°C. Thus, TGA results indicated the decomposition temperature of Pd (II) complex at 300~450°C in air. The DTA analysis indicated that the decomposition of Pd (II) complex is an exothermic process [26].

CONCLUSION

On the basis of elemental analysis, spectral data such as IR, UV-Visible, mass and 1H -NMR, the Pd (II) complexes of bidentate Schiff's bases exhibit square planar geometry.

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