



Synthesis and Characterization of New Palladium(II) Schiff Base Complexes Derived from β -Diketones and Diamines

MRIDULA GUPTA* and SHEELA M. VALECHA

Department of Chemistry, K.C. College, Churchgate, Mumbai-400020, India

*Corresponding author: E-mail: mridula.gupta@kccollege.edu.in

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A new series of heterocyclic Schiff bases were prepared from condensation of 1-phenyl-3-methyl-4-acetyl/benzoyl-pyrazolone with 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl ether, resulting in the formation of four novel Schiff base ligands. These ligands were then treated with ethanolic solution of PdCl₂, to form corresponding palladium(II) complexes. These complexes were characterized by elemental analysis, IR, ¹H NMR, TGA, magnetic susceptibility measurements and UV-visible absorption spectroscopy. All the Pd(II) complexes were found to have one coordinated water molecule. Schiff base ligands chelated with the metal atom through two donor sites N and O of azomethine (-C=N-) and phenolic (-OH) groups, respectively.

Keywords: Pyrazolone, Schiff base, Palladium(II) complexes.

INTRODUCTION

The design and synthesis of multidentate phenoxy Schiff base ligands and their metal complexes, have been a fascinating area of research, because of their wide range of biological activities. Their applications in conjunction with transition metals, is quite useful. They also serve as backbone for the synthesis of various heterocyclic compounds [1]. Tetradentate Schiff base is one of the most extensively studied ligands in coordination chemistry, as it can coordinate with a large number of transition metals [2,3]. It also possesses numerous interesting properties like antibacterial, antifungal, anti-inflammatory and other pharmacological properties [4].

Pyrazolone and its derivatives are an important class of heterocyclic compounds, which find applications in many drugs. They represent an interesting template for combinational and medicinal chemistry, due to their simple preparation and wide biological actions [5]. In fact, these heterocyclic compounds are of continued interests, due to their potent bioactivities and their application as therapeutic drugs. The importance of palladium, as a transition metal, lies in its wide spectrum of applications. The successful use of platinum (II) complexes, as potent anticancer drugs, has attracted interest of many scientists [6]. There is also much interest in palladium(II) complexes,

as they are very similar to platinum(II) complexes, in terms of coordination process and geometry. Palladium(II) complexes are frequently used as model complexes, to study the interaction of Pt(II) with DNA and to *mimic* the binding properties of various platinum(II) species [7]. Several palladium complexes have been reported with bidentate amine ligands, which have shown anticancer activity comparable to cisplatin [8].

Aniline-palladium complexes of type *trans*-[PdCl₂-(NH₂Ph)₂] were synthesized and studied for their role as catalyst, in the Heck reaction. These newly synthesized complexes could efficiently catalyze the Heck coupling of bromobenzene with acetonitrile and ethyl acrylate [9]. Ligand salicylideneimine and ligand triphenylphosphine were complexed with palladium(II) to form Schiff base complexes. These complexes were studied, for their role as catalyst in Suzuki-Miyaura coupling reactions of various aryl boronides and aryl boronic acids [10].

Reaction of a Schiff base cyclometalated derivative with triphosphine lead to the formation of ligand, which formed first penta-coordinated complexes with palladium(II). The geometry of these complexes was reported to be distorted trigonal bipyramidal [11]. New complexes of azomethine palladium(II) of type *cis*-[PdCl₂L], where L = PhN=NC(OMe), were synthesized and characterized. These complexes were also studied

for their biological activity and showed a considerable anti-tumour activity [12].

Several thiosemicarbazone ligands are complexed a variety of metal ions due to their variable donor properties, structural diversity and biological applications [13]. In view of the facts mentioned above and as part of our efforts to discover new potentially useful complexes, present research is focussed on the synthesis and characterization of palladium (II) complexes derived from novel Schiff base ligands, coordinated through N and O atoms.

EXPERIMENTAL

All the chemicals and solvents used in this research were of AR grade. Elemental analysis was performed on a Thermo-Finnigan CHNO analyzer (IIT-B). The FTIR spectra was recorded on Shimadzu IR-Prestige-21, spectrophotometer in the range of 4000-350 cm^{-1} . The UV-visible spectra of ligands and complexes were recorded in DMF/DMSO using Shimadzu UV 2600 in the range of 190-800 nm.

^1H NMR spectra was taken on NMR (300 MHz-NMR2). At room temperature, magnetic susceptibility was carried out on powdered samples, using a Sherwood Scientific Magnetic Susceptibility balance while thermal analysis was carried out on Perkin-Elmer, USA, Model Diamond TG/DTA. The samples were heated from 30 to 1020 $^{\circ}\text{C}$ at the rate of 10 $^{\circ}\text{C}/\text{min}$.

Synthesis of 3-methyl-1-phenylpyrazol-5-one: Schiff base, 3-methyl-1-phenylpyrazol-5-one was synthesized according to the reported method [14]. The yield of 3-methyl-1-phenylpyrazol-5-one was about 55 g (85 %).

Synthesis of 4-acetyl/benzoyl-3-methyl-1-phenylpyrazol-5-one: 4-Substitued-3-methyl-1-phenylpyrazol-5-ones were synthesized according to the reported method [15].

Synthesis of ligands (L1-L4): Ligands **L1**, **L2**, **L3** and **L4** were synthesized by the reaction of 4-acetyl/benzoyl-3-methyl-1-phenylpyrazol-5-one with two different diamines *viz.* 4,4'-diamino diphenyl methane and 4,4'-diamino diphenyl ether. Pyrazol-5-one derivative and amine were mixed in a 2:1 molar proportion, in solvent ethanol followed by the addition of few drops of conc. HCl to expedite the reaction. The reaction mixture was refluxed on water bath for 18-22 h. Upon cooling, the product separated out, which was filtered and then recrystallized from alcohol. The yields of the products were in the range of 55-60 %.

Synthesis of complexes: The ligand dissolved in DMF and the equimolar quantity of palladium(II) chloride was mixed in minimum quantity of ethanol. The ligand solution in DMF

was slowly added to an ethanolic solution of metal(II) chloride, with constant stirring on magnetic stirrer. The metal to ligand stoichiometry ratio was 1:1. The reaction was stirred for 4-5 h. To maintain pH in the range of 8.0-9.0, NaOH solution (1N) was added dropwise to the reaction mixture. After 4-5 h, solid complex separated out. It was filtered on suction pump and air dried.

RESULTS AND DISCUSSION

The synthesis of four ligands *viz.* 4',4''-bis[(1'-phenyl-3'-methyl-5'-oxodihydropyrazol-4'-yl)methylimino]diaminodiphenyl methane (**(HPMPZM)₂dpm, L1**), 4',4''-bis[(1'-methyl-3'-methyl-5'-oxodihydropyrazol-4'-yl)phenylimino]diaminodiphenyl methane (**(HPMPZP)₂dpm, L2**), 4',4''-bis[(1'-phenyl-3'-methyl-5'-oxodihydropyrazol-4'-yl)methylimino]diaminodiphenyl ether (**(HPMPZM)₂dpe, L3**) and 4',4''-bis[(1'-methyl-3'-methyl-5'-oxodihydropyrazol-4'-yl)phenylimino]diaminodiphenyl ether (**(HPMPZP)₂dpe, L4**) and their corresponding palladium(II) complexes were successfully synthesized. Table-1 shows the elemental analysis of all the palladium(II) complexes.

TABLE-1
ELEMENTAL ANALYSIS DATA OF PALLADIUM(II)
SCHIFF BASE COMPLEXES DERIVED FROM
 β -DIKETONES AND DIAMINES

Complexes	Elemental analysis (%): Calcd. (Found)		
	C	H	N
[PdL1(H ₂ O)]·7H ₂ O	50.54 (50.47)	5.40 (4.16)	9.57 (9.28)
[PdL2(H ₂ O)]·4H ₂ O	61.69 (61.60)	5.03 (3.93)	9.19 (8.90)
[PdL3(H ₂ O)]·7H ₂ O	51.04 (50.99)	5.43 (4.18)	9.92 (9.63)
[PdL4(H ₂ O)]·7H ₂ O	54.88 (54.83)	4.97 (3.82)	8.35 (8.10)

Infrared analysis: The IR data of key peaks of ligands **L1**, **L2**, **L3** and **L4** with their corresponding palladium(II) complexes are presented in Table-2. The IR spectra of the free ligands were characterized mainly by the broad bands at 3260-3000 and 3000-2340 cm^{-1} , which were assigned to symmetric and antisymmetric vibrations ν_{OH} , respectively which are low due to intermolecular or intramolecular hydrogen bondings [16]. The $\nu\text{CH}_{\text{arom.}}$ and $\nu\text{CH}_{\text{aliph.}}$ peaks were observed at 2930-2820 and 2380-2300 cm^{-1} , respectively. The strong bands around 1615-1580 cm^{-1} were assignable to $\nu\text{C}=\text{N}$ azomethine group (presence of this peak strongly indicated the condensation of aldehydic group of pyrazolone ring and primary amines [17] and $\text{C}=\text{N}$ pyrazolone groups [18,19]. The Schiff base ligands also showed distinct bands between 1250-1220 cm^{-1} due to δ_{OH} [19]. The bands observed at 1388-1360 cm^{-1} were attributed

TABLE-2
KEY IR BANDS (cm^{-1}) OF SYNTHESIZED SCHIFF BASE AND THEIR CORRESPONDING PALLADIUM(II) COMPLEXES

Ligand/complex	$\nu(\text{OH})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{N})$ azometh.	$\nu(\text{C}=\text{N})$ pyrazol.	$\nu(\text{C}-\text{O})$	$\delta(\text{OH})$	$\delta(\text{H}_2\text{O})$	$\nu(\text{Pd}-\text{N})$	$\nu(\text{Pd}-\text{O})$
(HPMPZM) ₂ dpm (L1)	3027-3065	—	1618.35	1580	1384.95	1225.82	—	—	—
[PdL1(H ₂ O)]·7H ₂ O	3028 br	3605-3420	1647.28	1571.09	1386.88	—	849.68	457.15	570.95
(HPMPZP) ₂ dpm (L2)	3027.41-3065.02	—	1628.95	1592.31	1384.95	1227.4	—	—	—
[PdL2(H ₂ O)]·4H ₂ O	3334.92	3536-3420	1647.28	1577.84	1382.06	—	849.68	458.11	564.2
(HPMPZM) ₂ dpe (L3)	3400 br	—	1626.06	1540.23	1384.9	1250.89	—	—	—
[PdL3(H ₂ O)]·7H ₂ O	3415.93-3498.87	3520.09-3888.49	1631.78	1571.09	1389.77	—	849.68	430.13	580.57
(HPMPZP) ₂ dpe (L4)	3033.19	—	1630.88	1573.98	1388.81	1246.07	—	—	—
[PdL4(H ₂ O)]·7H ₂ O	3031.26	3536.64-3031	1680.07	1527.69	1380.13	—	848.72	457.15	567.1

to vC-O phenolic group [20]. In the IR spectra of palladium(II) complexes with Schiff base ligands, all the bands shifted through a frequency range of 2-40 cm^{-1} indicated a successful complexation. The -C=N- peaks were clearly blue shifted, compared to ligand peaks, indicating conjugating effect between metal ions and ligands [17,19]. Presence of coordinated water in complexes was indicated by appearance of band in the region of 815-880 cm^{-1} [20,21]. All the palladium(II) complexes, showed a broad strong absorption peaks at 3880-3400 cm^{-1} indicating the presence of coordinated water molecule [14,15,20,22]. New bands with medium to weak intensities, appeared in the regions 700-500 and 490-400 cm^{-1} , which supports the formation of Pd-O ($\nu_{\text{M-O}}$) and Pd-N ($\nu_{\text{M-N}}$), respectively [18,23].

Thermal analysis: Thermal stability of palladium(II) complexes with Schiff base ligands and the thermal degradation steps of the complexes were studied through TGA. TG analysis of the samples was recorded in the temperature range of 30-1020 $^{\circ}\text{C}$. The significant weight loss observed from 80-120 $^{\circ}\text{C}$, which indicated a loss of lattice water molecules. The loss percentage indicated that seven water molecules of crystallization in the complexes, except for the complex with ligand **L2**, where four water molecules of crystallization were observed. Weight loss in the decomposition range 150-300 $^{\circ}\text{C}$ was in agreement with the removal of one coordinated water molecule in all the complexes. All the four complexes showed significant loss of weight in this range indicating the presence of one molecule of coordinated water. Significant mass loss of about 60-68 % was observed in the range of 300-600 $^{\circ}\text{C}$ (Table-3). This might be due to the disintegration of whole complex.

NMR analysis: ^1H NMR spectra of ligands and complexes were carried out in deuterated DMSO, as both ligands and Pd(II) complexes were insoluble in commonly organic solvents. The ligands **L1**, **L2**, **L3** and **L4** showed signals for phenolic OH at 12.662-12.933 ppm [18]. Phenolic 'H' peaks were not observed in the spectra of complexes indicated a deprotonation of phenolic OH. Peaks due to methylene (-CH₂-) group were seen in ligands

L1 and **L2** at δ 3.90-4.07 ppm and on complexation methylene peaks underwent shift to δ (3.56-3.98) ppm in complexes [PdL1(H₂O)]·7H₂O and [PdL2(H₂O)]·4H₂O. In ligands **L3** and **L4**, the methylene peaks were not seen as -CH₂- group was replaced by -O- (non-coordinated). Ligands **L2** and **L4** showed extra peaks at δ 6.16-6.99 ppm showed a replacement of acetyl group by benzoyl groups. These aromatic protonic peaks underwent shift on complexation to the range 6.24-6.96 in complexes [PdL3(H₂O)]·7H₂O and [PdL4(H₂O)]·7H₂O (Table-4).

UV-visible analysis: All the four Pd(II) complexes showed a magnetic moment in the range 1.4-2.3 B.M. indicated the presence of two unpaired electrons. The absorption spectra was recorded in DMSO in the wavelength region of 190-800 nm. The bands in the UV-Vis spectra of complexes were assigned upon comparison with the spectrum of the free ligand. For the free ligand, an absorption between 200-300 and 300-400 nm bands was assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (charge transfer), respectively. These transitions, also represent transitions, due to the presence of azomethine group (-C=N-). In ligands **L1** and **L4**, the peaks at 305-310 nm also shows a shoulder at 340-380 nm. Upon complexation, these bands underwent blue shift or red shift (Table-5). New weak bands appeared in the visible region of 450-800 nm in the complexes. These weak transitions were due to $d-d$ transitions.

Conclusion

Four new ligands and their corresponding palladium (II) complexes have been successfully synthesized and characterized. The characterization data proposed the probable structure of the metal complexes as shown in Fig. 1. This study indicates that stoichiometry of the complexes is 1:1 with ligand. The ligand coordinates with palladium(II) through N donor atom, which is part of the azomethine group and the phenolic -O of the ligands. Two deprotonated phenolic-O, which has negative charge, balances the +2 charge of palladium, thereby making the coordination sphere electrically neutral. All the complexes have one coordinated water molecule with the central metal

TABLE-3
THERMOGRAVIMETRIC ANALYSIS DATA OF PALLADIUM(II) SCHIFF BASE
COMPLEXES DERIVED FROM β -DIKETONES AND DIAMINES

Complex	Mass by formula	Loss of water of crystallization at 80-100 $^{\circ}\text{C}$		Loss of water of crystallization at 150-300 $^{\circ}\text{C}$	
		Found (%)	Calculated (%)	Found (%)	Calculated (%)
[PdL2(H ₂ O)]·7H ₂ O	844.42	15.0	14.92	2.0	2.13
[PdL2(H ₂ O)]·4H ₂ O	914.42	8.0	7.90	2.0	1.97
[PdL2(H ₂ O)]·7H ₂ O	846.42	14.5	14.88	2.0	2.13
[PdL2(H ₂ O)]·7H ₂ O	970.42	13.0	12.90	2.5	1.90

TABLE-4
NMR (δ ppm) DATA OF SYNTHESIZED SCHIFF BASE AND THEIR CORRESPONDING PALLADIUM(II) COMPLEXES

Ligand/complex	CH ₃ protons at 3,3'	-CH ₂ -	Phenyl	Phenolic proton
(HPMPZM) ₂ dpm (L1)	2.501-3.358	4.066	7.136-8.014	12.933
[PdL1(H ₂ O)]·7H ₂ O	2.511-3.362	3.852-3.975	7.009-8.251	-
(HPMPZP) ₂ dpm (L2)	2.501-3.370	3.8-3.9	6.844,6.872, 6.974 and 7.001-8.013	12.706
[PdL2(H ₂ O)]·4H ₂ O	2.504-3.362	3.587-3.561	6.2365-6.962, 7.088-8.250	-
(HPMPZM) ₂ dpe (L3)	1.00-2.389-3.369	-	7.141-8.022	12.912
[PdL3(H ₂ O)]·7H ₂ O	1.103-2.339-3.362	-	7.186-8.250	-
(HPMPZP) ₂ dpe (L4)	1.447-2.496-3.362	-	6.755,6.784, 6.988 and 7.017-8.022	12.662
[PdL4(H ₂ O)]·7H ₂ O	1.519-2.496-3.62	-	6.538, 6.905, 6.770 and 7.029-8.250	-

TABLE-5
ELECTRONIC SPECTRAL DATA BANDS OF SYNTHESIZED SCHIFF
BASE AND ITS CORRESPONDING PALLADIUM(II) COMPLEXES

Ligand/Complex	λ_1 n \rightarrow π^*	λ_1 $\pi \rightarrow \pi^*$	λ_4 d-d	λ_5 d-d	λ_6 d-d
(HPMPZM) ₂ dpm (L1)	271.59	346.91 (shoulder at 381.73)	–	–	–
[PdL1(H ₂ O)]·7H ₂ O	261.24	308.55	551.68	676.94	780.12
(HPMPZP) ₂ dpm (L2)	262.70	338.02	–	–	–
[PdL2(H ₂ O)]·4H ₂ O	260.19	316.10	559.80	646.27	768.51
(HPMPZM) ₂ dpe (L3)	289.36	349.79	–	–	–
[PdL3(H ₂ O)]·7H ₂ O	259.23	308.72	576.37	693.98	769.99
(HPMPZP) ₂ dpe (L4)	311.35	347.59 (shoulder at 382.07)	–	–	–
[PdL4(H ₂ O)]·7H ₂ O	263.97	310.85	623.94	703.95	786.33

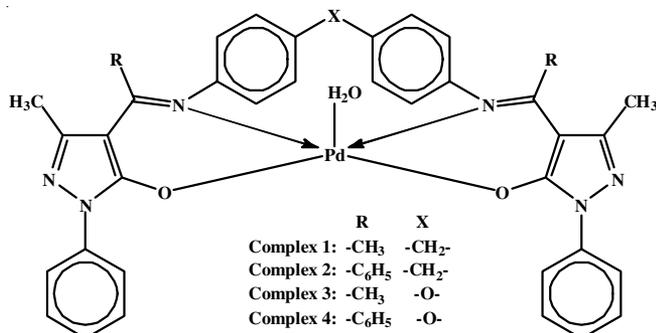


Fig. 1. Proposed structure of palladium(II) Schiff base complexes derived from β -Diketones and diamines

atom and 4 to 7 molecules of water of crystallization confirmed by IR and TGA.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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