

## Study on Palladium(II) Complexes of Schiff Base†

(MRS.) SHAILA DAGAONKAR and B.H. MEHTA\*

*Department of Chemistry*

*University of Bombay, Vidyanagari*

*C.S.T. Road, Santacruz (East), Bombay-400 098, India*

A series of eight complexes of palladium(II) have been synthesized using Schiff bases derived from 2-hydroxy-1-naphthaldehyde and various amines. The complexes have been characterized by elemental analysis, magnetic measurements, UV/visible absorption spectral studies, infrared spectral studies, diffused reflectance spectra and conductance measurements. All the complexes were assigned square-planar configuration.

### INTRODUCTION

Metal complexes of Schiff base ligands obtained from substituted benzaldehyde and various aromatic amines have been extensively studied<sup>1,2</sup>. However, systematic study on palladium(II) with various Schiff bases is not reported. The present study is attributed to the preparation and characterization of Pd(II) complexes derived from 2-hydroxy-1-naphthaldehyde and various amines.

### EXPERIMENTAL

Different Schiff bases were prepared by condensing 2-hydroxy-1-naphthaldehyde with various aromatic amines namely 2-amino-phenol (L1), 2-amino-4-chloro-phenol (L2), anthranilic acid (L3), *p*-toluidine (L4), *o*-toulidine(L5), sulphanic acid (L6), 4-amino-phenol (L7) and *o*-phenylene diamine (L8). The aldehyde and amine were taken in stoichiometric quantities and refluxed in ethanolic medium. Schiff bases were characterized by m.p., elemental and spectral analysis.

To prepare the metal complexes the aqueous solution of Pd(II) chloride was gradually added to 1% ethanolic solution of ligand in slight more than 1:2 stoichiometry composition. The mixture was refluxed for 3-4 h. On cooling, crystalline metal complex was separated, which was filtered, washed with alcohol and subsequently dried over fused CaCl<sub>2</sub> in vacuum at room temperature.

The metal complexes were characterized by elemental and spectral data. Palladium was estimated by gravimetric method<sup>3</sup> while nitrogen, carbon and hydrogen were estimated by microanalytical method. The result of these elemental analyses is given in Table-1. The conductance measurements of all the

†Presented in Sixth "Research Scholar's Meet" organised by Indian Chemical Society (Bombay branch) on 4th February 1994.

complexes in nitrobenzene were made on Toshniwal conductivity bridge. The IR spectra of ligands and complexes were recorded on FTIR 4200 Shimadzu spectrophotometer in the range 4000–400  $\text{cm}^{-1}$  using KBr pellet technique. The electron absorption spectra for these metal complexes are recorded on UV2100 Shimadzu spectrophotometer. While diffused reflectance spectra were recorded on CZ VSU2P spectrophotometer.

TABLE-1  
PHYSICAL AND ANALYTICAL DATA OF THE COMPLEXES

Complex (Colour)	% Analysis Found (Calcd.)		$\Omega_m$ mho $\text{cm}^{-2}/\text{mole}$	Electronic absorption spectra	
	N	Pd		UV/visible absorption peaks in kK	Diffused reflectance kK
Pd L <sub>1</sub> Pd(C <sub>17</sub> H <sub>11</sub> NO <sub>2</sub> ) (Green)	3.76 (3.80)	28.44 (28.88)	$2.500 \times 10^{-4}$	$\nu_1$ 22.82 $\nu_2$ 23.80 25.00	9.09, 10, 12.5, 20
Pd L <sub>2</sub> Pd(C <sub>17</sub> H <sub>10</sub> NO <sub>2</sub> Cl) (Brown)	4.08 (3.47)	27.58 (26.40)	$5.957 \times 10^{-4}$	$\nu_1$ 22.22 $\nu_2$ 25.00 30.76*	8.69, 10, 13.33, 20
Pd L <sub>3</sub> Pd(C <sub>18</sub> H <sub>13</sub> NO <sub>3</sub> ) (Brown)	3.48 (3.53)	27.10 (26.84)	$2.291 \times 10^{-4}$	$\nu_1$ 22.22 31.25*	9.09, 10, 11.11, 13.33, 20
Pd L <sub>4</sub> Pd(C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> ) <sub>2</sub> (Green)	4.30 (4.46)	17.90 (16.98)	$1.698 \times 10^{-4}$	$\nu_1$ 22.72 $\nu_2$ 24.09 30.76*	9.5, 10.5, 12.5, 14.2, 18.2
Pd L <sub>5</sub> Pd(C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> ) <sub>2</sub> (Brown)	4.28 (4.46)	17.69 (17.98)	$1.320 \times 10^{-4}$	$\nu_1$ 22.72 30.76*	9.09, 11.1, 14.2, 18.2
Pd L <sub>6</sub> Pd(C <sub>17</sub> H <sub>13</sub> NSO <sub>4</sub> ) <sub>2</sub> (Greenish black)	3.50 (3.69)	15.05 (14.02)	$4.651 \times 10^{-4}$	$\nu_2$ 23.80 31.25*	9.09, 10.5, 12.5, 15.3
Pd L <sub>7</sub> Pd(C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub> ) <sub>2</sub> (Greenish Black)	4.32 (4.44)	15.16 (16.81)	$1.730 \times 10^{-4}$	$\nu_2$ 24.69 31.25*	9.09, 10.5, 12.5, 15.3, 22.2
Pd L <sub>8</sub> Pd(C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O) <sub>2</sub> (Brown)	4.50 (4.23)	15.15 (16.11)	$7.142 \times 10^{-4}$	$\nu_1$ 22.27 $\nu_2$ 23.25 29.41*	8.69, 10, 13.33, 22.2

\*Charge transfer transitions

L<sub>1</sub> = 2-hydroxyl-naphthaldehyde 2-amino phenol.

L<sub>2</sub> = 2-hydroxyl-naphthaldehyde 2-amino-4-chloro phenol.

L<sub>3</sub> = 2-hydroxyl-naphthaldehyde anthranilic acid

L<sub>4</sub> = 2-hydroxyl-naphthaldehyde *p*-toluidine.

L<sub>5</sub> = 2-hydroxyl-naphthaldehyde *o*-toluidine.

L<sub>6</sub> = 2-hydroxyl-naphthaldehyde sulphanilic acid.

L<sub>7</sub> = 2-hydroxyl-naphthaldehyde-4-amino phenol

L<sub>8</sub> = 2-hydroxyl-naphthaldehyde *o*-phenylene diamine.

## RESULTS AND DISCUSSION

The result of elemental analysis (Table-1) suggests that Pd(II) complexes of ligands L1, L2, L3 have 1:1 stoichiometry, while those complexes derived from L4, L5, L6, L7, L8 exhibit 1:2 stoichiometry. These complexes are insoluble in common organic solvents. The molar conductance of these complexes in nitrobenzene at concentration of  $10^{-3}$  M falls in the range  $1.32 \times 10^{-4}$  to  $7.14 \times 10^{-4}$  mho  $\text{cm}^2/\text{mole}^{-1}$ . The low values of molar conductance of these complexes indicate that they are non-electrolytes in nature. All the complexes were found to be diamagnetic in nature. Pd(II) has completely filled 4d shell and hence its complexes are expected to be diamagnetic in nature. This also suggests that probably the ligand environment around Pd(II) is square-planar.

It is reported<sup>4</sup> that Pd(II) generally coordinates with square-planar stereochemistry and exhibits three absorption bands which are due to allowed d-d transition as follows:  $^1A_{1g} \rightarrow ^1B_{1g}$  ( $\nu_1$ ),  $^1A_{1g} \rightarrow ^1E_{1g}$  ( $\nu_2$ ),  $^1A_{1g} \rightarrow ^1A_2$  ( $\nu_3$ ).

The spectra of green coloured Pd(II) complexes show presence of broad d-d bands in the range 18–22 kK which are assignable to  $\nu_1$  transition while  $\nu_2$  transitions can be assigned to band appearing in the region 24–26 kK. It is reported that charge transfer transition generally appears around 30 kK. The spectra of Pd(II) complexes exhibit broad band in the region of 30 kK, which can be assigned to the charge transfer transition. The third d-d transition region overlaps with the charge transfer region. The fairly good agreement of these transitions suggests that Pd(II) complexes have square-planar environment of ligands. It is reported<sup>6</sup> that Pd(II) complexes with square-planar geometry crystallize as green colour complexes which support our findings.

TABLE-2.  
KEY IR FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE SCHIFF BASES AND  
THEIR Pd(II) COMPLEXES

	$\nu(\text{OH})$	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L1	3100	—	1638	—	—
PdL1		—	1630	549	480
L2	3400	—	1630	—	—
PdL2		—	1625	670	640
L3	3096	—	1618	—	—
PdL3		—	1610	650	605
L4	3096	—	1620	—	—
Pd(L4) <sub>2</sub>		—	1600	540	460
L5	3450	—	1620	—	—
Pd(L5) <sub>2</sub>		—	1600	720	650
L6	3076	—	1647	—	—
Pd(L6) <sub>2</sub>		—	1640	680	650

L7	3220	—	1630	—	—
Pd(L7) <sub>2</sub>	—	—	1622	680	650
L8	3000	2900	1640	—	—
Pd(L8) <sub>2</sub>	—	2851	1630	560	460

The salient features of IR spectra for ligands as well as Pd(II) complexes are summarised in Table-2. Infrared spectra of Schiff bases exhibit broad and highly intense band characteristic of  $\nu(\text{OH})$  stretching in the range  $3400\text{--}3000\text{ cm}^{-1}$ . The weak band of aromatic  $\nu(\text{C—H})$  stretching overlaps in the same region. However, absence of this band in the corresponding Pd(II) complexes indicates involvement of phenolic oxygen in coordination to metal. In ligands as well as in Pd(II) complexes the strong and sharp band is observed in the range  $1647\text{--}1600\text{ cm}^{-1}$ . This band is assigned to  $\nu(\text{C=N})$  stretching vibration. It is noticed that this band appears at lower frequency in complexes with respect to corresponding ligands. The lowering of this band suggests complexation through azomethine nitrogen<sup>7</sup>. The metal-nitrogen and metal-oxygen bonding are supported by new band appearing in the low frequency range  $700\text{--}550\text{ cm}^{-1}$  and  $650\text{--}450\text{ cm}^{-1}$  respectively<sup>8</sup>.

The band appearing in the spectrum of Schiff base L8 at  $2900\text{ cm}^{-1}$  with the weak intensity is assigned to  $\nu_{\text{NH}_2}$ . In corresponding metal complex this band is not splitted and makes it impreative that  $\text{—NH}_2$  group has not participated in the formation of coordinate bond.

On the basis of above structural investigation of Pd(II) complexes of Schiff bases it can be concluded that Pd(II) coordinates with ligands with square planar configuration.

### ACKNOWLEDGEMENT

One of the authors S.A. Dagaonkar is thankful to U.G.C. India for awarding fellowship.

### REFERENCES

1. A. Syamal and K.S. Kale, *Curr. Sci. (India)*, **44**, 254 (1975).
2. A. Syamal and B.K. Gupta, *Indian J. Chem.*, **23A**, 260 (1984).
3. A.I. Vogel, *Text Book of Quantitative Inorganic Analysis*, Longman Green and Co. Ltd., London (1975).
4. R.C. Saxena, C.L. Jain, R. Benjamin and S.K. Sangal, *J. Indian Chem. Soc.*, **63**, 435 (1986).
5. C.P. Gupta, P.K. Kanungo and R.K. Mehta, *J. Indian Chem. Soc.*, **56**, 826 (1979).
6. K. Dey and R.L. De, *J. Inorg. Nucl. Chem.*, **37**, 1530 (1975).
7. B.R. Singhvi, M.R. Mali and R.K. Mehta, *Curr. Sci. (India)*, **46**, 636 (1977).
8. G.T. Behanke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).