

## ARTICLE

## Synthesis and Characterization of Schiff Base Ligands and Their Palladium(II) Complexes

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**Abstract:** This paper is concerned with the preparation and characterization of Schiff base ligands derived from the condensation of salicylaldehyde with three different diamines, namely, ethylenediamine, *o*-phenylenediamine, and *trans*-1,2-diaminocyclohexane. The Schiff base ligands were characterized by elemental analysis, melting point, FTIR, UV-Vis, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The Schiff base ligands are reacted with palladium(II) ion via direct reaction or using a template method. Identical complexes were obtained from the two methods with the same percentage yields. The formulas obtained for the complexes are PdC<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>, [PdL<sup>1</sup>]Cl<sub>2</sub>; PdC<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>2</sub>, [PdL<sup>1</sup>]Br<sub>2</sub>; PdC<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, [PdL<sup>1</sup>](BF<sub>4</sub>)<sub>2</sub>; PdC<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>, [PdL<sup>2</sup>]Cl<sub>2</sub>; PdC<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>2</sub>, [PdL<sup>2</sup>]Br<sub>2</sub>; PdC<sub>20</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>·BF<sub>4</sub>, [PdL<sup>2</sup>]BF<sub>4</sub>; PdC<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>, [PdL<sup>3</sup>]Cl<sub>2</sub>; PdC<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Br<sub>2</sub>, [PdL<sup>3</sup>]Br<sub>2</sub>; PdC<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O, [PdL<sup>3</sup>]·2H<sub>2</sub>O. The isolated compounds were characterized based on their melting points, elemental analyses, conductivity measurements, nuclear magnetic resonance, FTIR and electronic absorption spectra.

**Keywords:** Schiff base ligand, Palladium (II) complexes.

### Introduction

Recently, there has been some interest in the preparation of various Schiff base ligands due to their preparative accessibilities, structural varieties and varied denticities<sup>[1]</sup>. Metal-chelate Schiff base complexes have played an important role in developing stereochemical models in main group and transition metal coordination chemistry, mainly due to their stability, ease of preparation and structural variability<sup>[2–6]</sup>. Schiff bases are generally excellent chelating agents and have multidisciplinary applications in chemical, biological and pharmacological fields<sup>[7]</sup>. This class of compounds also exhibited remarkable activity against a wide range of organisms and are known to have medicinal importance, and found, thus, applications in pharmacology and in drug design<sup>[8]</sup>. The applications of Schiff base ligands and their complexes, especially in biology, including antibacterial, antifungal, anticancer, antioxidant,

and anti-inflammatory applications, have been reported<sup>[9–16]</sup>.

Our group is interested in the synthesis of novel, mixed-donor Schiff base ligands and their complexes<sup>[17,18]</sup>. Recently, we have reported the crystal structure of the Schiff base N,N'-[bis(pyridin-2-yl)formylidene]ethane-1,2-diamine (bpdf), and studied the non-covalent supramolecular chemistry involved in the crystal structure of bpdf ligand<sup>[18]</sup>. The significant role of the Schiff base ligands in the area of coordination chemistry as chelating ligands, along with the importance of palladium(II) complexes as catalysts, prompted us to prepare and characterize palladium(II) complexes of N,N'-bis(salicylidene) ethylenediamine (C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>1</sup>), N,N'- bis (salicylidene) -1,2-phenylenediamine (C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>2</sup>) and N,N'-bis(salicylidene)-1,2-diaminocyclohexane (C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>3</sup>) Schiff base ligands. Elemental analysis, conductivity measurements, FT-IR, UV-visible, <sup>1</sup>H and <sup>13</sup>C NMR of these complexes

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are presented and discussed. The catalytic activities of these new palladium complexes are under ongoing investigation.

## Materials and Methods

The solvents used were of analytical reagent grade and were used as purchased. The compounds ethylenediamine, *o*-phenylenediamine, *trans*-1,2-diaminocyclohexane, salicylaldehyde, and tetrakis(acetonitrile)palladium(II) tetrafluoroborate,  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ , were purchased from Aldrich, and palladium(II) chloride and palladium(II) bromide were purchased from BDH, England. The starting complexes, *cis*-dichlorobis(benzonitrile)palladium(II), *cis*- $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ , and *trans*-dibromobis(benzonitrile)palladium(II), *trans*- $[\text{Pd}(\text{PhCN})_2\text{Br}_2]$ , were synthesized as described in the literature<sup>[19]</sup>.

The melting point was measured on an electrothermal melting point apparatus. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, USA. The infrared spectra were recorded as potassium bromide pellets over the range 4000–500  $\text{cm}^{-1}$  on a Maltson 5000 FTIR spectrometer. Conductivity measurements were carried out using a microprocessor conductivity meter model LF 537 at 25 °C to  $1 \times 10^{-3}$  M-solutions in dimethyl sulfoxide (DMSO). Electronic absorption spectra were recorded on a Perkin Elmer Lambda 25 UV/Vis Spectrometer using  $1 \times 10^{-5}$  M solutions in DMSO. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR experiments were conducted on a Bruker 400-MHz instrument (400 MHz Bruker Ultra Shield) at Jordan University of Science and Technology with tetramethyl silane (TMS) as a reference and deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) or (CDCl<sub>3</sub>) as a solvent.

### General Procedure for the Preparation of the Schiff Base Ligands L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup>

The following Schiff base ligands, namely, N,N'-bis(salicylidene)ethylenediamine (C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>1</sup>); N,N'-bis(salicylidene)-1,2-phenylenediamine (C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>2</sup>); and N,N'-bis(salicylidene)-1,2-diaminocyclohexane (C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>, L<sup>3</sup>) were prepared according to the literature<sup>[20]</sup> by the following general procedure. To a stirring solution of the diamines (ethylenediamine, *o*-phenylenediamine and *trans*-1,2-diaminocyclohexane; 2.30 mmol) in 25 ml ethanol, a solution of salicylaldehyde (4.60 mmol) in ethanol (10 ml) was dropwise added

over a period of 1 hour. The yellow-orange precipitate appeared after 30 min of the addition. The reaction mixture was stirred for another 24 h. For ligand L<sup>2</sup>, the reaction mixture was refluxed for 36 h. The product was filtered off, washed with diethyl ether, and dried in oven at 40 °C. The Schiff base ligands were solid. L<sup>1</sup> and L<sup>3</sup> were yellow, while L<sup>2</sup> had an orange color. The percentage yield was found to be 70% for L<sup>1</sup> and 85% for both L<sup>2</sup> and L<sup>3</sup>. The ligands were characterized by elemental analysis, m.p., UV-visible, FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The analytical and physical data for the prepared ligands are presented in Table 1.

### General Procedure for the Preparation of the Complexes by the Direct Method.

A solution of L<sup>n</sup> (L<sup>1</sup> = C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>; L<sup>2</sup> = C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>; L<sup>3</sup> = C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>; 0.100 mmol) and sodium acetate trihydrate (0.200 mmol) in acetonitrile (20 ml) was dropwise added to a stirred solution of  $[\text{Pd}(\text{PhCN})_2\text{X}_2]$  (X = Cl, Br; 0.100 mmol) or  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  in 10 ml acetonitrile over a period of 1–2 h. The reaction mixture was stirred for another 24 h. The yellow-orange solid was filtered off and washed with diethyl ether. Formulas of complexes obtained were verified using elemental analysis and spectroscopic data to have the general formulas  $[\text{PdL}^n]\text{X}_2$  (where L<sup>n</sup> = L<sup>1</sup>, X = Cl, Br and BF<sub>4</sub>; L<sup>2</sup> = Br; L<sup>3</sup>, X = Cl and Br),  $[\text{PdL}^2\text{Cl}]\text{Cl}$ ,  $[\text{PdL}^2]\text{BF}_4$ , and  $[\text{PdL}^3] \cdot 2\text{H}_2\text{O}$ .

### General Procedure for the Preparation of the Complexes by the Template Method.

A solution of the diamine (ethylenediamine, *o*-phenylenediamine, *trans*-1,2-diaminocyclohexane; 0.390 mmol) in acetonitrile (10 ml) was added dropwise over a period of 1–2 h, to a stirred mixture solution of salicylaldehyde (0.780 mmol) and  $[\text{Pd}(\text{PhCN})_2\text{X}_2]$  (X = Cl, Br; 0.390 mmol) in 20 ml acetonitrile. The reaction mixture was stirred for another 24 h. A yellow-orange solid was filtered and washed with diethyl ether. Identical products were obtained in the direct method with the same percentage yield.

All the products were dried under vacuum at 40 °C. The analytical and physical data of the new complexes are summarized in Table 2. The yields were calculated based on the metal salt.

**Table 1. Melting points, Elemental analysis, FTIR bands<sup>a</sup>, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR chemical shifts<sup>b</sup>, and UV-visible spectra for the Schiff base ligands<sup>c</sup>.**

Ligand / Formula	M.P. (°C)	Elemental Analysis Calculated (found)%			FT-IR bands <sup>a</sup>		<sup>1</sup> H-NMR <sup>b</sup> (δ, ppm)	<sup>13</sup> C-NMR <sup>b</sup> (δ, ppm)	λ <sub>max</sub> <sup>c</sup> (nm)	Assignment
		%C	%H	%N	(cm <sup>-1</sup> )	Assignment				
L <sup>1</sup> C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	121–123	71.62 (71.69)	6.01 (5.88)	10.44 (10.48)	3445br	ν O-H	13.25(s, 2H), 8.36 (s, 2H), 7.34–7.25 (dt, 4H), 6.99– 6.88 (dd, 4H), 3.94 (s, 4H).	59.5, 117.2, 118.5, 131.2, 132.3, 133.0, 160.9, 166.5	251 260 319	LC LC LC
					2901w	ν C-H, aliph.				
					1636s	ν C=N, imine				
					1578m, 1499m	ν C=C arom.				
					1285m	ν C-O phen.				
750s	ν (C-H, arom. deformation)									
L <sup>2</sup> C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	160–162	75.93 (74.50)	5.10 (4.85)	8.86 (8.88)	3445br	ν O-H	13.04(s, 2H), 8.61 (s, 2H), 7.38–7.31 (m, 4H), 7.24– 7.20 (m, 2H), 7.05–7.02(d, 2H), 6.93–6.90(td, 4H)	117.9, 119.0, 119.1, 119.8, 127.8, 132.4, 133.4, 143.0, 162.0, 163.8	260 sh 276 320 334	LC LC LC LC
					1614vs	ν C=N, imine				
					1526s, 1481s	ν C=C arom.				
					1276m, 1192m	ν C-O phen.				
					760s	δ C-N=C				
L <sup>3</sup> C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	88–90	74.51 (74.57)	6.88 (7.07)	8.69 (8.73)	2922m, 2849m	ν C-H, aliph.	13.25(s, 2H), 8.24(s, 2H), 7.25–7.19(m, 2H), 7.14– 7.11(m, 2H), 6.88–6.85(d, 2H), 6.80–6.75(td, 2H), 3.31–3.28(m, 2H), 1.89– 1.85(m, 4H), 1.45 (m, 4H)	24.2, 33.1, 72.8, 116.8, 118.6, 131.5, 132.2, 147.8, 161.0, 164.7	260 sh 276 320 334	LC LC LC LC
					1630vs	ν C=N, imine				
					1582m, 1503m	ν C=C arom.				
					1281s	ν C-O phen.				
					760w	δ C-N=C				

<sup>a</sup> Potassium bromide pellets were used to obtain the FTIR spectra in the range 4000–500 cm<sup>-1</sup>.

<sup>b</sup> <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were obtained in CDCl<sub>3</sub> as a solvent with TMS as the internal standard at 400 MHz and 100 MHz, respectively.

<sup>c</sup> UV-Vis was measured for 10<sup>-5</sup> M in DMSO. Molar absorptivity (ε × 10<sup>-3</sup>) in the range 11–52 l.mol<sup>-1</sup>cm<sup>-1</sup>. br, br; d, doublet; dd, doublet of doublet; m, multiplet; s, singlet; t, triplet; m, medium; s, strong; vs, very strong; w, weak.

**Table 2. Physical, chemical and spectroscopic properties of the prepared complexes<sup>a</sup>.**

Complex/Formula	M.P. °C	Yield (%)	Color	Elemental Analysis Calculated (found)%			$\Lambda_M^b$	FT-IR bands		<sup>1</sup> H-NMR ( $\delta$ , ppm)	$\lambda_{max}$ (nm)	Assignment
				%C	%H	%N		cm <sup>-1</sup>	Assignment			
[PdL <sup>1</sup> ]Cl <sub>2</sub> / PdC <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	310–312	67	yellow	43.12 (42.89)	3.62 (3.56)	6.29 (6.20)	74.3	3432b 1628w 1540s, 1495m 1235w, 1140w 760s 675w, 531w	$\nu$ O-H, $\nu$ C=N, imine $\nu$ C=C arom. $\nu$ C-O phen. $\delta$ C-N=C $\nu$ M-N	8.25 (s), 8.22 (s), 7.76 (d), 7.44 (m), 7.22 (dd), 5.00 (s), 3.91 (s).	259, 285 sh 317 sh, 372 sh 398	LC LC LMCT
[PdL <sup>1</sup> ]Br <sub>2</sub> / PdC <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Br <sub>2</sub>	290–292	85	pale brown	35.95 (35.74)	3.02 (3.00)	5.24 (5.16)	75.8	1640m 1562s, 1413s 644w 524w	$\nu$ C=N, imine $\nu$ C=C, arom. $\delta$ N=C-C $\nu$ M-N	8.15 (s), 8.12 (s), 7.74 (d), 7.46 (m), 7.20 (dd), 5.06 (s), 3.90 (s)	257, 278 sh 364 sh 401 sh	LC LC LMCT
[PdL <sup>1</sup> ](BF <sub>4</sub> ) <sub>2</sub> / PdC <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>	230–233	89	green	35.04 (34.39)	2.94 (2.65)	5.11 (4.79)	66.4	1636s 1541m, 1448m 1340w, 1303w 1084s	$\nu$ C=N, imine $\nu$ C=C, arom. $\nu$ C-O $\nu$ B-F	8.10 (s), 7.66 (d), 7.52 (t), 7.08 (t), 5.0 (s), 3.92 (s)	259, 282 sh 312 sh 400	LC LC LMCT
[PdL <sup>2</sup> Cl]Cl/ PdC <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	239–241	52	yellow	48.66 (47.52)	3.27 (3.15)	5.67 (5.38)	18.5	3435b 1626w 1539s, 1498m 1238w, 1145w 763s 678w, 532w	$\nu$ O-H $\nu$ C=N, imine $\nu$ C=C arom. $\nu$ C-O phen. $\delta$ C-N=C $\nu$ M-N	8.95 (s), 8.82 (s), 8.60 (s), 8.43–8.28 (m), 8.17 (d), 8.09 (s), 7.94 (s), 7.86 (s), 6.13 (s), 5.83 (d)	258, 275, 282, 294, 317, 335, 456 sh	LC LC LMCT
[PdL <sup>2</sup> ]Br <sub>2</sub> / PdC <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Br <sub>2</sub>	280–282	52	pale orange	41.23 (40.64)	2.77 (2.69)	4.81 (4.63)	91.1	3435b 1639s 1564s, 1413s	$\nu$ O-H, $\nu$ C=N, imine $\nu$ C=C arom.	8.85 (s), 8.78 (s), 8.55 (s), 8.40–8.21 (m), 8.17 (d), 8.10 (s), 7.91 (s), 7.84 (s), 6.12 (s), 5.81 (d)	258, 281 sh 381 sh	LC LMCT
[PdL <sup>2</sup> ]BF <sub>4</sub> / PdC <sub>20</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> .BF <sub>4</sub>	328–330	58	orange	47.20 (47.20)	2.97 (3.14)	5.51 (5.68)	20.6	3433b 1606s 1518m, 1437w 1180m 1080s 754w 540w	$\nu$ O-H, $\nu$ C=N, imine $\nu$ C=C arom. $\nu$ C-O phen. $\nu$ B-F $\delta$ C-N=C $\nu$ M-N	9.25(s), 8.39(m), 7.79-7.77(d), 7.50– 7.46(m), 7.08– 7.05(d), 6.77-6.73(t)	258, 294, 304, 318, 333, 354, 380sh, 470	LC LC LMCT

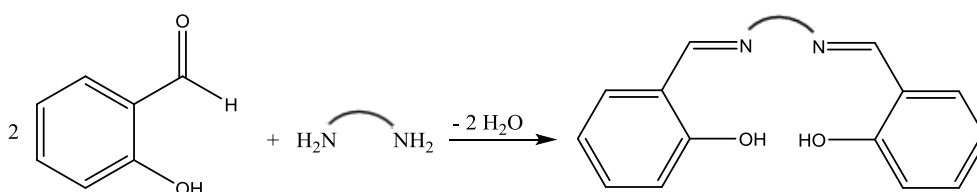
Complex/Formula	M.P. °C	Yield (%)	Color	Elemental Analysis Calculated (found)%			$\Lambda_M^b$	FT-IR bands		$^1\text{H-NMR}$ ( $\delta$ , ppm)	$\lambda_{\text{max}}$ (nm)	Assignment
				%C	%H	%N		$\text{cm}^{-1}$	Assignment			
[PdL <sup>3</sup> ]Cl <sub>2</sub> / PdC <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	310–312	80	yellow	48.07 (47.90)	4.44 (4.28)	5.61 (5.62)	57.2	2935m, 2858w 1629s 1513s, 1448s 1190m, 1151m 748m 563w	$\nu_{\text{C-H}}$ , arom. $\nu_{\text{C=N}}$ , imine $\nu_{\text{C=C}}$ , arom. $\delta_{\text{C-O}}$ , phenolic $\delta_{\text{C-N=C}}$ $\nu_{\text{M-N}}$	8.38 (br.s), 8.10 (br.s), 7.54 (br.s), 7.29 (br.s), 6.84(br.s), 6.55(br.s), 2.74(br.s), 1.85-1.24 (m), 0.81(br.s)	259, 275, 322 383 sh, 403	LC LMCT
[PdL <sup>3</sup> ]Br <sub>2</sub> / PdC <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> Br <sub>2</sub>	285–288	85	pale yellow	40.81 (40.64)	3.77 (3.60)	4.78 (4.69)	69.9	1640m 1562m, 1413w 696w	$\nu_{\text{C=N}}$ , imine $\nu_{\text{C=C}}$ , arom. $\delta_{\text{N=C-C}}$	ND <sup>c</sup>	257, 315 sh 342 413 sh	LC LC LMCT
[PdL <sup>3</sup> ].2H <sub>2</sub> O/ PdC <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> .2H <sub>2</sub> O	300–302	86	yellow	51.90 (52.40)	5.23 (4.61)	6.05 (6.05)	9.1	3445b 2937w 1631s 1533m, 1450w 1190m, 1151m 750w 665w	$\nu_{\text{O-H}}$ , $\nu_{\text{C-H}}$ , arom. $\nu_{\text{C=N}}$ , imine $\nu_{\text{C=C}}$ , arom. $\delta_{\text{C-O}}$ , phen. $\delta_{\text{C-N=C}}$ $\delta_{\text{N=C-C}}$	8.15 (s), 7.56 (d), 7.36 (t), 6.88(d), 6.60(m), 3.52 (br.s), 2.76(d), 1.85 (br.s), 1.60-1.52(m)	258, 280,318, 405	LC LMCT

<sup>a</sup> Potassium bromide pellets were used to obtain the FTIR spectra in the range 4000–500  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  was obtained in DMSO- $d_6$  as a solvent with TMS as the internal standard at 400 MHz. UV-visible was measured for  $10^{-5}$  M in DMSO. Molar absorptivity ( $\epsilon \times 10^{-3}$ ) in the range 5–70  $\text{l.mol}^{-1}\text{cm}^{-1}$ . <sup>b</sup> Molar conductance for  $10^{-3}$  M solutions in DMSO at 25 °C in ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ). <sup>c</sup> Not determined; br, broad; d, doublet; dd, doublet of doublet; m, multiplet; s, singlet; t, triplet; m, medium; s, strong; vs, very strong; w, weak.

## Results and Discussion

### Preparation and Physical Properties of Schiff Base Ligands and their Complexes

The Schiff bases used in the preparation of the complexes were prepared using the reported methods. The condensation of salicylaldehyde with the diamines (ethylenediamine, 1,2-phenylenediamine, and *trans*-1,2-diaminocyclohexane) gives the corresponding Schiff base ligands<sup>[21]</sup>. The elemental analyses, the important FT-IR bands along with their assignments, as

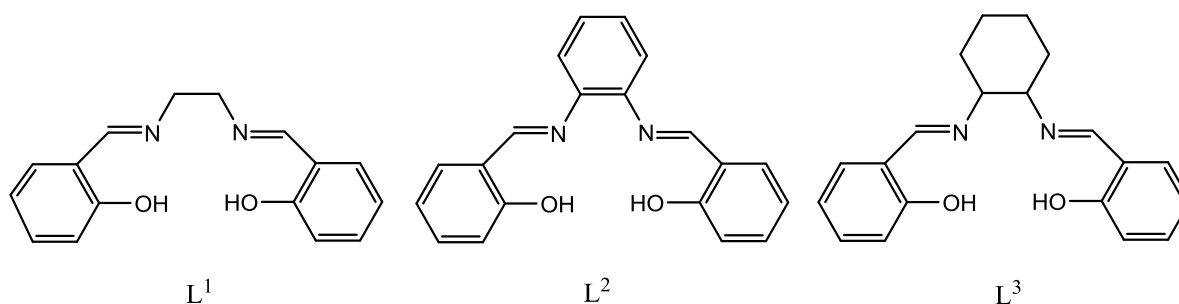


**Figure 1.** Synthesis of Schiff base ligands;  $\text{H}_2\text{N}-\text{NH}_2$  = ethylenediamine for  $\text{L}^1$ , *o*-phenylenediamine for  $\text{L}^2$  and *trans*-1,2-cyclohexanediamine for  $\text{L}^3$ .

Furthermore, the Schiff base ligands were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra. The  $^1\text{H}$ -NMR spectra for the isolated ligands give signals corresponding to the aromatic protons occurring in the range 6.90–7.38 ppm<sup>[20,24]</sup>. The signal at 13.04–13.25 ppm for the ligands  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$  may be explained by intramolecular hydrogen bonding<sup>[20,21ab,28]</sup>. The  $-\text{CH}=\text{N}-$  proton appears as a singlet in the range 8.24–8.61 ppm<sup>[20]</sup>. However,  $^1\text{H}$ -NMR signals arising from ethylene and cyclohexane protons for the ligands  $\text{L}^1$  and  $\text{L}^3$  appear in the region 3.94–1.45 ppm<sup>[22,28]</sup>. The  $^{13}\text{C}$ -NMR spectra support the formation of the Schiff base ligands. The  $^{13}\text{C}$ -NMR signals

well as the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR data for the prepared ligands are listed in Table 1. The FTIR spectra of the ligands showed medium to weak bands in the region of 2920–2843  $\text{cm}^{-1}$  which are due to the C-H stretching vibrations. Very strong to strong bands in the region of 1636–1614  $\text{cm}^{-1}$  assigned to the C=N azomethine group<sup>[20–23]</sup>. The bands that appear in the region 1582–1480  $\text{cm}^{-1}$  are due to the C=C stretching vibrations<sup>[24–27]</sup>. Figure 1 shows the formation of these Schiff base ligands.

corresponding to the aromatic carbons are visible in the region 117–166 ppm. Signals corresponding to the aliphatic carbons appear in the region 21–70 ppm<sup>[21c–28]</sup>. The electronic absorption bands for the ligands with their assignments are presented in Table 1. The ligand centered (LC) or  $\pi-\pi^*$  transitions usually occur in the ultraviolet region of the spectrum in the ranges of 251–334 nm. Based on these data, the isolated ligands have indicated the formation of the proposed Schiff base ligands as shown in Figure 2. These data are similar to previous reports for such Schiff base ligands<sup>[20,21bc,28]</sup>.



**Figure 2.** Structure of Schiff Base Ligands,  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$ .

These ligands were reacted with *cis*- $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ , *trans*- $[\text{Pd}(\text{PhCN})_2\text{Br}_2]$ , and  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ . The resulting complexes were identified by elemental analysis, melting point, molar conductivity, FTIR, electronic

absorption spectroscopy and  $^1\text{H}$ -NMR. The isolated complexes along with some of their physical properties are listed in Table 2. All isolated products are colored solids, stable in air, soluble only in DMSO and insoluble in most

common organic solvents. The yield was in the range of 52–86% (Table 2). The molar conductivity values for  $1 \times 10^{-3}$  M solutions of the complexes are given in Table 2 and were found to be in good agreement with those reported for similar complexes<sup>[29,30]</sup>.  $[\text{PdL}^3] \cdot 2\text{H}_2\text{O}$  behaves as a non-electrolyte, while  $[\text{PdL}^2\text{Cl}]\text{Cl}$  and  $[\text{PdL}^2]\text{BF}_4$  act as 1:1 electrolytes. The complexes  $[\text{PdL}^1]\text{Cl}_2$ ,  $[\text{PdL}^1]\text{Br}_2$ ,  $[\text{PdL}^1](\text{BF}_4)_2$ ,  $[\text{PdL}^2]\text{Br}_2$ ,  $[\text{PdL}^3]\text{Cl}_2$ , and  $[\text{PdL}^3]\text{Br}_2$  behave as a 1:2 electrolytes<sup>[30b]</sup>.

The electronic absorption for the complexes with their assignments is presented in Table 2. The assignment of the bands was done based on band intensity and location on the energy scale with similar previously characterized complexes. The intense ligand-metal charge transfer (LC)  $\pi$ - $\pi^*$  bands usually occur in the ultraviolet region, while those bands due to metal-ligand charge transfer appear in the region from near-UV to the end of the visible region. Complexes of Pd(II)

are suggested to have square planar geometry and are expected to be diamagnetic. The spectra of  $d^8$  square planar complexes are usually characterized by a strong band in the yellow to blue region (600–450 nm) and another band near the ultraviolet region, which is usually masked by the charge transfer band<sup>[31–33]</sup>. The electronic spectra for all complexes show a strong band in the range of (240–378) nm which is due to an intra-ligand charge transition (LC) or  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions<sup>[26]</sup>. Also, there are absorption bands in the range of (380–456) nm due to the existence of metal-ligand charge transfer (LMCT) transition. No d-d transition has been detected as they are possibly obscured by the broad charge transfer transitions. LMCT transitions are responsible for the characteristic brown, yellow or orange colors of metal ions complexes<sup>[34–36]</sup>. Figure 3 shows the UV-Vis spectrum of  $\text{L}^2$  and  $[\text{PdL}^2]\text{BF}_4$ .

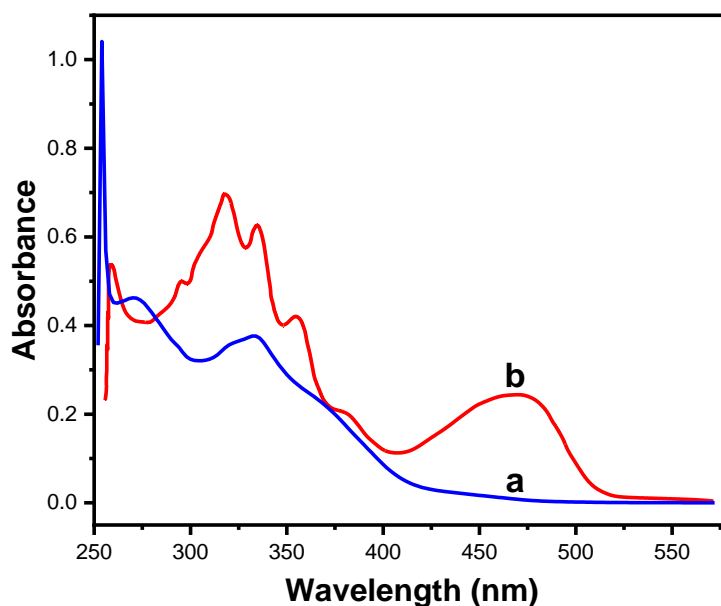


Figure 3. Electronic Spectrum of a)  $\text{L}^2$  and b)  $[\text{PdL}^2]\text{BF}_4$  complex.

The details of the FTIR spectra of the ligands and their complexes are summarized in Tables 3 and 4. The complexes of  $\text{L}^1$ ,  $\text{L}^2$ , and  $\text{L}^3$  showed medium to strong bands in the range 1606–1640  $\text{cm}^{-1}$  which are due to the stretching vibration of the azomethine group ( $\text{C}=\text{N}$ )<sup>[21,23–28]</sup>. The medium to strong bands that appear at the range 1562–1413  $\text{cm}^{-1}$  are assigned to the  $\text{C}=\text{C}$  stretching vibrations of the aromatic ring of the ligands<sup>[23–28,30]</sup>. Also, the azomethine group ( $\text{C}=\text{N}$ ) bond stretching shifts from a strong band

at 1614–1636  $\text{cm}^{-1}$  in the free ligands to a lower or higher region in the complexes at 1606–1640  $\text{cm}^{-1}$ . This shift is supporting the coordination of the ligand through the imine group nitrogen. The phenolic  $\text{C}-\text{O}$  stretching frequency is shifted from a medium band at 1285  $\text{cm}^{-1}$  in the free ligands to a weak band in the complexes at 1145–1340  $\text{cm}^{-1}$  which supports the coordination of the ligand through the phenolic oxygen<sup>[20,37]</sup>. The weak band appearing at 524–678  $\text{cm}^{-1}$  is assigned to the  $\text{Pd}-\text{N}$  bond, confirming the

coordination of the ligand to palladium(II)<sup>[23,26]</sup>. The strong band appearing for  $[\text{PdL}^1](\text{BF}_4)_2$  and  $[\text{PdL}^2]\text{BF}_4$  at  $1070\text{--}1084\text{ cm}^{-1}$  was assigned to B–F stretching in these complexes<sup>[24]</sup>. Furthermore, the broad band that appears in the range  $3430\text{--}3450\text{ cm}^{-1}$  for the complexes is due to the O–H stretching frequency of the phenolic group ( $\nu_{\text{O-H}}$ )<sup>[23]</sup>.

The  $^1\text{H-NMR}$  measurements of the Pd(II) complexes were carried out and are summarized in Table 3. The  $^1\text{H-NMR}$  spectra of complexes show signals in the range  $8.10\text{--}9.25\text{ ppm}$  corresponding to the  $-\text{CH}=\text{N}-$  protons, and  $6.50\text{--}7.76\text{ ppm}$  assigned to aromatic protons<sup>[24,38–40]</sup>. The

signal for  $-\text{CH}=\text{N}-$  protons is shifted downfield upon coordination to Pd(II). These signals indicate the presence of  $\text{L}^{1-3}$  coordinated to Pd(II). Furthermore, the  $^1\text{H-NMR}$  signals arising from the ethylene protons of  $\text{L}^1$  complexes are shifted upfield and appear at  $3.90\text{--}3.92\text{ ppm}$ . Also, the  $^1\text{H-NMR}$  signals arising from the cyclohexane protons of the  $\text{L}^3$  complexes appear in the region  $2.78\text{--}1.52\text{ ppm}$ . There is a peak for water appearing at  $3.40\text{ ppm}$  for  $[\text{PdL}^3]\cdot 2\text{H}_2\text{O}$ . Thus, the  $^1\text{H-NMR}$  measurements further support the formation of the proposed Schiff base complexes presented in Figure 4.

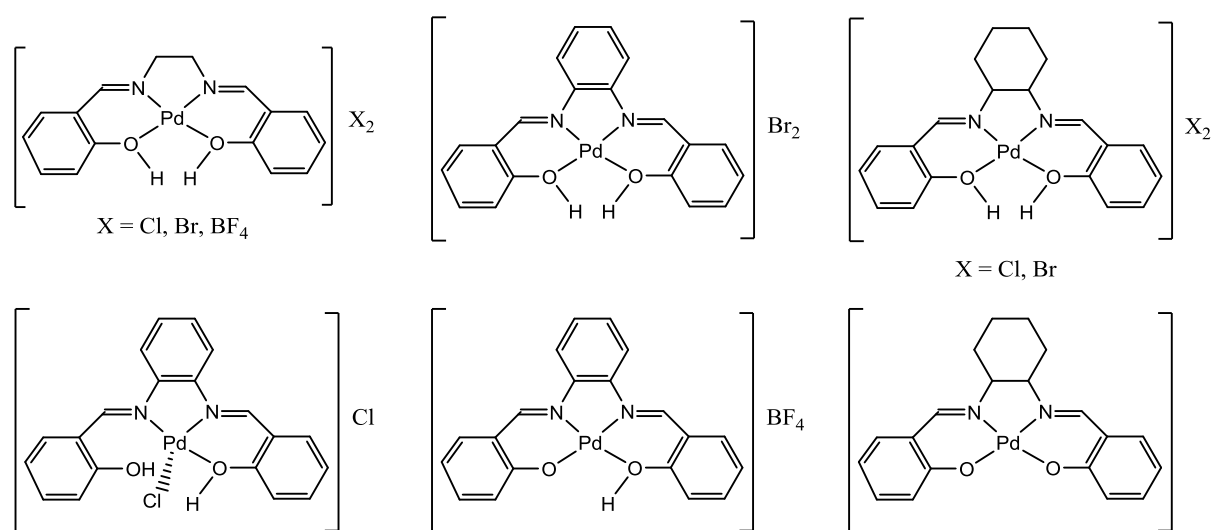


Figure 4. Proposed structure of synthesized complexes.

## Conclusion

In this study, new Schiff base complexes of palladium(II) were prepared and characterized. Based on the results obtained, the formulas for the complexes are  $[\text{PdL}^n]\text{X}_2$  (for  $\text{L}^n = \text{L}^1$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{BF}_4$ ; for  $\text{L}^2$ ,  $\text{X} = \text{Br}$ ; for  $\text{L}^3$ ,  $\text{X} = \text{Cl}$ , and  $\text{Br}$ ),  $[\text{PdL}^2\text{Cl}]\text{Cl}$ ,  $[\text{PdL}^2]\text{BF}_4$ , and  $[\text{PdL}^3]\cdot 2\text{H}_2\text{O}$ . The proposed structures of these

new complexes are shown in Figure 4. These complexes are expected to have good applications in catalytical, biological, and medical fields due to the oxidation-reduction properties of the palladium metal ion used in the preparation of these complexes. The catalytic activities of the prepared complexes are under ongoing investigation.

## References

- [1] Rahaman, S. H.; Ghosh, R.; Ghosh, B. K., *Inorg. Chem. Commun.*, **2006**, *9*, 1011–1014.
- [2] Karmakar, T. K.; Ghosh, B. K.; Usman, A.; Fun, H. K.; Riviere, E.; Mallah, T.; Aromi, G.; Chandra, S. K., *Inorg. Chem.*, **2005**, *44*, 2391–2399, and references therein.



- [3] Vigato, P. A.; Tamburini, S.; Bertolo, L., *Coord. Chem. Rev.*, **2007**, *251*, 1311–1492.
- [4] Drozdak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F., *Coord. Chem. Rev.*, **2005**, *249*, 3055–3074.
- [5] Lewinski, J.; Zachara, J.; Justyniak, I.; Dranka, M., *Coord. Chem. Rev.*, **2005**, *249*, 1185–1199.
- [6] Che, C.-M.; Huang, J. S., *Coord. Chem. Rev.*, **2003**, *242*, 97–113.
- [7] (a) Nawaz, H.; Akhter, Z.; Yameen, S.; Siddiqi, H. M.; Mirza, B.; Rifat, A., *J. Organomet. Chem.*, **2009**, *694*, 2198–2203; (b) Roy, G. B., *Inorg. Chim. Acta*, **2009**, *362*, 1709–1714.
- [8] Chaturvedi, D.; Kamboj, M., *Chem. Sci. J.*, **2016**, *7*, 1000e114 (2 pages).
- [9] Abu-Dief, A. M.; Mohamed, I. M. A., *Beni-Suef Univ. J. Basic Appl. Sci.*, **2015**, *4*, 119–133.
- [10] More, M. S.; Joshi, P. G.; Mishra, Y. K.; Khanna, P. K., *Mater. Today. Chem.*, **2019**, *14*, 100195 (22 pages).
- [11] Prakash, A.; Adhikari, D., *Int. J. Chem. Tech. Res.*, **2011**, *3*, 1891–1896.
- [12] Kajal, A.; Bala, S.; Kamboj, S.; Sharma, N.; Saini, V., *J. Catalysts*, **2013**, *2013*, 893512 (14 pages).
- [13] Brodowska, K.; Łodyga-Chruścińska, E., *Chemik*, **2014**, *68*, 129–134.
- [14] Utreja, D.; Vibha, B.S.P.; Singh, S.; Kaur, M., *Curr. Bioact. Comp.*, **2015**, *11*, 215–230.
- [15] Chaudhary, N. K., *BIBECHANA*, **2013**, *9*, 75–80.
- [16] Nasir Uddin, M.; Ahmed, S. S.; Alam, S. M. R., *J. Coord. Chem.*, **2020**, *73*, 3109–3149.
- [17] Zaitoun, M. A.; El-Qisairi, A. K.; Zoubi, J.; Momani, K. A.; Jaradat, Q. M.; Allimoun, M. O.; Lataifeh, A.; Al-Mazaideh, G. M.; Qaseer, H. A., *Jordan J. Chem.*, **2017**, *12*, 71–84.
- [18] El-Qisairi, A. K.; Qaseer, H. A.; Alshahateet, S. F.; Hasan Qaseer, M. K.; Zaghal, M. H.; Al-Btoush, W.; Dawe, L. N., *Croat. Chem. Acta*, **2014**, *87*, 123 – 128.
- [19] Hartely, F. R., *Organomet. Chem. Rev. A*, **1970**, *6*, 119–137.
- [20] Khandar, A. A.; Nejati, K., *Polyhedron*, **2000**, *19*, 607–613.
- [21] (a) Yang, S.; Kou, H.; Wang, H.; Cheng, Ke.; Wang, J., *New J. Chem.*, **2010**, *34*, 313–317; (b) de Toledo, T. A.; Pizani, P. S.; da Silva, L. E.; Teixeira, A. M. R.; Freire, P. T. C., *J. Mol. Struct.*, **2015**, *1097*, 106–111; (c) Roy, N.; Pramanik, H. A. R.; Paul, P. C.; Singh, T. S., *J. Fluoresc.*, **2014**, *24*, 1099–1106; (d) Ghann, W.; Sobhi, H.; Kang, H.; Chavez-Gil, T.; Nesbitt, F.; Uddin, J., *J. Materials Sci. Chemical Eng.*, **2017**, *5*, 46–66.
- [22] Waldo, H. C.; Scott, J. L., *Molecules*, **2004**, *9*, 513–519.
- [23] Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5<sup>th</sup> ed., Wiley, New York, 1997.
- [24] Surrah, A. S.; Thewalt, U.; Rieger, B., *J. Organomet. Chem.*, **1999**, *587*, 58–66.
- [25] Haghghi, S.; Mc Aulift, C. A.; Hill, W. E.; Koril, H. H.; Friedman, M. E., *Inorg. Chim. Acta*, **1980**, *43*, 113–119.
- [26] Emara, A. A. A.; Saleh, A. A.; Adly, O. M. I., *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, **2007**, *68*, 592–604.

- [27] Gaballa, A. S.; Asker, M. S.; Barakat, A. S.; Teleb, V. S. M., *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, **2007**, *67*, 114–121.
- [28] Khandar, A. A.; Shaabani, B.; Belaj, F.; Bakhtiari, A., *Polyhedron*, **2006**, *25*, 1893–1900.
- [29] Geary, W. J., *Coord. Chem. Rev.*, **1971**, *7*, 8–122.
- [30] (a) Qaseer, H. A., *Croat. Chem. Acta*, **2005**, *78*, 79–84; (b) Tyagi, M.; Chandra, S., *Open J. Inorg. Chem.*, **2012**, *2*, 41–48.
- [31] Fujimoto, A.; Junzuka, K., *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, **1988**, *44*, 1035–1043.
- [32] Martin, L. Y.; Dehayes, L. J.; Zompa, L. J.; Busch, P. H., *J. Am. Chem. Soc.*, **1974**, *96*, 4046–4048.
- [33] Alcock, N. W.; Balakrishnan, K. P.; Berry, A.; Moore, P.; Reader, C. J., *J. Chem. Soc., Dalton Trans.*, **1988**, 1089–1093.
- [34] Ali, B. F.; Zaghal, M. H.; Mhaidat, R. M.; Qaseer, H. A.; El-Qisairi, A. K., *Polyhedron*, **2013**, *54*, 237–242.
- [35] Yadav, S.; Ahmed, M.; Siddiqi, K. S., *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, **2012**, *98*, 240–246.
- [36] El-Qisairi, A. K.; Qaseer, H. A.; Zaghal, M. H.; Magaireh, S.; Saymeh, R.; Yousef, Y. A., *Jordan J. Chem.*, **2007**, *2*, 255–264.
- [37] Nworie, F. S., *J. Anal. Pharm. Res.*, **2016**, *3*, 00076 (9 pages), and references therein.
- [38] Ruiz, J.; Rodriguez, V.; Cutillas, N.; Lopez, G.; Perez, J., *Organometallics*, **2002**, *21*, 4912–4918.
- [39] Rîmbu, C.; Danac, R.; Pui, A., *Chem. Pharm. Bull.*, **2014**, *62*, 12–15.
- [40] Login, C.C.; Bâldea, I.; Tiperciuc, B.; Benedec, D.; Vodnar, D. C.; Decea, N.; Suciuc, S., *Oxidative Medicine and Cellular Longevity*, **2019**, 1607903, 11 pages.