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Pd (II) Complexes of New Tetra Dentate Schiff Base Ligands: Synthesis, Spectral Characterization and Catalytic Activity

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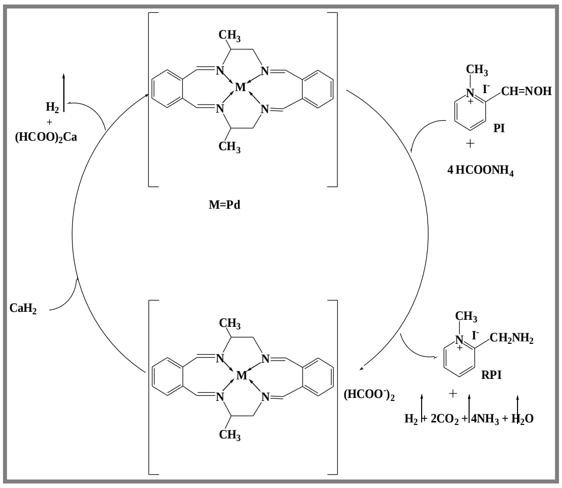
ABSTRACT

New Schiff base ligands containing N and O donor atoms are prepared by the condensation of ortho-phthalaldehyde with different diamines and amino acids. Further, these ligands on reaction with Pd(II) solution produced yellow crystalline complexes. Both tetra dentate Schiff base ligands and their metal complex have been well characterized by the analytical and IR, ^{1}H NMR, ^{13}C NMR and Mass spectral data. All these complexes are studied for their catalytic activity on the reduction of prolidoxime iodide drug and the reaction mechanism also proposed.

Graphical Abstract



Catalytic cycle of Schiff base Pd(II) complexes in the reduction of PI.

Keywords: Schiff bases, Pd(II) complexes, Spectral characterization, Catalytic activity.

INTRODUCTION

Design and synthesis of Schiff bases and their transition metal complexes is much attractive areas of current research round the globe owing to their catalytic applications in chemistry [1-7]. Metal complexes make these compounds effective as specific catalysts towards oxidation [8, 9], reduction [10, 11], hydrolysis [12], biological activity [13-15] and other transformations of organic reactions. Different synthetic path ways to synthesis Schiff bases and their metal complexes have been expanded by many scientists in this field [16, 17]. Based on literature noteworthy research has been done on Schiff bases and their complexes[18, 19]; though it is noted that work in the synthesis, characterization, catalytic activity studies of Schiff bases exclusively derived from OPA and diamines and amino acids is inadequate[20, 21]. In this context new Schiff bases were designed and synthesized in ethanol medium with less reaction times and high product yields. The combination of medicinally valuable orthophthalaldehyde and respective diamines and amino acids is used to create an adaptable Schiff-base arrangement [22-24].In extension of our continuing work is planned to synthesize and characterize the new Schiff base ligands containing N and O donor atoms and then these ligands on treating with Pd(II) salt to give respective Schiff base-metal complexes. Further these complexes have been used as catalysts for the reduction of prolidoxime iodide.

MATERIALS AND METHODS

Ortho-phthalaldehyde (OPA), amino acids, ortho-nitro benzaldehyde and chiral diamines were acquired from Aldrich, USA and all other organic solvents, metal salts used in this study were of analytical grade products from Merck. The solvents were distilled by standard procedure before use. The water used in this study was essentially double distilled water.

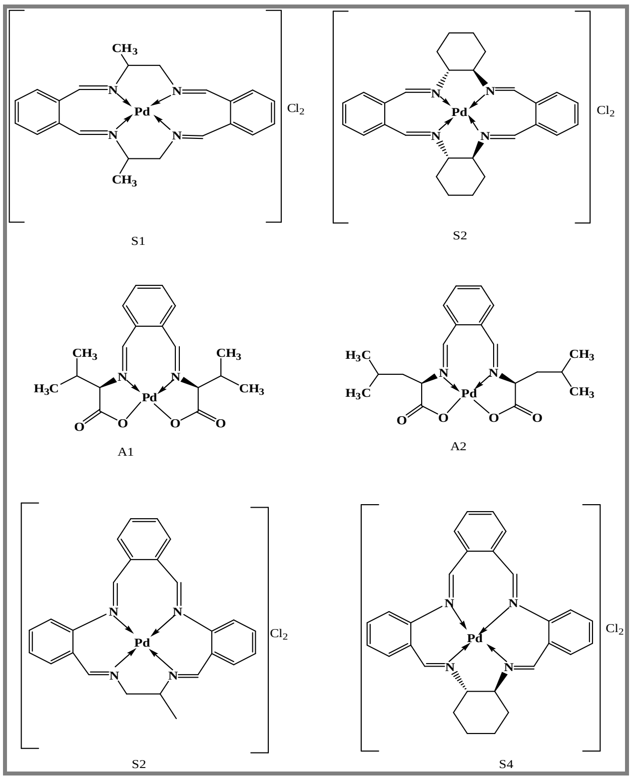
The melting points were obtained on a Buchi-510 melting point apparatus. The percentages of carbon, hydrogen, nitrogen were determined by using a Perkin-Elmer CHN analyzer at 24°C. UV-Visible spectra were recorded with Shimadzu UV-160A, a UV-Visible double beam spectrophotometer with matched quartz cells of path length 1 cm. The IR spectra were recorded in KBr pellets on a Perkin-Elmer 283 spectrophotometer. Brucker WH 300(400 MHz) and Varian Gemini (100 MHz) spectrometers were used for ^{1}H NMR and ^{13}C NMR spectra. Mass spectra were recorded on CEC-21-110B and Finnegan MAT-1210 mass spectrometers. Conductance measurements were done on 10^{-3} M solution of compounds in dichloromethane at 25°C using Dig sun Digital conductivity meter model DL-909. TGA curves were recorded on Mettler Toledo star system.

Synthesis of Schiff base Ligands: A ethanolic solution of ortho-phthalaldehyde (1.70 g, 0.01268 mol) was added drop wise to a stirred warm absolute ethanol solution of 1,2-diamino propane (0.94 g, 0.0126 mol) for ligand S1 and ethanol solution of OPA (1.8 g, 0.0134 mol)was added to ethanol solution of 1.5 g (0.0134 mol) of (1R, 2R)-(-)1,2-diamino cyclohexane for ligand S2.The resulting solution was refluxed for few hours (TLC checked). After the completion of the reaction the solution was concentrated on rotary evaporator and the ligand was precipitated by petroleum ether. The product was purified by recrystallization and dried in vacuum.

To an aqueous solution of L-valine 1.39 g (0.011 mol) NaOH 0.47g (0.011 mol) ortho-phthalaldehyde 0.8 g (0.0059 mol) in 5 mL ethanol was added drop wise with constant stirring for ligand A1 and to an aqueous solution of L-leucine 1.95 g (0.014 mol) NaOH 0.59 g (0.014 mol) ortho-phthalaldehyde 1.0 g (0.007 mol) in 5 mL ethanol was added drop wise with constant stirring for ligand A2. The reaction mixture was refluxed for 3-4 h then completion of the reaction was monitored by TLC and product formed was filtered washed with ethanol then with ether. Product was dried and stored in vacuum desicator over anhydrous calcium chloride.

S3 ligand was prepared by dissolving intermediate(product of ortho-amino benzaldehyde and 1,2-diamino propane) 1.04 g (0.0037 mol) in absolute ethanol was added drop wise to a stirred ethanol solution of ortho-phthalaldehyde 0.5 g (0.0037moles) and S4 ligand was prepared by dissolving intermediate (product of ortho amino benzaldehyde and (1R, 2R)-(-)1,2-diamino cyclohexane) 1.194 g (0.0037 mol) in absolute ethanol was added drop wise to a stirred ethanol solution of ortho-phthalaldehyde 0.5 g (0.0037 mol). The resulting mixture was refluxed for 3-5 h. The completion of the reaction was monitored by TLC. The reaction solution was concentrated on rotary evaporator and the ligand was precipitated by petroleum ether.

Synthesis of Schiff base Pd(II) metal complexes: Palladim(II) chloride (0.532 g, 0.003 mol) dissolved in methanol (20 mL) and added to corresponding ligand solutions (0.003 mol.) viz. S1 S2 A1 A2 S3 S4 in methanol (20 mL). The reaction mixture was stirred for 4-6 h then resulting solution was concentrated under reduced pressure, a few mL of diethyl ether was added to initiate crystallization. The resulting precipitate was filtered and washed with diethyl ether. The product obtained was recrystallized from dichloromethane and diethyl ether solvent mixture.



Scheme 1. Tentative structures of Schiff base Pd(II) complexes.

Catalytic reduction of pralidoxime iodide by Schiff base Pd(II) Complexes: 5 mL of pralidoxime iodide and 0.01 mmol of Pd(II) complex was taken into a 100 mL round bottom flask. The mixture was refluxed for 20 min at 70°C. The round bottom flask was cooled to room temperature and the contents of the flask were collected into separate 20 mL calibrated tubes. Slowly the new color was developed when 1 mL of ninhydrin solution was added to the tubes and heated for 5 min. at 70°C [25]. Then tubes were cooled to room temperature and the total volumes of the tubes were made up to 20 mL with double distilled water and kept aside for 10 min. The absorbance value of the colored solution was determined at 600 nm against the reagent blank [26].Calibrated curve was plotted and the amount of RPI formed during the oxidation process was estimated. The same method was employed for the remaining Schiff base metal complexes and prepared standard stock pharmaceutical solutions.

RESULTS AND DISCUSSION

In the present investigations, six new Schiff base ligands were synthesized by condensation of ortho-phthalaldehyde with different amines and amino acids in alcohol medium. By using these Schiff bases new hexa coordinated Schiff base Pd(II) complexes were synthesized by treating $PdCl_2$, with N_2O_2

and N_4 donor Schiff base ligands separately and all the complexes are stable in air and soluble in ethanol. The percentages of carbon, hydrogen and nitrogen were determined experimentally using CHN analyzer. The physical and analytical data (Table 1) for the newly synthesized compounds is in good agreement with the proposed molecular formulae.

Mass spectral analysis: The mass spectra of ligands viz., S1 S2 and S3 showed the (M^++Na) ion peaks where as A1, A2 and S4 ligands exhibitted (M^++1) molecular ion peaks. The mass spectra of Schiff base complexes have been shown molecular ion peaks with respect to (M^+) ion. This data is in good agreement with the respective molecular formulae. The molecular ion peak values (m/z) of all compounds are given in Table 1.

Table 1. Physical data of Schiff base Pd(II) metal complexes

S. No.	Compound	Molecular Formula	Analysis (%)Found (Calculated)				Mass
			C	H	N	Pd	
1	S1	$C_{22}H_{24}N_4$	75.36 (76.71)	6.98 (7.02)	16.08 (16.27)	--	367 (M^++Na)
2	S2	$C_{28}H_{32}N_4$	78.69 (79.21)	7.54 (7.60)	12.89 (13.20)	--	447 (M^++Na)
3	A1	$C_{18}H_{24}N_2O_4$	64.58 (65.04)	7.12 (7.28)	8.36 (8.43)	--	333 (M^++1)
4	A2	$C_{20}H_{28}N_2O_4$	65.69 (66.64)	7.69 (7.83)	7.65 (7.77)	--	361 (M^++1)
5	S3	$C_{25}H_{22}N_4$	78.67 (79.34)	5.74 (5.86)	14.35 (14.80)	--	401 (M^++Na)
6	S4	$C_{28}H_{26}N_4$	79.80 (80.35)	6.15 (6.26)	13.27 (13.39)	--	419 (M^++1)
7	[Pd(S1)Cl_2]	$C_{22}H_{24}Cl_2N_4Pd$	50.41 (50.64)	4.59 (4.64)	10.63 (10.74)	20.29 (20.40)	522 (M^+)
8	[Pd(S2)]Cl_2	$C_{28}H_{32}Cl_2N_4Pd$	55.58 (55.87)	5.21 (5.36)	9.21 (9.31)	17.53 (17.68)	602 (M^+)
9	[Pd(A1)]	$C_{18}H_{22}N_2O_4Pd$	48.97 (49.49)	5.37 (5.08)	6.29 (6.41)	24.05 (24.36)	436 (M^+)
10	[Pd(A2)]	$C_{20}H_{26}N_2O_4Pd$	50.98 (51.68)	6.01 (5.64)	5.97 (6.03)	22.47 (22.89)	464 (M^+)
11	[Pd(S3)]Cl_2	$C_{25}H_{22}Cl_2N_4Pd$	54.02 (54.01)	3.99 (3.90)	10.08 (10.01)	19.15 (19.12)	555 (M^+)
12	[Pd(S4)]Cl_2	$C_{28}H_{26}Cl_2N_4Pd$	56.44 (56.39)	4.40 (4.25)	9.40 (9.30)	17.86 (17.82)	595 (M^+)

Infrared spectral analysis: In infrared spectral studies were carried out and compared with corresponding Schiff bases. The azomethine($\upsilon_{C=N}$) band shifted towards lower side, is appeared with medium intensity in the range of 1620-1610 cm^{-1} which supports the coordination of ligand to the metal ion which is also further confirmed by a medium intensity band at 519-535 cm^{-1} responsible to metal nitrogen bond (υ_{M-N}).

In the Schiff base complexes [Pd(A1)]and [Pd(A2)]two bands observed in the range of 1586-1598 & 1370-1356 assignable to symmetric and asymmetric vibrations of carboxylate ion suggesting the coordination of the carboxylate oxygen to the metal atom which is also confirmed by the disappearance of a band in the range of 2943-2925 cm^{-1} is due to υ_{OH}. A medium intensity band found in the far IR region of 438-426 cm^{-1} corresponding to metal oxygen bond (υ_{M-O}) which also supports the above fact.

Aromatic stretching frequencies are observed for all the ligands in the range of 3062-3035 cm^{-1} and 1525-1471 cm^{-1}. There were no significant changes observed for aromatic ring frequencies in all the complexes [31]. The selected infrared spectral data of all the ligands is presented in table 2 and complexes in table-3.

Table 2. Infrared spectral data of Schiff bases ligands

S. No.	Compound	Selected IR bands (cm^{-1})			
		$\upsilon_{(C=N)}$	$\upsilon_{(OH)}$	$\upsilon_{(C=O)}$	Aromatic
1	S1	1648	-	-	3039/1471
2	S2	1643	-	-	3052/1485
3	A1	1631	2925	1721	3035/1474
4	A2	1636	2943	1710	3062/1525
5	S3	1652	-		3054/1483
6	S4	1645	.		3058/1495

Table 3. Infrared spectral data of Schiff base Pd(II) complexes

S. No.	Pd(II) complex	Selected IR bands (cm^{-1})			
		υ(C=N)	υ(COO-) asym/sym	υ(Pd-N)	υ(Pd-O)
1	[Pd(S1)]Cl_2	1620	--	520	--
2	[Pd(S2)]Cl_2	1617	--	534	--
3	[Pd(A1)]	1613	1586, 1370	528	438
4	[Pd(A2)]	1610	1598, 1356	535	426
5	[Pd(S3)]Cl_2	1618	--	519	--
6	[Pd(S4)]Cl_2	1620	--	532	--

^{1}H NMR spectral analysis: The ^{1}H NMR spectra of six newly synthesized Schiff base ligands was recorded and the integral intensities of every signal were found to be in agreement with the number of different types of protons. All the ligands exhibited a singlet in the range of 8.72-8.10δ responsible to CH=N protons (2H) suggests that the condensation of OPA with amines which was also confirmed by the absence of aldehydes proton peaks around 9.98 δ. In the spectra of Ligand S1 and S4 two peaks were observed for azomethine protons at different chemical shift values due to two chemically non-equalant environment where as Ligand S3 shown three peaks. In the case of ligand S2, all -CH_2 groups and chiral protons of cyclohexane were appeared as multiplates in the range of 2.21-1.15δ and 5.24δ. Schiff bases A1 and A2 have been shown a broad peak at ~11.0 δ corresponding to the –OH group of amino acids. Ligand S3 had shown a doublet peak at 1.42 δ corresponding to methyl group protons, multiplate in the range of 4.25-3.90δfor diastereotopic protons and multiplate at 3.55δ due to chiral proton. For ligand S4 multiplets appeared in the range of 2.18-1.52δ corresponding to methylene groups of cyclohexane and another at 5.28δ was owing to chiral protons. Multiplates exhibited in the range of 7.95-7.10δ were due to the aromatic protons. The significant^{1}H NMR data of selected protons for all the ligands are given in table 4.

Table 4. ^{1}H NMR spectral data of Schiff base Pd(II) complexes

Comp. No.	Pd(II) Complex	^{1}H NMR peak position (δ ppm)
1	[Pd(S1)]Cl_2	8.15 (s, 2H, -N=CH), 7.95 (s, 2H, -N=CH), 7.85-7.15 (m, 8H, Ar-H), 4.09-3.92 (m, 4H, -CH_2-), 3.45-3.03 (m, 2H, -CH), 1.32-1.29 (d, 6H, -CH_3)
2	[Pd(S2)]Cl_2	7.80 (s, 2H, -N=CH), 7.86-7.51 (m, 8H, Ar-H), 5.19 (m, 4H, -CH), 2.16-1.91 (m, 8H, -CH_2), 1.50-1.11 (m, 8H, -CH_2).
3	[Pd(A1)]	7.25 (s, 2H, -N=CH), 7.72-7.41 (m, 4H, Ar-H), 3.80 (d, 2H, -CH-CO-), 2.28 (m, 2H, -C$\underline{H}$-CH-CO-), 1.5-1.0 (d, 12H, -CH_3).
4	[Pd(A2)]	7.42 (s, 2H, -N=CH), 7.75-7.32 (m, 4H, Ar-H), 4.5-4.02 (t, 2H, 2-CH-CO-), 1.68-1.63 (t, 4H, -CH_2-), 1.45-1.41 (m, 2H,-CH), 1.4-1.01 (d, 12H, -CH_3).
5	[Pd(S3)]Cl_2	8.10 (s, 2H, -N=CH), 7.98 (s, 1H, -N=CH), 7.92 (s, 1H, N=CH), 7.65-6.93 (m, 12H, Ar-H), 4.20-4.05 (d, 2H, J = 6.0 Hz, CH_2), 3.54-3.45 (m, 1H, CH), 1.39-1.35(d, 3H, J = 5.3 Hz, CH_3).
6	[Pd(S4)]Cl_2	7.52 (s, 2H, -N=CH), 7.40 (s, 2H, -N=CH), 7.41-6.22 (m, 12H, Ar-H), 5.12 (m, 2H, -CH), 2.02-1.63 (m, 4H,-CH_2-), 1.52-1.22 (m, 4H, -CH_2-).

^{13}C NMR spectral analysis: The ^{13}C NMR spectra for all the ligands have been recorded and contain signal around 164.1-161.4δ indicating the presence of azomethine carbon which indicating the condensation between OPA and amine group. All ligands have contained asymmetric carbons which were exhibited signals in the range of 74.2-58.7δ. The spectra of ligands S1 and S3 shown a signal at 62.3-60.2δ corresponding to methylenic carbon adjacent to nitrogen atom, proves that the being there of N-CH$_2$ linkage. The spectra of A1 and A2 ligands have been exhibited signals around ~175δ attributed to carboxyl carbon of amino acids. For all the ligands arylic carbons were appeared in the around 142.5-120.6δ. The ^{13}C NMR spectral data of all the ligands are represented in table 5.

Table 5. ^{13}C NMR spectral data of Schiff base ligands

S. No.	Schiff base	^{13}C NMR peak position (δ ppm)
1	S1	163.1 (4C, -N=CH-), 141.7-132.5 (12C, Aromatic), 62.3 (2C, =N-CH$_2$-), 60.1 (2C, =N-CH-), 18.5 (2C, -CH$_3$).
2	S2	163.7 (4C, -N=CH-), 140.2-130.2 (12C, Aromatic),73.8 (4C, =N-CH-), 28.6 (4C, -CH-$\underline{C}H_2$-CH$_2$-), 23.9 (4C, -CH$_2$-$\underline{C}H_2$-CH$_2$-),
3	A1	175.3(2C,-CO-OH),161.4(2C,-N=CH-),142.5-128.3(6C, Aromatic),73.5(2C,=N-$\underline{C}$H-CO-),30.2(2C,-$\underline{C}$H-CH$_3$),19.1(4C,-CH3).
4	A2	176.1 (2C, -CO-OH), 162.2 (2C, -N=CH-), 140.2-131.4 (6C, Aromatic), 72.8(2C, =N-$\underline{C}$H-CO-), 31.3(2C, -$\underline{C}$H-CH$_3$), 22.4 (2C, -CH-$\underline{C}H_2$-CH-), 20.2(4C, -CH3).
5	S3	164.1 (4C, -N=CH-), 142.5-121.8 (18C, Aromatic), 60.2(1C,-CH$_2$-N=), 58.7 (1C,=N-CH-), 20.8 (1C, -CH$_3$).
6	S4	163.3 (4C, -N=CH-), 141.5-120.6 (18C, Aromatic), 74.2(2C,-CH-N=), 28.6 (2C,-CH-$\underline{C}H_2$-CH$_2$-), 25.1 (2C, -CH$_2$-$\underline{C}H_2$-CH$_2$-).

Thermal analysis: The thermogravimetric analysis of all Pd(II) complexes was carried out by taking >10 mg of the compound. These complexes indicate that they are stable up to 220°C and hence exist in anhydrous state. The DTA curves show no endothermic peaks up to 225°C confirming the absence of lattice or coordinated water molecules in the complexes. The sharp decomposition corresponding to the loss of organic moiety in complexes can be seen in the DTA curves which contained one sharp endothermic peak falling in the range of 225-252°C. The final product of decomposition of all the complexes above 600°C corresponds to metal oxide.

Electronic spectral studies: The electronic spectra of the Pd(II) metal complexes were recorded in DMF as solvent. Theoretically three ligand field bands are expected for square planar Pd(II) metal complexes at about 15000, 20000 and 25000 cm^{-1}, but all these three are not observed in most of the complexes. The Pd(II) metal complexes have been found to show a broad d-d transition band in the region of 22450-20460 cm^{-1} [445-488 nm] assignable to $^{1}B_{1g}\leftarrow{}^{1}A_{1g}$ transition typical for the square planar geometry Further, a relatively strong charge transfer band has been observed in the spectra of all the Pd(II) metal complexes in the range of 34540-31260 cm^{-1} [289-319 nm]. From the electronic spectral data(Table 6) and the diamagnetic behavior of the complexes, the square planar geometry has been proposed to all the Pd(II) metal complexes.

Table 6. Electronic spectral data of Co(II) complexes

S. No.	Complex	υ_1(cm^{-1})	υ_2(cm^{-1})
1	[Pd(S1)]Cl$_2$	464 (21510)	319 (31260)
2	[Pd(S2)]Cl$_2$	485 (20600)	307 (32550)
3	[Pd(A1)]	480 (20830)	289 (34540)
4	[Pd(A2)]	488 (20460)	300 (33270)
5	[Pd(S3)]Cl$_2$	445 (22450)	438(22831)
6	[Pd(S4)]Cl$_2$	625(16000)	295 (33890)

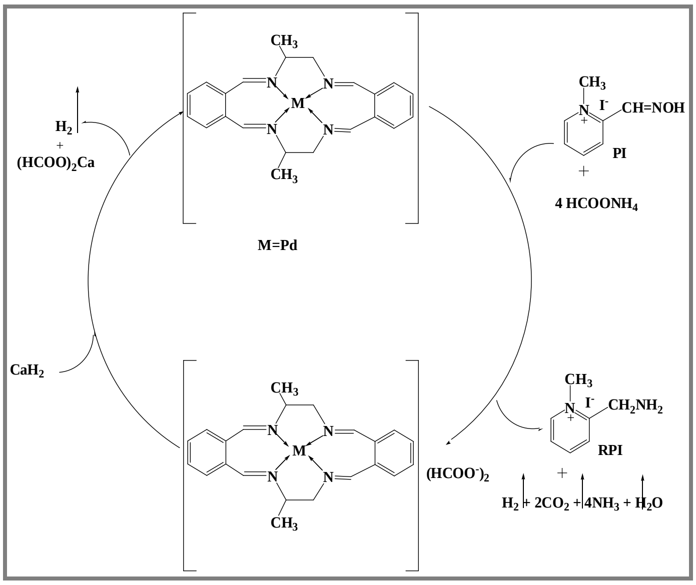
Conductance measurements: All Pd(II) complexes were subjected to molar conductance studies by using dichloromethane as solvent. The very low conductance values (Table 7) indicating non-electrolytic behavior nature of the complexes.

Table 7. Molar conductance data of Schiff base Pd(II) complexes

S. No.	Pd(II) complex	$\Lambda_M(\Omega^{-1} cm^2 mol^{-1})$
1.	$[Pd(S1)]Cl_2$	52.2
2.	$[Pd(S2)]Cl_2$	48.5
3.	[Pd(A1)]	13.0
4.	[Pd(A2)]	26.5
5.	$[Pd(S3)]Cl_2$	58.6
6.	$[Pd(S4)]Cl_2$	58.6

Magnetic properties: The magnetic susceptibility measurements have been carried out for Schiff base Pd(II) complexes and these compounds were found to be diamagnetic as expected for square planar and hence Pd(II) ion is in low spin configuration

Catalytic studies: In the infrared spectrum a peak responsible for the stretching frequency of -C=N band found at 1621 cm^{-1} in Pralidoxime iodide (PI). The disappearing of this peak and a new peak observed at 1472 cm^{-1} confirms the conversion of C=N to C-N bond. Similarly, the disappearance of a band at 3460 cm^{-1} owing to the presence of N-O bond supports the absence of oxygen atom in RPI. The presence of primary amino groups in RPI supported by a strong absorption band around 3350 cm^{-1} observed and attributed to the N-H stretching of aliphatic primary amino group. In the ^1H NMR spectra of PI two peaks observed at 8.65 and 8.48 δ due to CH=N and N-O-H protons. However, in the ^1H NMR spectra of RPI, these peaks were disappeared representing the absence of these protons. On the other hand, two new peaks were found at 3.18 and 5.26 δ responsible to $–CH_2–$ and $–NH_2$ protons, correspondingly and supporting the presence of aliphatic primary amino group in RPI. In the ^{13}C NMR spectra of PI a peak observed at 154.8 δ responsible for the imine carbon in CH=N group whereas this peak was disappeared in RPI, additionally a new peak was noticed at 43.6 δ confirming modifications of CH=N-OH group to CH_2-NH_2 group.



Scheme 1. Catalytic cycle of Schiff base Pd(II) complexes in the reduction of PI.

Table 8. Percent yields of RPI formed by using Schiff base Pd(II) complexes

S. No	Catalyst	Product Yield (%)
1	$[Pd(S1)]Cl_2$	85
2	$[Pd(S2)]Cl_2$	79
3	[Pd(A1)]	80
4	[Pd(A2)]	78
5	$[Pd(S3)]Cl_2$	63
6	$[Pd(S4)]Cl_2$	68

APPLICATION

This catalytic reduction process contains many advantages such as mild reaction conditions, simple work-up and good selectivity when compared to conventional hydrogenation or reduction techniques. Therefore, it was shown to be capable for reduction of many drugs. Hence, in quality control laboratories this method might be regarded as the best option for the reduction of drugs.

CONCLUSION

Schiff base Pd(II) complexes were synthesized by treating $PdCl_2$ with the six Schiff bases individually. In Palladium(II) complexes all the ligands (except A1 and A2 ligands) were coordinate through four nitrogen atoms of C=N group, remaining ligands A1 and A2 coordinates to the metal ion through two nitrogen atoms of C=N group and two oxygen atoms of carboxylates. All the complexes were shown to have non-electrolytic nature. Square planar structures were proposed to for all the complexes based on elemental and spectral data.

A catalytic method has been developed based on the reduction of the oxime group of PI in the presence of newly synthesized Schiff base Pd(II) catalysts. This catalytic reduction process contains many advantages such as mild reaction conditions, simple work-up and good selectivity when compared to conventional hydrogenation or reduction techniques, therefore it was shown to be capable for reduction of many drugs. Hence, in quality control laboratories this method might be regarded as the best option for the reduction of drugs.

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