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Palladium complexes of NO type Schiff bases: synthesis, characterization and antioxidant activities

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Abstract

The reaction of o-aminophenol with para hydroxy and methoxy substituted benzaldehydes yielded two Schiff bases. These Schiff bases functioning precursors were turned into palladium complexes by treating palladium acetate. The structural formulas based on spectral methods (elemental analysis, FT-IR spectroscopy, NMR spectroscopy and QTOF-LC/MS spectroscopy) were suggested for obtained both complexes. According to the structural characterization methods, one of the complexes had also an acetate co-ligand along with the hydroxy substituted Schiff base ligand. In the other complex, the palladium central ion was proposed to be coordinated with two methoxy substituted Schiff bases. Besides, DPPH scavenging activities of the all synthesized compounds were determined and compared to well-known antioxidant standards. According to the results, antioxidant activities of the palladium complexes was mild but lower than parent Schiff bases.

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1. Introduction

Schiff bases are frequently studied compound group ever since Hugo Schiff reported preparation of the first example in 1864. Schiff bases, so called imines or azomethines, are of great importance due to their wide application areas varying from polymer, dye, pharmaceutical and food industry to agrochemical and sensor applications [1–13]. The structural stability and versatility in addition to easy synthesis of imine compounds induced gaining wide currency of this substance class. Among its various features, bioactivity of Schiff bases especially comes to the forefront in consequence of interactions and hydrogen bonds between the azomethine group and certain sites in the cell structure beside structural factors like solubility, dipole moment and cell permeability [14]. Also, electrons in sp^2 hybrid orbitals of azomethine nitrogen play a crucial role in biological applications [15].

Schiff bases can effectively coordinate metal ions, especially if they contain electron donor groups such as -OH, -NH, -SH in positions proper for coordination in conjunction with azomethine group. Various transition metal ions like nickel(II), copper(II), zinc(II), palladium(II) etc. can be used to synthesize complex structures with Schiff bases and resulted complexes have wide industrial and biological coverage. Among biological applications of Schiff base complexes, antibacterial, antioxidant, antifungal and anticancer activities can be mentioned [16-22].

Recently, researchers have been working extensively on natural-source or synthetic antioxidants to reduce the effect of oxidative stress on living cells. These antioxidant materials have protected the living cells by acting as free radical scavengers and metal chelators. There are many palladium Schiff base complexes synthesized for this purpose in the literature. It was stated that these complexes generally exhibited average antioxidant activity and antioxidant property of the complexes were greater than Schiff bases [23–26].

In this research, two new palladium complexes of NO type Schiff bases were prepared and proposed two different complex structures based on the results of spectroscopic methods (FT-IR, NMR, QTOF-LC/MS, elemental analysis) and previous studies [27,28]. DPPH scavenging activities of the synthesized compounds were determined. The compounds were compared to the standard antioxidants (Butylated hydroxyanisole (BHA), Butylated hydroxytoluene (BHT), Trolox and α-Tocopherol).

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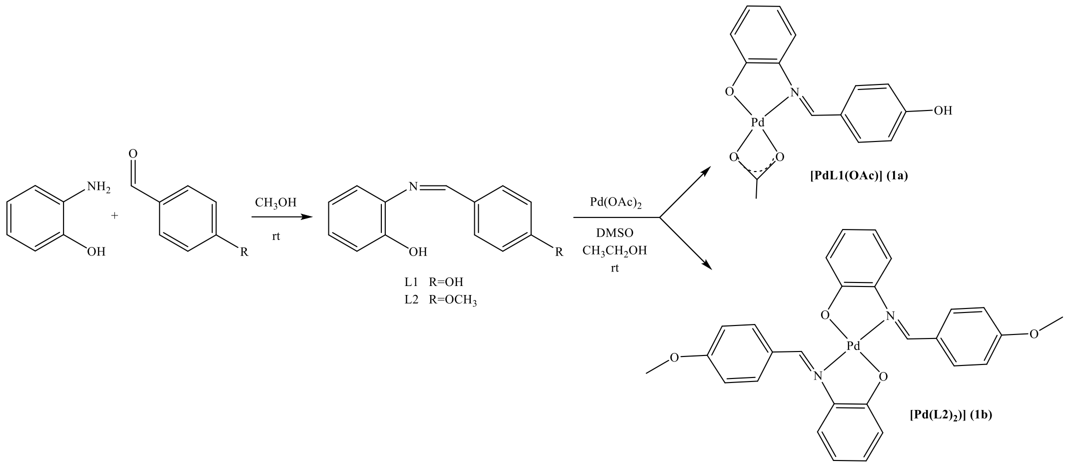

Scheme 1. Reaction scheme for Schiff bases and palladium complexes along with proposed complex structures

2. Materials and Methods

2.1. Apparatus

All chemicals were used as received from commercial sources. The FT-IR spectra were measured by using a Jasco FT-IR 4700 spectrometer in the range of 400-4000 cm^{-1}. Elemental analyses were recorded on a Elementar Vario Micro Cube elemental analyzer. ^{1}H- and ^{13}C-NMR spectra of all imine compounds were saved using AC Bruker 400 MHz NMR spectrometer in $CDCl_3$ at ambient temperature. Mass spectra were obtained by using Agilent 6530 Accurate-Mass QTOF-LC/MS Spectrometer.

2.2. Synthesis of the Schiff bases

The synthesis of the Schiff bases was carried out according to the literature methods with slight modifications [29]. Methanol solutions of o-hydroxyaniline and benzaldehyde derivatives in equivalent amounts were mixed at room temperature. Reaction completion was followed by TLC method. When starting materials were all consumed, ethanol was evaporated and the product was extracted with chloroform for three times. The final product was dried with Na_2SO_4, filtered and obtained as oily compounds. The structural characterization results were in harmony with the previous study [29].

2.3. Synthesis of the Palladium complexes (1a and 1b)

Schiff bases (1 mmol) and palladium acetate (1eq) solved in ethanol (20 mL) and DMSO (10 mL) was mixed in a round-bottom flask at room temperature. Red-brown precipitate was observed immediately. Reaction mixture was stirred for 48 hours at room temperature. After all of the Schiff base was consumed, the reaction mixture was filtered and obtained precipitate was washed with ethanol and diethyl ether.

[PdL1(OAc)] (1a): Yield 64%. FT-IR (cm^{-1}): 3568-3088 (O-H), 3055,3004 (C-H$_{arom.}$), 2927,2890 (C-H$_{aliph.}$), 1580 (C=O), 1538 (azomethine, C=N), 1296 (C-O); ^{1}H-NMR (DMSO-d6, δ, ppm): 2.08 (3H, s, CH_3-acetate), 6.38-6.27 (4H, m, CH), 6.86-6.80 (2H, m, CH), 7.11 (1H, d, 3J_H 8.21 Hz, CH), 7.21 (1H, d, ^3J_H 7.99 Hz, CH), 8.19 (1H, s, CH), 10.05 (1H, s, OH). ^{13}C-NMR (DMSO-d6, δ, ppm): 21.53, 112.06, 113.88, 116.82, 120.62, 122.26, 130.61, 131.68, 136.40, 145.08, 159.71, 161.20, 161.67, 171.30, 172.48. Anal. calcd. for $C_{15}H_{13}NO_4Pd$ (377.69 g/mol): C, 47.70; H, 3.47; N, 3.71. Found: C, 47.85; H, 3.63; N, 3.96%.

[Pd(L2)$_2$] (1b): Yield 58%. FT-IR (cm^{-1}): 3053 (C-H$_{arom.}$), 2995,2934,2833 (C-H$_{aliph.}$), 1537 (azomethine, C=N); ^{1}H-NMR (DMSO-d6, δ, ppm): 3.74 (6H, s, CH_3), 6.29-6.35 (6H, m, CH), 6.59-6.56 (2H, m, CH), 6.91-6.85 (4H, m, CH), 7.24-7.22 (4H, m, CH), 8.25 (2H, s, CH). ^{13}C-NMR (DMSO-d6, δ, ppm): 55.56 (2C), 109.72 (2C), 114.00 (2C), 117.09 (2C), 120.78 (2C), 121.10 (2C), 131.01 (2C), 131.33 (2C), 136.22 (2C), 146.90 (2C), 160.68 (2C), 160.93 (2C), 161.06 (2C), 171.61 (2C). Anal. calcd. for $C_{28}H_{24}N_2O_4Pd$ (558.93 g/mol): C, 60.17; H, 4.33; N, 5.01. Found: C, 59.93; H, 4.50; N, 5.22%.

2.4. Antioxidant activity

2.4.1. Preparation of samples and antioxidant standards

The antioxidant activities of the prepared phenolic Schiff bases and palladium complexes were determined by using some in vitro tests with intend to create the structure-activity connection. For this aim, all samples and well known antioxidant standards (BHA, BHT, trolox and α-tocoferol) were prepared as 1000 ppm stock solutions and diluted to specific concentrations before use.

2.4.2. DPPH scavenging activity

DPPH scavenging activities of the phenolic compounds were determined by decolorizing of purple-colored ethanol solution of 1,1-diphenyl-1-picrylhydrazyl (DPPH) as a result of treatment with test compounds [30]. The aliquots in four different concentrations (10-100 ppm) were prepared from the test compounds and the standards. 1 mL DPPH solution in 1 mM concentration was added to each aliquot prepared in 3 mL ethanol. The absorbance at 517 nm was measured against ethanol after 30 min of incubation in dark at room temperature. The inhibition activities were calculated by the following:

$$\%Inhibition = \left(1 - {A_{sample}}/{A_{control}}\right) x100 \qquad (1)$$

3. Results and Discussion

Two new palladium Schiff base complexes were prepared by interacting o-aminophenol Schiff bases with palladium acetate. The Schiff bases and the complexes were stable at room conditions. While the Schiff bases had high solubility in common alcohols (ethanol, methanol,...etc.) and organic solvents ($CHCl_3$, CH_2Cl_2,…etc.), the palladium complexes were soluble in DMSO, but had low solubility in common alcohols. The possible structural formulas for the complexes were proposed in accordance with elemental analysis, FT-IR, NMR (^{1}H- and ^{13}C-) and QTOF-LC/MS data. According to the characterization methods, it is proposed that acetate ion behaved as a co-ligand to complete the coordination sphere in 1a while two Schiff base ligands formed the coordination environment in 1b.

3.1. FT-IR spectral studies

Figure 1 includes the FT-IR spectra of 1a and starting Schiff base L1, comparatively. The majority of the main groups belonging to the Schiff base were also observed in the spectra of the resulting palladium complexes with shifts in their positions.

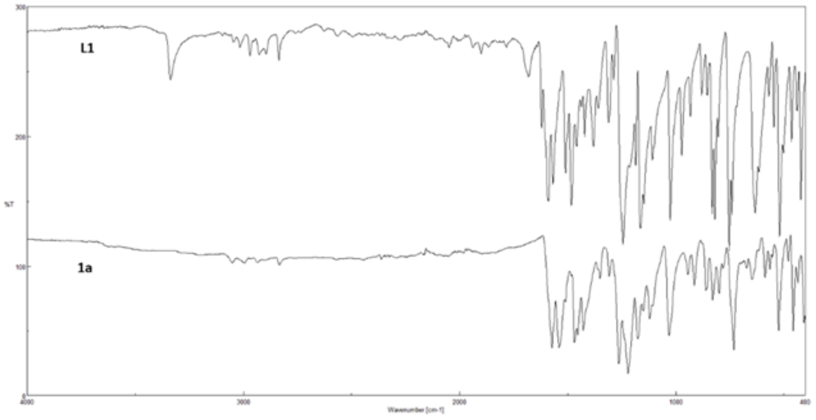

Figure 1. The FT-IR spectra of **1a** and **L1**.

All the Schiff bases and their palladium complexes exhibited similar spectra with little differences. In the spectrum of 1a, the sharp O-H stretching band around 3300 cm^{-1} disappeared because of deprotonation of the hydroxyl group as a result of coordination. νC=N stretches of two palladium complexes between 1550-1650 cm^{-1} shifted to lower wave numbers in harmony with the literature [32]. The involvement of the acetate group as co-ligand to the complex structure ended up with birth of two new bands in the spectra of the complex 1a: υC=O (1580 cm^{-1}) and υC-O (1296 cm^{-1}). Remaining characteristic groups like aliphatic and aromatic C-H groups, ether groups etc. were observed with expected shifts in the spectra of the synthesized compounds.

3.2. ^{1}H- and ^{13}C-NMR spectral studies

NMR spectra of the palladium complex **1a** and starting Schiff base ligand L1 recorded in DMSO-d6 at room temperature were shown in Figure 2. Full NMR data belonging to ^{1}H- and ^{13}C-NMR were shown in the experimental section.

When the NMR spectra of 1a and L1 were compared, the formation of a new singlet at 2.08 ppm has drawn attention because of the participation of the acetate ligand to the coordination environment. Because only one of the two hydroxyl groups belonging to L1 ligand was deprotonated, a singlet pointing out the hydroxyl group was observed around 10 ppm in the spectrum of the complex 1a.

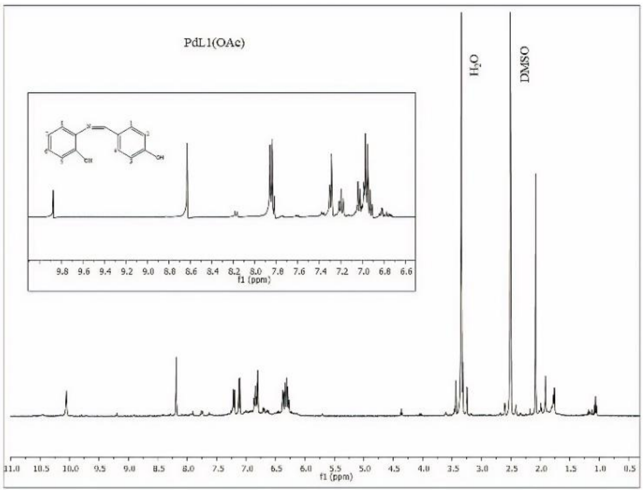

Figure 2. NMR spectra of **1a** and **L1** (inside window).

While the singlet at 8.19 ppm was designated to the azomethine proton, aromatic protons 1 and 2 appeared at 7.21 and 7.11 ppm as multiplets. Besides, the multiplet between 6.86 and 6.80 ppm was attributed to aromatic protons 6 and 7. When it comes to remaining aromatic protons, they overlapped in the range of 6.38 to 6.27 ppm. ^{13}C-NMR spectrum was verified the expected structure for 1a, too. Imin carbon atom was observed at 171.31 ppm while methyl and carbonyl carbon peaks indicating the existence of acetate ligand appeared at 21.53 and 172.48 ppm. Other carbons appeared in the area expected for aromatic carbons.

Figure 3 demonstrates the NMR spectra of the complex 1b and Schiff base L2 measured in DMSO-d6 at ambient temperature. Full NMR data belonging to ^{1}H- and ^{13}C-NMR were shown in the experimental section. Two singlet peaks at 3.74 ppm and 8.25 ppm in the spectrum were induced by methoxy and imin protons, respectively.

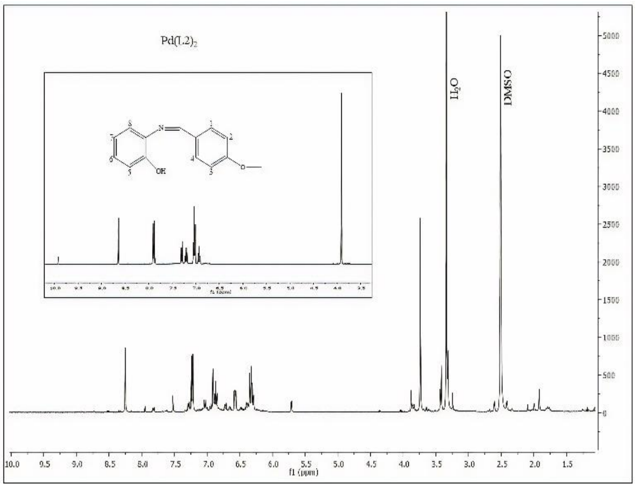

Figure 3. NMR spectra of **1b** and **L2** (inside window).

Aromatic ring protons were observed similar ways and range with complex 1a, as expected. While the resonances belonging to aromatic protons 3 and 4 appeared at 7.24-7.22 ppm interval, the multiplet in the range of 6.91 to 6.85 ppm pointed out 6 and 7. ^{13}C-NMR spectrum was verified the structure, too. Imin carbon and methoxy carbon were observed at 171.61 and 55.56 ppm, respectively. Other carbons appeared in the area expected for aromatic carbons.

3.3. Mass spectral studies

QTOF-LC/MS spectra of the palladium complexes were consistent with proposed formulas. In the spectra of the both complexes, a signal corresponding to [Pd(PhNH$_2$OH)(DMSO)] fragment at 294 was observed because of the usage of DMSO as solvent in the QTOF-LC/MS spectra (Figure 4). Also, the peak appeared at 228 in the spectrum of 1b was attributed to the Schiff base L2. While the molecule ion peak was found at 558 for 1b, 1a had a molecular ion peak at 360 in response to [PdL1(OAc)-OH] fragment.

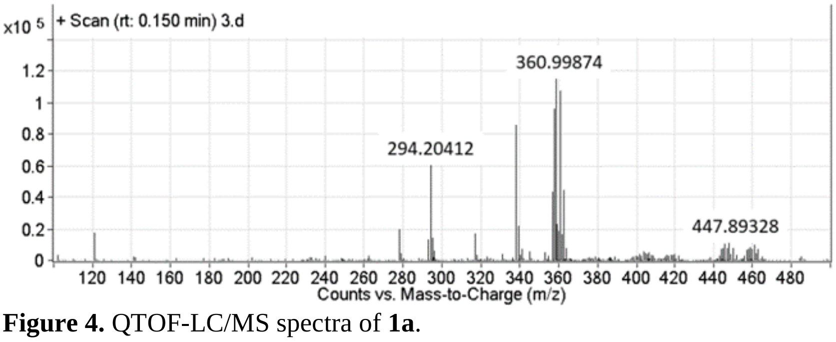

Figure 4. QTOF-LC/MS spectra of **1a**.

3.4. Antioxidant activity studies

Antioxidant activities of the synthesized compounds were expressed by the IC50 value which is the concentration that can scavenge %50 of a free radical. Calculated IC50 values of the compounds were compared with well-known positive controls BHA, BHT and α-Tocopherol and tabulated in Table 1.

Table 1. IC50 values of the test compounds for DPPH scavenging assay

Test compounds	IC50
L1	19.21
Complex 1a	57.77
L2	10.48
Complex 1b	80.20
BHA	5.42
BHT	5.97
Trolox	13.66
α -tocopherol	4.39

The antioxidant capacities of the Schiff bases and their palladium complexes were examined by DPPH scavenging assay. DPPH scavenging activity has a great importance because the compounds exhibiting DPPH scavenging activity are the anticancer and the anti-inflammatory agents as well [33]. For this reason, these type compounds have been attracting attention as potential anticancer drugs. According to the results of DPPH assay, L1 and L2 exhibited great scavenging activity towards DPPH (for L2 even greater than Trolox standard). When it comes to complexes 1a and 1b, it appeared that the complexation had a negative effect on DPPH scavenging activities of Schiff bases L1 and L2. Nevertheless, 1a and 1b had mild activity to scavenge DPPH. This finding is also in accordance with a previous study revealing the close relationship between redox and antioxidant properties of the metal complexes [34].

4. Conclusions

In conclusion, two Schiff bases derived from o-aminophenol were converted to palladium complexes by reacting palladium acetate in this study. The combined evaluation of the structural characterization methods (FT-IR, ^{1}H- and ^{13}C-NMR, elemental analysis, QTOF-LC/MS) revealed two different formulas for synthesized palladium complexes. An acetate ligand was coordinated to palladium ion in combination with Schiff base ligand **L1** in complex **1a**. When it comes to 1b, coordination sphere was composed of two Schiff base ligand L2. Antioxidant capacities of the prepared complexes were determined by DPPH scavenging assay. The results exhibited good antioxidant activity for the Schiff base ligands L1 and L2 compared to well-known antioxidant standards BHA, BHT, Trolox and Alpha-tocopherol. The scavenger capacities of the prepared palladium complexes were mild.

Conflicts of interest

The authors state that did not have conflict of interests

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