



Synthesis, Spectroscopic, Antibacterial and Antioxidant Activities of Pd(II) Mixed-Ligand Complexes Containing Tridentate Schiff Bases



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Pd(II) complexes of the form [PdLNH₃] (where L = N-salicylidene-o-aminophenol (L1), N-(5-methoxysalicylidene-o-aminophenol) (L2) and N-(2-hydroxy-1-naphthalidene)-o-aminophenol) (L3) containing ammonia and ONO tridentate Schiff bases were synthesized. These complexes were characterized by elemental analysis, infrared, ultraviolet-visible, proton and carbon-13 spectroscopies. The NMR spectra showed that the Schiff bases coordinated to the palladium(II) ion through the two deprotonated phenolic oxygen and azomethine nitrogen atoms. The presence of ammonia molecules in these complexes were indicated by the IR and ¹H NMR spectra. The spectral data suggested a square planar geometry for the complexes. The biological studies revealed that the complexes displayed better antibacterial and antioxidant activities than the parent Schiff bases.

Keywords: Schiff base, complex, Palladium(II) ion, antibacterial, antioxidant

Introductio

Schiff bases are compounds with an imine or azomethine, (HC=N) group [1]. They function as excellent chelating ligands with wide range of properties tunable by introduction of substituents with different electron-donating or electron-withdrawing groups on either the carbonyl or amine ring. Intra- and intermolecular hydrogen bonds can be formed from Schiff bases obtained from various substituted salicylaldehydes and 2-hydroxy-1-naphthaldehyde and these usually determine their chemical and physicochemical properties. The resultant imines are involved in binding with metal ions via nitrogen lone pair electrons. Schiff bases have played essential roles in understanding the coordination chemistry of transition metal ions. The azomethine moiety is

significant for biological activities, it is a very useful active centre of many biological systems [2, 3]. Studies showed that Schiff bases derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde including their derivatives and their complexes with some transition metals displayed significant biological properties because of the presence of nitrogen and oxygen atoms which are active donor atoms in the molecules of these compounds. These biological properties make Schiff bases and the complexes gain attention, some of the reported properties are antimicrobial, analgesic, antioxidants, antimalarial, anticonvulsant and anti-inflammatory [3-8].

Many complexes have been synthesized for their pronounced biological activities. There are many studies on Pd(II) complexes with Schiff

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base ligands because they play important roles in bioinorganic chemistry and redox enzyme systems. They can act as catalyst and provide the basis of models for active sites of biological systems [3]. However, literature search showed that reports on complexes bearing ammonia are extremely limited. Hence this study, the synthesis, spectroscopic, antibacterial and antioxidant activities of Pd(II) complexes of tridentate Schiff bases.

Experimental

Materials

Salicylaldehyde, 5-methoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-aminophenol, palladium(II) acetate, ammonium hydroxide and formic acid were purchased from Merck (Germany) which were used as supplied. The solvents were of pure grade except ethanol and water that were distilled.

Instruments

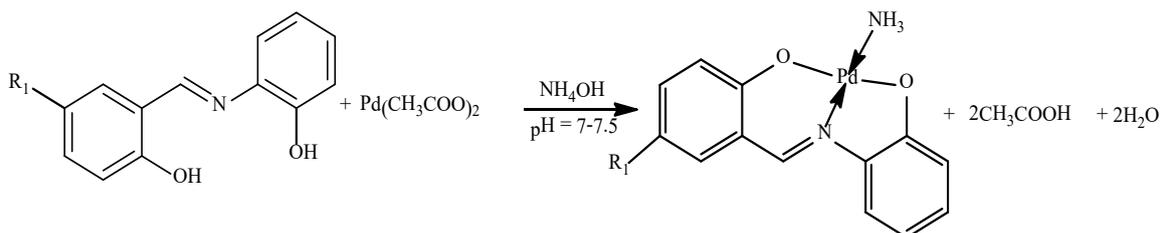
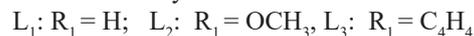
A Thermo Finnigan Flash EA 1112 Series was used for the elemental analyses (C, H, N). The Infrared spectroscopy analyses were carried

out using the attenuated (ATR) technique with a Perkin-Elmer 400 FT-IR/FT-FIR spectrometer. A MPD Mitamura Riken Kogyo (Japan) electrothermal was used to determine the melting points. The nuclear magnetic resonance spectra were carried out on a Bruker Avance III 600 Spectrometer in solution with DMSO- d_6 and tetramethylsilane (TMS) as internal standard at 600 MHz. The UV-Visible were recorded in 1.0×10^{-4} M DMSO solution using Shimadzu UV 1800 Spectrophotometer on 250-900 nm.

Synthesis

The Schiff bases syntheses

5.0 mmol of the 2-aminophenol in 10 ml of ethanol was added in drops to 5.0 mmol of the corresponding salicylaldehyde in 20 ml of the same solvent. The resulting solution was stirred for 2 hours on addition of three drops of formic acid. The coloured solids precipitated were separated by filtration and recrystallized from hot ethanol.



Scheme 1. Synthetic route of the Schiff base ligands.

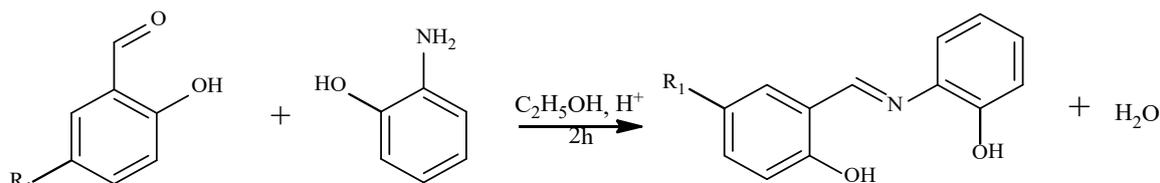
Synthesis of the Pd(II) complexes

A methanolic solution of $Pd(CH_3COO)_2$ (5.0 mmol) was added in drops to the corresponding Schiff base solution (5.0 mmol) while stirring in 10 ml of the same solvent. Some drops of ammonia hydroxide were added to modify the pH of the resulting mixture to 7-7.5 and refluxed at $60^\circ C$ for 4 hours. The coloured solids precipitated were filtered by vacuum filtration, washed with distilled water, diethyl ether and methanol. These were dried over silica gel in a desiccator for two days

and recrystallized from DMSO.

Antibacterial study

The antibacterial potentials of the compounds were measured against some Gram-positive and Gram-negative bacterial strains by agar-well diffusion method. The Gram-positive bacterial strains were *Streptococcus agalactiae* and *Staphylococcus aureus* while *Escherichia coli*, *Klebsiella pneumonia*, *Proteus mirabilis*, *Pseudomonas aeruginosa* and *Salmonella*



Scheme 2. Synthetic route of the Pd(II) complexes.

typhimurium were the Gram-negative bacterial strains used. The Nutrient agar medium was used to sub-culture the isolates of bacterial strains which were nurtured at 37 °C for 24 hours. 20 ml of disinfected Nutrient agar medium was dispensed in each germfree Petri dish after modifying the bacterial strains cultures to 0.5 McFarland standard, these were allowed to gel. The dishes were swabbed with the inocula of the bacterial strains and left for 15 minutes to adsorb onto the gel. Varying concentrations of the samples (5 mg/ml, 10 mg/ml, 15 mg/ml) were filled into the wells that were drilled on the seeded agar dishes by a sterile cork borer of 6 mm diameter. These were kept for 1 hour in the refrigerator to allow for thorough circulation of the samples into the medium and then nurtured for 24 hours at 37 °C before observing the inhibition zones. Antimicrobial activities were expressed as inhibition diameter zones in millimeter (mm). Standard Gentamycin (10 µg/ml) was employed as control [9-11].

Phosphomolybdate Total Antioxidant Capacity (PTAC) Assay

The total antioxidant capacities (TAC) of the compounds were determined by phosphomolybdenum assay and ascorbic acid was used as the standard. 1.0 ml of reagent (0.6 M sulphuric acid, 28 µM sodium phosphate and

4 µM ammonium molybdate) was reacted with a fractional part of the extract solution (1.0 ml of 1000 µg). The covered tubes were incubated at 95 °C in a water bath for 90 minutes after which the samples were cooled to room temperature and a UV spectrophotometer was used to measure the absorbance of the aqueous solution of each at 695 nm. The procedure was repeated for an empty solution containing 1.0 ml of reagent solution. The TAC studies were expressed as equivalents of ascorbic acid [12].

Results and Discussion

The physicochemical data of the synthesized Schiff bases and the complexes are presented in Table 1. The Schiff base ligands and the complexes were stable and coloured solids. The complexes were not soluble in water and almost all organic solvents except in DMSO and DMF. The complexes have higher melting points than the parent Schiff base ligands, this showed that they have better stability than the Schiff bases. The elemental analysis data confirmed the formation of 1:1:1 [Palladium: Schiff base: ammonia] molar ratio. The crystals obtained in DMSO were not suitable for X-ray diffraction measurement. No crystal was obtained in DMF. Attempts to isolate single crystal suitable for X-ray diffraction measurement were not successful.

TABLE 1. The physicochemical data of the Schiff bases and the Pd(II) complexes.

| Compounds | Molecular formula | Molecular weight | Colours | Melting points (°C) | % Yield | Elemental analysis (%) | | |
|----------------------------------|--|------------------|---------|---------------------|---------|------------------------|----------------|----------------|
| | | | | | | Found (Calculated) | | |
| | | | | | | C | H | N |
| L ₁ | C ₁₃ H ₁₁ NO ₂ | 213.14 | Orange | 187 | 97 | 73.25 (73.23) | 5.21 (5.20) | 6.60 (6.57) |
| PdL ₁ NH ₃ | C ₁₃ H ₁₂ N ₂ O ₂ Pd | 334.67 | Orange | >260 | 75 | 46.69 (46.66) | 3.64 (3.61) | 8.38 (8.37) |
| L ₂ | C ₁₄ H ₁₃ NO ₃ | 243.14 | Wine | 157 | 95 | 69.10 (69.12) | 5.38 (5.39) | 5.77 (5.76) |
| PdL ₂ NH ₃ | C ₁₄ H ₁₄ N ₂ O ₃ Pd | 364.69 | Orange | >260 | 72 | 46.13 (46.11) | 3.88 (3.87) | 7.69 (7.68) |
| L ₃ | C ₁₇ H ₁₃ NO ₂ | 263.29 | Yellow | 249 | 86 | 77.56 (77.55) | 5.00 (4.98) | 5.29 (5.32) |
| PdL ₃ NH ₃ | C ₁₇ H ₁₄ N ₂ O ₂ Pd | 384.73 | Brown | >260 | 82 | 53.08 (53.07) | 3.66 (3.67) | 7.27 (7.28) |

*Spectroscopic studies**FT-IR spectra*

The IR spectral data of the compounds are presented in Table 2. The free Schiff base (L_1 , L_2 and L_3) spectra showed the azomethine, $\nu(-HC=N)$ vibrational frequencies at 1627, 1617 and 1626 cm^{-1} respectively, these wave numbers shifted backward (1604-1597 cm^{-1}) in the Pd(II) complexes (Figs. 1-3). This revealed the involvement of the azomethine nitrogen atoms in coordination with the Pd(II) ions and the palladium–ligand bonds formation. Absorption bands at 1274, 1228 and 1247 cm^{-1} in the free Schiff bases spectra were attributed to the phenolic C–O stretching vibrations of L_1 , L_2 and L_3 respectively. These bands shifted to higher wave numbers at 1306-1261 cm^{-1} in the Pd(II) complexes, these showed the involvement of the oxygen atoms of the phenolic groups in coordination with the Pd(II) ion. The free Schiff bases (L_1 , L_2 and L_3) exhibited

hydroxyl $\nu(O-H)$ vibrational frequencies at 3746, 3747 and 3119-2427 cm^{-1} respectively, these were absent in the complexes which further confirmed the removal of the phenolic groups protons and the attachment of oxygen to the Pd(II) ion [3, 13]. The complexes showed new absorption bands at 3353, 3340 and 3332 cm^{-1} respectively assigned to $\nu(N-H)$ stretching vibrations of ammonia ($-NH_3$) groups, these indicated the presence of $-NH_3$ groups in the complexes and showed the attachment of the nitrogen atoms of the $-NH_3$ groups to the Pd(II) ion [14]. The bands around 489-471 cm^{-1} and 544-508 cm^{-1} were attributed to the stretching vibrations of the palladium–oxygen, $\nu(Pd-O)$ and palladium–nitrogen, $\nu(Pd-N)$ bands respectively. These confirmed the attachment of the Schiff bases to the Pd(II) ion via the oxygen and nitrogen atoms of the phenolic and azomethine groups respectively [3, 9, 13, 15].

Table 2. The IR data of the Schiff bases and the Pd(II) complexes.

| Schiff bases/Complexes | IR bands(cm^{-1}) | | | | | |
|------------------------|------------------------------|------------|------------|------------|------------|------------|
| | $\nu(O-H)$ | $\nu(N-H)$ | $\nu(C=N)$ | $\nu(C-O)$ | $\nu(M-O)$ | $\nu(M-N)$ |
| L_1 | 3746 | – | 1627 | 1274 | – | – |
| Pd L_1 NH $_3$ | – | 3332 | 1597 | 1306 | 489 | 525 |
| L_2 | 3747 | – | 1626 | 1247 | – | – |
| Pd L_2 NH $_3$ | – | 3353 | 1604 | 1304 | 488 | 544 |
| L_3 | 3119-2427 | – | 1617 | 1228 | – | – |
| PdNAPNH $_3$ | – | 3340 | 1600 | 1261 | 471 | 508 |

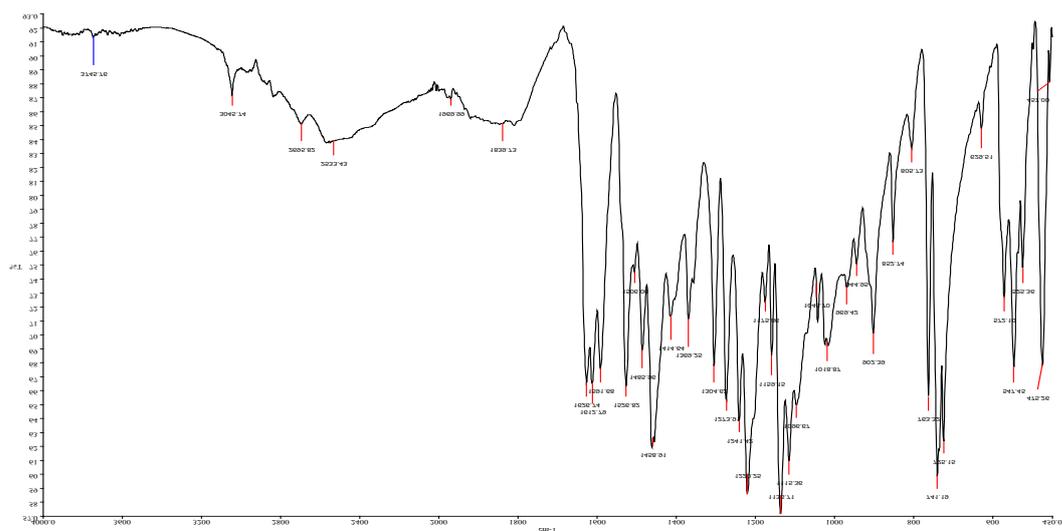
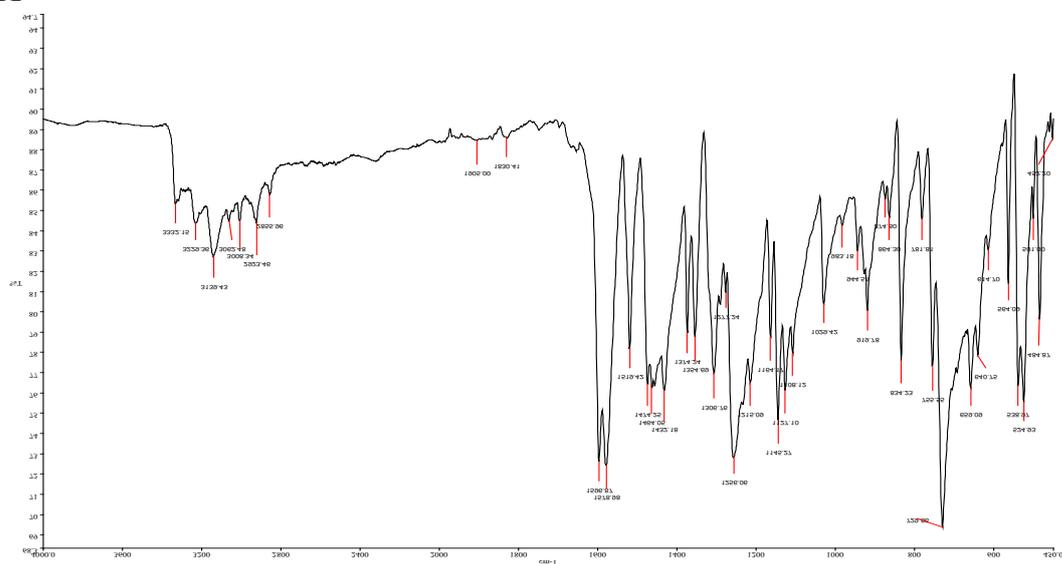
**A****B**

Fig. 1. IR spectra of L₁ (A) and PdL₁NH₃ (B).

NMR spectra

The NMR data (^1H and ^{13}C) of the compounds are presented in Table 3. The free Schiff bases displayed two singlet signals for the two phenolic $-\text{OH}$ protons at δ 13.78-13.07 ppm and δ 10.31-9.68 ppm. The spectra showed singlet signals at δ 8.92 ppm (L_1), 8.89 ppm (L_2) and 9.47 ppm (L_3) attributed to the azomethine ($-\text{HC}=\text{N}$) protons. The protons of the aromatic rings appeared as multiplets around δ 8.34-6.70 ppm [4, 16, 17]. The three protons of the methoxy ($-\text{OCH}_3$) groups in ' L_2 ' appeared as a sharp singlet signal at δ 3.71 ppm [18, 19]. A comparison of the ^1H NMR spectra of the parent Schiff bases with the Pd(II) complexes spectra (Figs. 4-6) revealed that the two phenolic $-\text{OH}$ protons in the parent Schiff bases were not present in the Pd(II) complexes. This indicated the detachment of the Schiff bases $-\text{OH}$ protons before coordinating with the Pd(II) ion. It also corroborated the coordination of oxygen atoms to Pd(II) ion. Moreover, the coordination of the azomethine nitrogen atoms of the parent Schiff bases to the Pd(II) ion were indicated by the displacements of the chemical shifts of the azomethine hydrogen to upfield region at δ 9.42-8.75 ppm. The aromatic protons appeared as multiplets around δ 8.57-6.53 ppm for the complexes [4, 17]. The new singlet signals at δ 3.56 ppm, δ 3.51 ppm and δ 3.50 ppm in the Pd(II) complexes were assigned to the three

hydrogen atoms of $-\text{NH}_3$ groups [14]. The three $-\text{OCH}_3$ group protons of ' L_2 ' in the Pd(II) complexes appeared as a sharp singlet signal at δ 3.70 ppm [18, 20]. Signals at 3.33 ppm and 2.45-2.50 ppm are for $\text{H}_2\text{O}/\text{DMSO}$ and DMSO respectively in all the spectra.

s=singlet, m= multiplets, Ar= aromatic.

The ^{13}C NMR spectra of the palladium(II) complexes are consistent with the proton NMR of the complexes. The ^{13}C NMR spectrum of PdL_1NH_3 (Fig. 7) showed a peak at δ 167.47 ppm which confirmed the presence of azomethine carbon in the complex. The aromatic carbons' peaks appeared in the range δ 162.98-114.79 ppm [17]. In PdL_2NH_3 ^{13}C NMR spectrum (Fig. 8), the azomethine carbon appeared at δ 167.39 ppm and the aromatic carbons' peaks appeared in the range δ 156.49-114.79 ppm while the carbon peak for $-\text{OCH}_3$ group appeared at δ 55.96 ppm [18, 19]. PdL_3NH_3 ^{13}C NMR spectrum (Fig. 9) showed the azomethine carbon's peak at δ 167.18 ppm and the aromatic carbons' peaks in the range δ 163.60-111.71 ppm [9].

Table 3. The ^1H and ^{13}C NMR spectra data of the Schiff bases and Pd(II) complexes.

| Schiff Bases and Complexes | ^1H NMR | |
|----------------------------|-----------------------------|-----------------------------------|
| | δ (ppm) | Assignment |
| L_1 | 13.78 | (s, 1H, $-\text{OH}$) |
| | 9.73 | (s, 1H, $-\text{OH}$) |
| | 8.92 | (s, 1H, $-\text{HC}=\text{N}$) |
| | 7.56-6.84 | (m, 8H, CH_{Ar}) |
| PdL_1NH_3 | — | — |
| | — | — |
| | 8.75 | (s, 1H, $-\text{HC}=\text{N}$) |
| | 7.90-6.50 | (m, 8H, CH_{Ar}) |
| | 3.51 | (s, 3H, $-\text{NH}_3$) |
| | 162.98-114.79 | (12C, C_{Ar}) |
| 167.47 | (1C, $\text{HC}=\text{N}$) | |

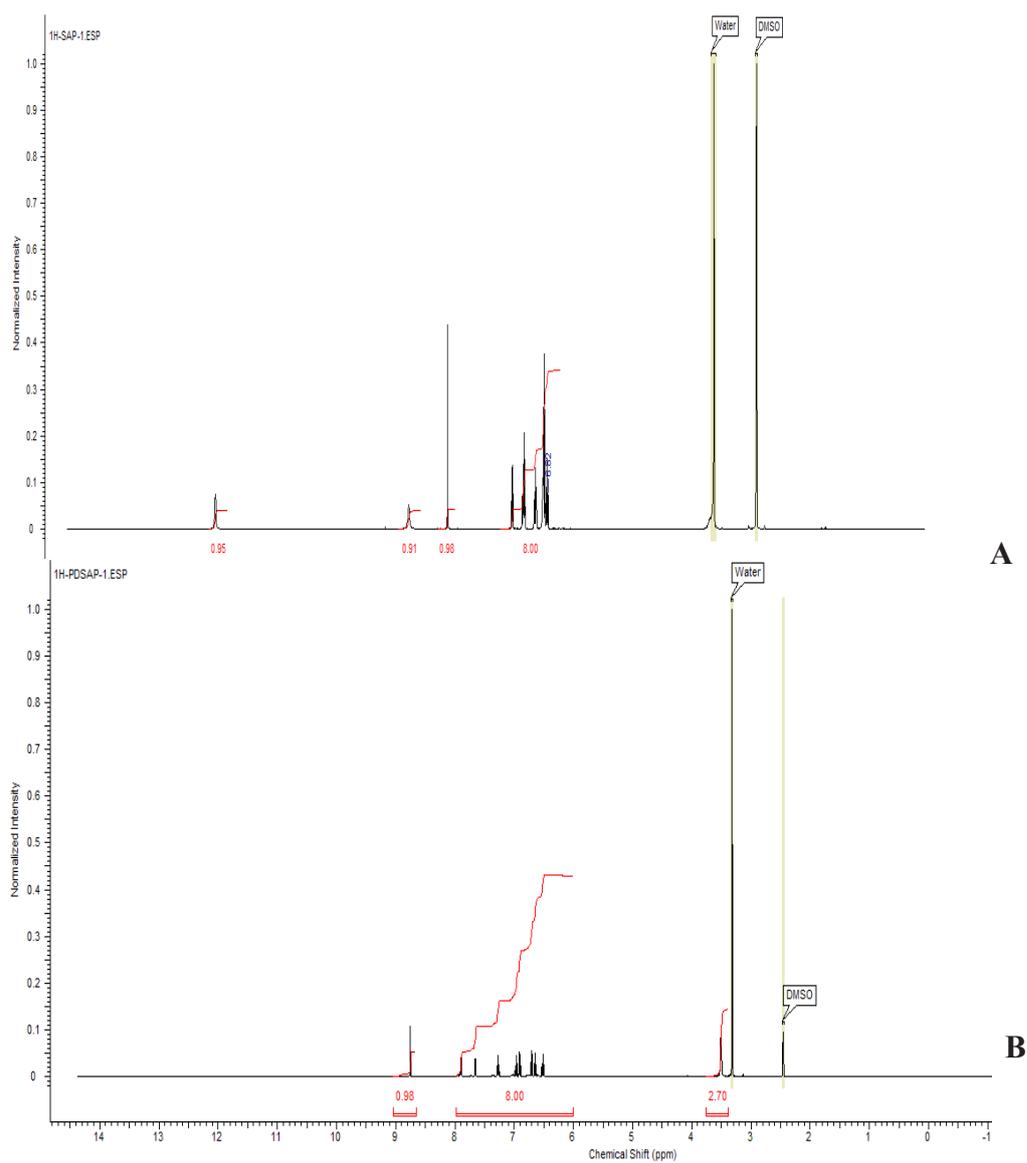


Fig. 4. ^1H NMR spectra of L_1 (A) and PdL_1NH_3 (B).

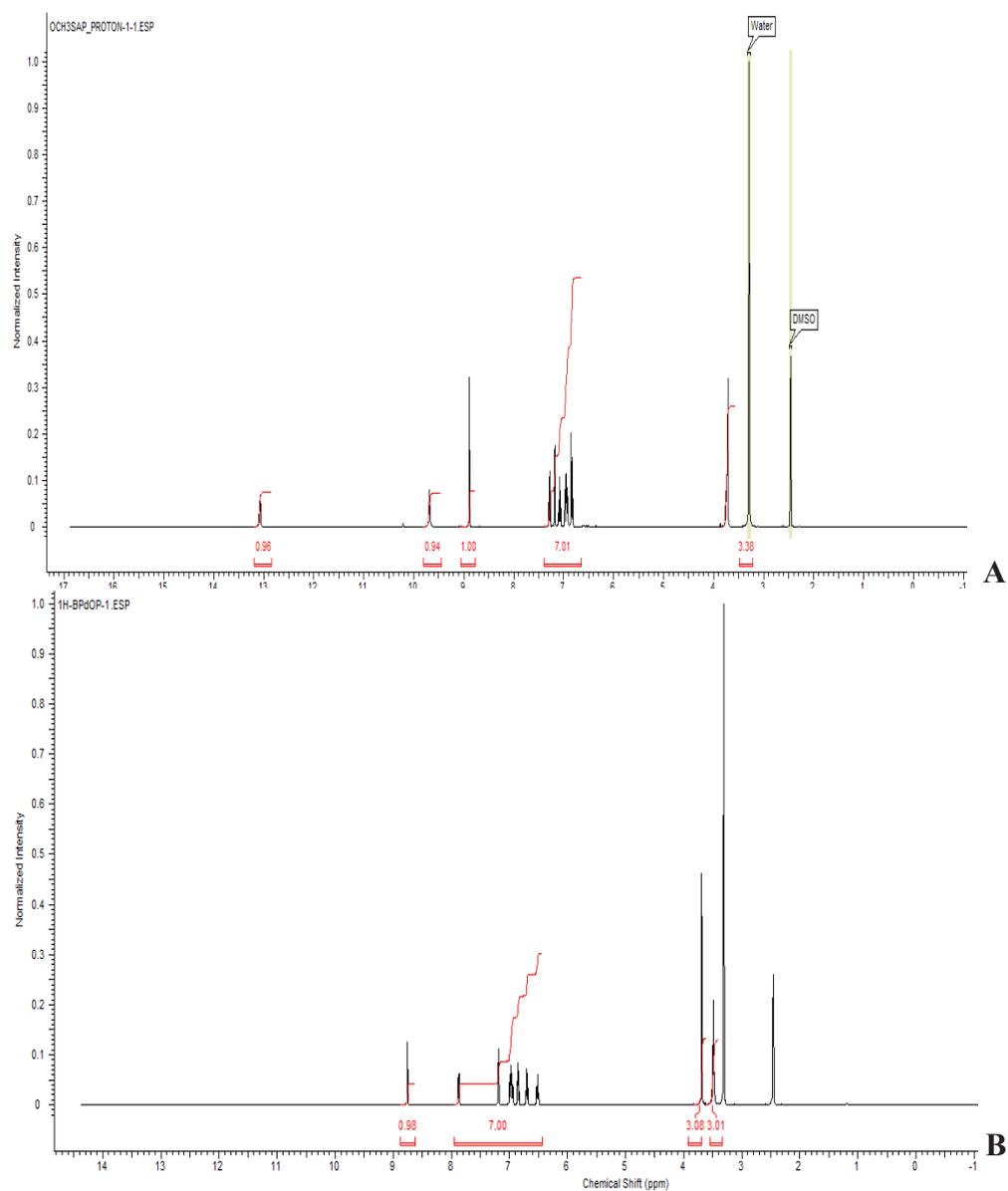


Fig. 5. ^1H NMR spectra of L_2 (A) and PdL_2NH_3 (B).

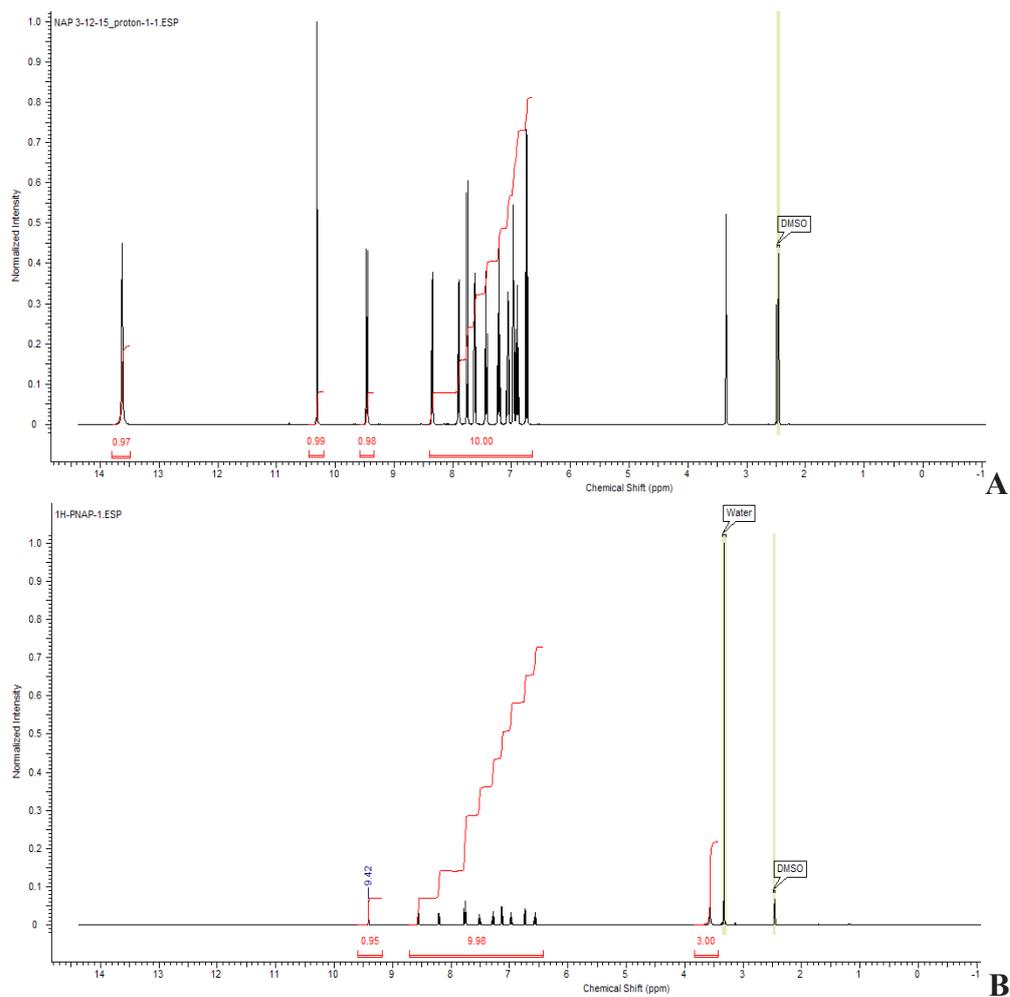


Fig. 6. ^1H NMR spectra of L_3 (A) and PdL_3NH_3 (B).

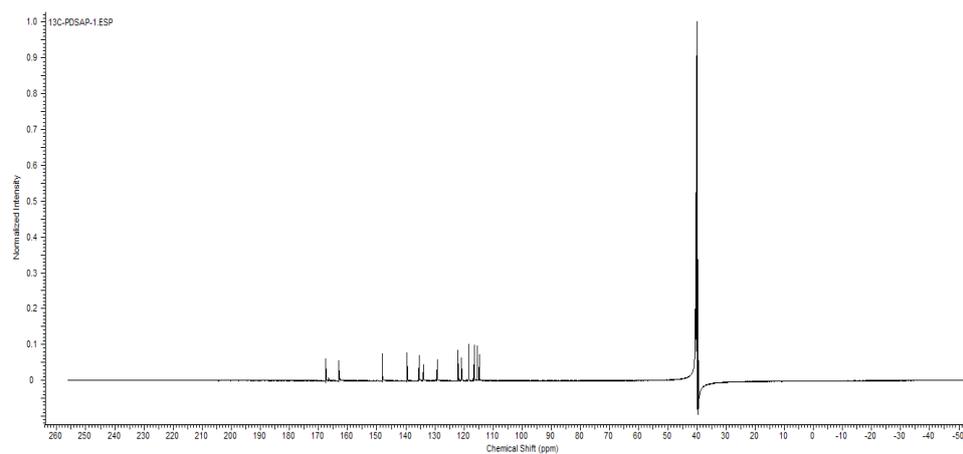


Fig. 7. ^{13}C NMR of PdL_1NH_3 complex.

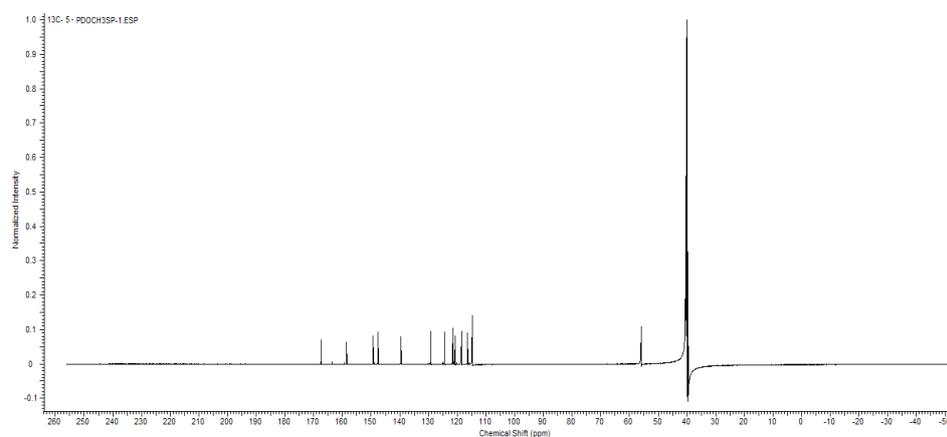


Fig. 8: ^{13}C NMR of PdL_2NH_3 complex.

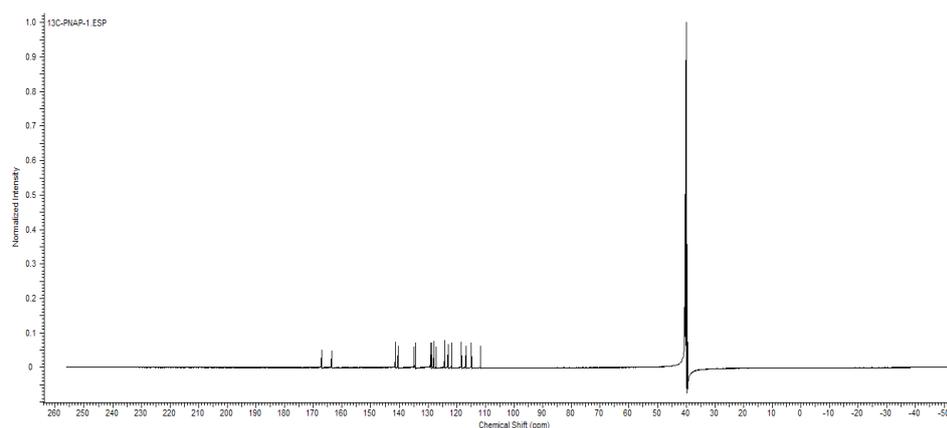


Fig.9. ^{13}C NMR of PdL_3NH_3 complex.

UV-Visible spectra

The UV-Visible spectral data of the compounds are presented in Table 4. The parent Schiff bases spectra showed two absorption bands around $37027.04\text{--}36625.03\text{ cm}^{-1}$ and $28328.61\text{--}22271.71\text{ cm}^{-1}$ which were attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively [9, 18, 20]. These moved to lower frequencies in the complexes spectra corroborating the attachment of the Schiff base ligands to the Pd(II) ions. PdL_1NH_3 displayed three bands at 32467.53 cm^{-1} , 23752.97 cm^{-1} and 22624.43 cm^{-1} attributed to $\pi\rightarrow\pi^*$, ${}^1\text{A}_{1g}\rightarrow{}^1\text{E}_{1g}$ and ${}^1\text{A}_{1g}\rightarrow{}^1\text{B}_{1g}$ transitions respectively [17]. PdL_2NH_3 spectrum displayed two absorptions at 32154.34 cm^{-1} and 21551.72 cm^{-1} assigned to $\pi\rightarrow\pi^*$ and ${}^1\text{A}_{1g}\rightarrow{}^1\text{B}_{1g}$ transitions respectively [19]. PdL_3NH_3

spectrum revealed three absorptions at 31152.65 , 22471.91 and 21186.44 cm^{-1} assigned to $\pi\rightarrow\pi^*$, ${}^1\text{A}_{1g}\rightarrow{}^1\text{E}_{1g}$ and ${}^1\text{A}_{1g}\rightarrow{}^1\text{B}_{1g}$ respectively. The UV-Visible spectra data revealed that all the complexes displayed absorption bands above 16666.67 cm^{-1} (below 600 nm). The absence of absorption band below 16666.67 cm^{-1} (above 600 nm) revealed a large crystal-field splitting which is characteristic of square planar geometry [16]. Therefore, a square planar geometry was proposed for the Pd(II) complexes. Furthermore, the complexes displayed sharp signals in their proton NMR spectra which is also characteristics of square planar geometry [21], thereby corroborating the proposed square planar geometry for the complexes.

Table 4. Electronic spectral data of the salicylaldimines and the Pd(II) complexes.

| Compounds | Bands in cm ⁻¹ | Assignments |
|----------------------------------|------------------------------|---|
| L ₁ | 36625.03, 28328.61 | $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ |
| PdL ₁ NH ₃ | 32467.53, 23752.97, 22624.43 | $\pi \rightarrow \pi^*$, ${}^1A_{1g} \rightarrow {}^1E_{1g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ |
| L ₂ | 37027.04, 27027.03 | $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ |
| PdL ₂ NH ₃ | 32154.34, 21154.34 | $\pi \rightarrow \pi^*$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ |
| L ₃ | 30769.23, 26859.00 | $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ |
| PdL ₃ NH ₃ | 31152.65, 22471.91, 21186.44 | $\pi \rightarrow \pi^*$, ${}^1A_{1g} \rightarrow {}^1E_{1g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ |

Antibacterial activities

The antibacterial activities results of the compounds are summarized in Table 5. The results revealed that all the synthesized Schiff base ligands and the Pd(II) complexes exhibited antibacterial activities. The Pd(II) complexes displayed better inhibitory effects against the bacterial strains than the parent Schiff bases. This showed that the antibacterial activities of the parent Schiff bases increase on coordination with the Pd(II) ion. This can be related to chelation theory and probably the synergistic effect of ammonia molecules in the complexes. On chelation, ligands become more potent, consequently destroying or restricting the growth of more bacterial strains than the free ligands. Chelation reduces the polarity of the metal ion thereby easing the inflow of the complexes across the bacteria's cell wall [5, 18, 20, 22, 23].

In comparison with standard Gentamycin, PdL₂NH₃ exhibited more inhibitory effects against the bacterial strains than standard Gentamycin. Moreover, all the complexes showed more potent activities against *S. agalactiae* than standard Gentamycin which was inactive against it. The methoxy-substituted Pd(II) complex (PdL₂NH₃) exhibited the most potent activity among the complexes.

Total antioxidant capacity

The TAC results of the compounds are presented in Table 6. The results revealed that the Pd(II) complexes exhibited higher TAC than the Schiff base ligands, this could be related to the coordination of the Pd(II) ions and probably the synergistic effect of ammonia molecules in the complexes. The bonding of the central metal ion to the ligands facilitates their abilities to make unpaired electrons stable, thereby help remove free radicals [17, 24]. Hence, making the complexes better antioxidants than the parent ligands. PdL₂NH₃ exhibited the highest TAC among the Pd(II) complexes.

Table 5. Antibacterial activities of the Schiff bases and the complexes.

| Schiff bases/ Complexes | mg | <i>E. coli</i> | | <i>K. pneumoniae</i> | | <i>P. aeruginosa</i> | | <i>S. agalactiae</i> | | <i>S. aureus</i> | | <i>S. typhimurium</i> | | <i>P. mirabilis</i> | | |
|----------------------------------|----|----------------|----|----------------------|----|----------------------|----|----------------------|----|------------------|----|-----------------------|----|---------------------|----|----|
| | | 5 | 10 | 15 | 5 | 10 | 15 | 5 | 10 | 15 | 5 | 10 | 15 | 5 | 10 | 15 |
| L ₁ | 16 | 16 | 17 | 15 | 16 | 16 | 17 | 19 | 14 | 14 | 16 | 16 | 16 | 14 | 14 | 14 |
| PdL ₁ NH ₃ | 18 | 18 | 22 | 16 | 17 | 17 | 18 | 18 | 20 | 22 | 17 | 19 | 18 | 14 | 14 | 14 |
| L ₂ | 22 | 22 | 22 | 20 | 20 | 30 | 30 | 30 | 22 | 22 | 30 | 30 | 18 | 25 | 25 | 25 |
| PdL ₂ NH ₃ | 24 | 24 | 24 | 22 | 24 | 32 | 32 | 32 | 24 | 25 | 32 | 32 | 20 | 28 | 28 | 28 |
| L ₃ | 14 | 14 | 18 | 14 | 14 | 14 | 14 | 10 | 12 | 15 | 17 | 17 | 17 | 12 | 12 | 13 |
| PdL ₃ NH ₃ | 16 | 16 | 19 | 16 | 16 | 17 | 17 | 12 | 14 | 16 | 16 | 18 | 18 | 16 | 16 | 16 |
| DMSO | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | | | 20 | | | | | | | | 20 | | | | | 20 |

- = Resistant, not sensitive (< 8 mm), sensitive (9–14 mm), very sensitive (15–19 mm) and ultrasensitive (> 20 mm) [11].

Table 6. Total antioxidant capacities of the Schiff bases and the Pd(II) complexes.

| Schiff bases/Complexes | TAC μg per mg AA |
|----------------------------------|-----------------------------|
| L ₁ | 0.68 |
| PdL ₁ NH ₃ | 0.72 |
| L ₂ | 0.78 |
| PdL ₂ NH ₃ | 1.41 |
| L ₃ | 0.62 |
| PdL ₃ NH ₃ | 0.77 |

Conclusion

Pd(II) complexes containing ammonia, N-(salicylidene)-*o*-aminophenol, N-(5-methoxysalicylidene)-*o*-aminophenol and N-(2-hydroxy-1-naphthalidene)-*o*-aminophenol were synthesized. They were characterized by different spectroscopic methods which confirmed their formation. A square planar geometry was suggested for the complexes. The antibacterial activities of the complexes follow the order: PdL₂NH₃ > PdL₁NH₃ > PdL₃NH₃ while the TAC follow the order PdL₂NH₃ > PdL₃NH₃ > PdL₁NH₃.

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