SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF PALLADIUM(II) COMPLEXES WITH TETRADENTATE N_2O_2 AND BIDENTATE NO-DONOR SALICYLALDEHYDE SCHIFF BASE LIGANDS

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ABSTRACT

In this study, a salen-type (*R*)- and (*S*)-N-5-*tert*-butyl-salicylidene-1-phenylethylamine Schiff base ligands and their Pd(II) complexes were synthesized and characterized by ESI-MS, IR and NMR spectroscopies. The ligands were synthesized from the condensation of ethylenediamine with 5-fluoro-salicylaldehyde and (*R*)- or (*S*)-1-phenylethylamine with 5-*tert*-butyl-salicylaldehyde with high yields of 96,3-97.5 %. Their corresponding Pd(II) complexes were formed with yields around 76 %.

Keywords: Pd(II)-complexes, synthesis, characterization.

1. INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and typically prepared by the condensation of a primary amine with an aldehyde or ketone. They have been studied extensively because of their selectivity and sensitivity towards various metal ions [1]. Schiff bases have been widely used in many fields e.g., as chelating ligands in coordination chemistry, as catalysts in catalytic reactions, as anti-oxidative, anti-bacterial, anti-biotics, anti-inflammatory agents in biological activities, etc. A large number of Schiff base complexes have been reported so far, and their catalytic and biological properties have also been studied intensively. Metal complexes of Schiff bases have found diverse applications in addition to interesting structural chemistry, such as catalysis in polymerization reaction, reducing thionyl chloride reaction, reducing reaction of cetone, Henry reaction, epoxidation of alkenne and Diels - Alder reaction etc. [2 - 7]. Besides, in recent years, some metal complexes containing Schiff

base ligands have been identified as a very promising class of anti-bacrian, anti-fungal and anti-cancer activating compounds [8 - 10].

Among Schiff bases, tetradentate (N_2O_2) and bidentate (NO) ligands are more attractive to scientist due to they are not only rich property but also capable of creating complexes with most transition metals. We report in this study the synthesis, spectral properties of several Pd(II) complexes of tetradentate (N_2O_2) and bidentate (NO) ligands.

2. EXPERIMENTAL

2.1. Chemicals and instruments

The pure chemicals used in this study were 4-flourophenol 97 % 4-*tert*-butyl phenol 97 %; 1,2-ethylenediamine 99 %, (*R*)- or (*S*)-1-phenylethylamine 99 %, potassium tetrachloro palladium(II) 47.5 % Pd, and solvent CH_3Cl, DMSO 99 % manufactured by Merck (Germany) and Aldrich (USA). Industrial solvents as C_2H_5OH, CH_3OH, CH_2Cl_2, *n*-hexane, ethylacetate (EtOAc) were distilled before used.

The structure of the compounds were determined by the combination of modern spectroscopic methods such as infrared spectra (FT-IR): Instrument is IMPACT-410, Nicolet-Carl Zeiss Jena (Germary); mass spectrum ESI-MS: Instrument is 5989B MS Engine (Hewlett Packard); nuclear magnetic resonance spectrum: Instrument is Bruker Avance 500 MHz, (^{1}H NMR, ^{13}C NMR, HSQC and HMBC). All experimental data and measurements were carried out at the Institute of Chemistry, Vietnam Academy of Science and Technology.

2.2. Synthesis of ligands

2.2.1. Synthesis of ligand N,N'-bis(5-flouro-salicylidene)-1,2-ethylendiamine - ***$H_2$5Fsed (1)***

A solution of 1 mmol (61.9 mg) of 1,2-ethylenediamine in 25 ml of dichloromethane was charged in a round bottom flask (100 ml). Then 2 mmol (288.7 mg) of 5-fluoro-salicylaldehyde was slowly added and the mixture was stirred at room temperature for 3 h. The reaction progress was controled by thin layer chromatography (TLC). After that, 0.142 g Na_2SO_4 anhydrous (99 %) was added to absorb water eliminated during the reaction. Filter the solution after extraction with CH_2Cl_2 and distilled water, rotates in vacuum to recover the solvent and collected the product. The solution obtained after filtering was then evaporated in vacuum to remove solvent. The resulting solid was washed with cold n-hexane and C_2H_5OH several times and dried. The yield of this reaction is 97.5 %.

^{1}H-NMR ($CHCl_3$, 500 MHz), δ_H (ppm), *J* (Hz): 12.84 (1H, *s*, O<u>H</u>), 8.30 (1H, *s*, H-7), 7.04-7.00 (1H, *m*, H-6), 6.92 (1H, *dd*, *J* = 3.0; 8.5, H-4), 6.88 (1H, *d*, *J* = 8.5, H-3), 3.95 (2H, *s*, H-8). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ_C (ppm): 165.58, 165.56 (*d*, C-2); 157.25 (C-7); 156.48, 154.60 (*d*, C-5); 119.65, 119.47 (*d*, C-4); 118.48, 118.43 (*d*, C-3); 118.17, 118.11 (*d*, C-1); 116.61, 116.43 (*d*, C-6); 59.71 (C-8). **(+)ESI-MS** (*m/z*): 304.9 $[M+H]^+$. **IR** (KBr): 3100, 2939, 2911-2853, 1634, 1364, 1139 cm^{-1}.

2.2.2. Synthesis of ligands (R)- and (S)-N-5-tert-butyl-salicylidene-1-phenylethylamine - ***(R)-H5tbspa (2); (S)-H5tbspa (3)***

2.5 mmol (309.7 mg) of (*R*)- or (*S*)-1-phenylethylamine in 10 ml of C_2H_5OH was taken in a

round bottom flask (100 ml). To this solution 2.5 mmol (459.3 mg) of 5-*tert*-butyl-salicylaldehyde was slowly added and the mixture was stirred at room temperature. The progress of reaction was monitored by TLC. After completion of reaction, 2.5 mmol (355.1 mg) of Na_2SO_4 anhydrous was added to absorb water eliminated during reaction. The product mixture were separated by column chromatography using *n*-hexan : EtOAc (9:1) as eluent. The desired product was then washed with C_2H_5OH. The complex is lemon yellow. Yield: 96.5 % (2); 96.3 % **(3).**

✍ **(*R*)-H5*t*bspa ligand**

^{1}H-NMR (DMSO-d_6, 500 MHz), δ_H (ppm), *J* (Hz): 13.26 (1H, *s*, OH); 8.67 (1H, *s*, H-7); 7.44 (1H, *d*, *J* = 2.5, H-6); 7.39-7.34 (5H, *m*, H-10-H-14); 7.28-7.25 (1H, *m*, H-4); 6.81 (1H, *d*, *J* = 8.5, H-3); 4.64 (1H, *q*, *J* = 6.5, H-8); 1.55 (3H, *J* = 7.0, H-15); 1.25 (9H, *s*, H-17; H-18; H-19). **^{13}C NMR** ($CDCl_3$, 125 MHz), δ_C (ppm): 164.79 (C-7); 158.07 (C-2); 144.05 (C-9); 140.86 (C-5); 129.45 (C-4); 128.55 (C-11, C-13); 128.09 (C-6); 127.05 (C-12); 126.27 (C-10, C-14); 117.93 (C-1); 115.90 (C-3); 66.91 (C-8); 33.68 (C-16); 31.17 (C-17; C-18, C-19); 24.21 (C-15). **(+)ESI-MS** (*m/z*): 282.0 $[M-H]^+$. **IR** (KBr): 3068, 3027, 2966-2867, 1634, 1323, 1156 cm^{-1}.

✍ **(*S*)-H5*t*bspa ligand**

^{1}H-NMR ($CDCl_3$, 500 MHz), δ_H (ppm), *J* (Hz): 13.30 (1H, *s*, OH); 8.41 (1H, *s*, H-7); 7.36-7.32 (5H, *m*, H-11-H-14); 7.26 - 7.21 (2H, *m*, H-4; H-6); 6.89 (1H, *dd*, *J* = 9.0, H-3); 4.54 (1H, *q*, *J* = 6.5, H-8); 1.62 (3H, *s*, H-15); 1.29 (9H, *s*, H-17; H-18; H-19). **^{13}C NMR** ($CDCl_3$, 125 MHz), δ_C (ppm): 163.84 (C-7); 158.75 (C-2); 143.98 (C-9); 141.35 (C-5); 129.62 (C-4); 128.65 (C-11; C-13); 127.82 (C-6); 127.21 (C-12); 126.43 (C-10; C-14); 118.12 (C-1); 116.52 (C-3); 68.48 (C-8); 33.97 (C-16); 31.44 (C-17; C-18, C-19); 24.89 (C-15). **(+)ESI-MS** (*m/z*): 279.9 $[M-H]^+$ (%). **IR** (KBr): 3058; 3027; 2953-2868; 1634; 1378; 1135 cm^{-1}.

2.3. Synthetic complexes

2.3.1. Synthetic complex of Pd(II) with N,N'-bis(5-flouro-salicylidene)-1,2-ethylendiamine [Pd(5Fsed)] ***1a***

To solution of 0.5 mmol (163 mg) K_2PdCl_4 in 10 ml DMSO, 0.5 mmol (156.8 mg) of ligand N,N'-bis(5-fluoro-salicylidene)-1,2-ethylenediamine 97 % in 10ml DMSO was added. The resulting reaction mixture was stirred slowly and 139 mg K_2CO_3 dissolved in H_2O was added. Thereafter, the reaction mixture was continuously stirred at 60 ^oC for 3h in dark environment at pH = 9.The progress of reaction was checked by TLC. When the starting material was dim in thin layer, the reaction was stopped. The reaction mixture was cooled. The precipitation was filtered and washed with distilled water for removing DMSO solvent. Washing the precipitation on filter paper by cooled *n*-hexane, then certain time by: C_2H_5OH; CH_3OH; EtOAc; CH_2Cl_2. The obtained complex is yellow solid, which isn't soluble in solvents as CH_2Cl_2, EtOAc, MeOH, DMSO. Yield: 76.3 %.

^{1}H-NMR (DMSO-d_6, 500 MHz), δ_H (ppm), *J* (Hz): 8.16 (1H, *s*, H-7); 7.22-7.19 (1H, *dd*, *J* = 3.0, 9.0, H-4); 7.22-7.19 (1H, *d*, *J* = 2,5, H-6); 6.84-6.81 (1H, *m*, H-3); 3.84 (1H, *s*, H-8).**^{13}C-NMR** (DMSO-d_6, 125 MHz), δ_C (ppm): 161.53 (C-2); 159.48 (C-7); 152.44, 150.62 (*d*, C-5); 122.04; 120.98 (*d*, C-3), 122.18, 121.99 (*d*, C-4); 119.20, 119.14 (*d*, C-1); 116.86, 116.68 (*d*, C-6); 59.36 (C-8). **(+)ESI-MS** (*m/z*): 408.9 $[M+H]^+$. **IR** (KBr): 3100, 2926-2873, 1634, 1306, 1145, 777; 471 cm^{-1}.

2.3.2. Synthetic complex of Pd(II) với (R)-N-5-tert-butyl-salicylidene-1-phenylethylamine [Pd(R-5tbspa)$_2$] ***2a***

1 mmol (289.1 mg) of ligand 97 % of (*R*) or (*S*)-N-5-*tert*-butyl-salicylidene-1-phenylethylamine in 10 ml DMSO was added into a round bottom flask (50 ml) along with 0.5 mmol (163.2 mg) K_2PdCl_4 in 100 ml. The resulting mixture was stirred slowly and 1 mmol (109.2 mg) of K_2CO_3 in H_2O was added. The reaction was stirred for about 3h at 60 ^{0}C, in dark environment with pH = 9. The reaction was checked by TLC. Filter the solution after extraction with CH_2Cl_2 and distilled water to remove DMSO solvent and water. The organic solution is dissolved in CH_2Cl_2. The organic phase was evaporated under low pressure to remove solvent. The product was purified by column chromatography using *n*-hexane: EtOAc (9: 1) as eluent. The obtained complex is bright red solid with a yield of 76.9 %.

^{1}H-NMR ($CDCl_3$, 500 MHz), δ_H (ppm), *J* (Hz): 7.47 (3H, *m*, H-7, H-11; H-13); 7.39-7.36 (2H, *m*, H-10; H-14); 7.32-7.29 (1H, *m*, H-12); 7.27-7.25 (1H, *dd*, *J* = 2.5; 8.5, H-4); 6.92 (1H, *d*, *J* = 2.5, H-6); 6.81 (1H, *d*, *J* = 9.0, H-3); 6.14 (1H, *q*, *J* = 7.5, H-8); 1.75 (3H, *d*, *J* = 6.5, H-15); 1.22 (9H, *s*, H-17, H-18, H-19). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ_C (ppm): 162.25 (C-7); 161.51 (C-2); 142.59 (C-9); 137.35 (C-5); 132.80 (C-4); 129.47 (C-11, C-13); 128.60 (C-6); 128.12 (C-12); 127.35 (C-10, C-14); 120.16 (C-1); 119.96 (C-3); 57.07 (C-8); 33.61 (C-16); 31.33 (C-17); 29.71 (C-18, C-19); 21.33 (C-15) . **(+)ESI-MS** (*m/z*): 667.2 $[M+H]^+$. $\boldsymbol{\alpha_D^{23}}$ = +44 (c 1.0; CH_3OH). **IR** (KBr): 3020; 2960-2855; 1619; 1329; 1148; 695; 461 cm^{-1}.

*2.3.3. Complex Pd(II) with (S)-N-5-tert-butyl-salicylidene-1-phenylethylamine [Pd(S-5tbspa)$_2$] **3a***

The complex was prepared in a pathway similar to [Pd(*R*-5*t*bspa)$_2$] **2a** as above. The obtained complex is bright red solid with a yield of 76.3 %.

^{1}H-NMR (DMSO-d_6, 500 MHz), δ_H (ppm), *J* (Hz): 8.67 (1H, *s*, H-7); 7.44 (1H, *d*, *J* = 2.5, H-6); 7.39-7.34 (5H, *m*, H-4, H-10, H-11, H-13, H-14); 7.24 (1H, *m*, H-12); 6.81 (1H, *d*, *J* = 8.5, H-3); 4.64 (1H, *q*, *J* = 7.5, H-8); 1.55 (3H, *d*, *J* = 7.5, H-15); 1.25 (9H, *s*, H-17, H-18, H-19). **^{13}C-NMR** (DMSO-d_6, 125 MHz), δ_C (ppm): 164.78 (C-7); 158.06 (C-2); 144.04 (C-9); 140.85 (C-5); 129.44 (C-4); 128.54 (C-11, C-13); 128.08 (C-6); 127.04 (C-12); 126.26 (C-10, C-14); 117.92 (C-1); 115.89 (C-3); 66.91 (C-8); 33.67 (C-16); 31.16 (C-17, C-18, C-19); 24.20 (C-15). **(+)ESI-MS** (*m/z*): 667.1 $[M+H]^+$. $\boldsymbol{\alpha_D^{23}}$ = -42 (c 1.0, CH_3OH). **IR** (KBr):3030, 2961-2862, 1618, 1328, 1147, 662, 461 cm^{-1}.

3. RESULTS AND DISCUSSION

The most important bands and their tentative assignment in the IR spectrum of the free ligands and its complexes are presented in Table 1. IR spectra, the wavelength range with weak intensityin the region 3020–3100 cm^{-1} have been recorded for the ligands and theirs complexes which may be due to the C-H group. The absorption in the region 2961–2853 cm^{-1} can be attributed to the valence oscillation of saturated C-H. In the IR spectra, the strong absorption at 1634–1635 cm^{-1} is due to C=N imino stretching vibrations. This is also shifted to a lower value than that of the complexes at 1618–1634 cm^{-1} confirming the coordination of the imino nitrogen to the Pd(II) ion. The medium intensity at 1148–1135cm^{-1} is due to the valence oscillation of C=C. The IR spectrum of the ligands show absorption band at 2939–3027cm^{-1} which may be due to the OH group that is linked with aromatic ring. The OH stretching for the complexes are not appeared on the region at (2939 to 3027 cm^{-1}). On the other hand, the IR spectra of the complexes exhibited new non-ligand bands in the range 777–662cm^{-1} and in the range 471–461cm^{-1} assigned as Pd-O and Pd-N stretching vibrations, respectively.

Table 1. IR spectrum data (cm^{-1}) of the ligands and their complexes

Compounds	ν(C-H) aromatic	νOH	ν(C-H) saturate	ν(C=N)	ν(C-O)	ν(C=C)	ν(M-O)	ν(M-N)
$H_2$5Fsed **1**	3100	2939	2911-2853	1635	1364	1139	-	-
[Pd(5Fsed)] **1a**	3100	-	2926-2873	1634	1306	1145	777	471
(*R)*-H5*t*bspa **2**	3068	3027	2966-2867	1634	1323	1156	-	-
[Pd(*R*-5*t*bspa)$_2$] **2a**	3020	-	2960-2855	1619	1329	1148	695	461
(*S)*-H5*t*bspa **3**	3058	3027	2953-2868	1634	1378	1135	-	-
[Pd(*S*-5*t*bspa)$_2$] **3a**	3030	-	2961-2862	1618	1328	1147	662	461

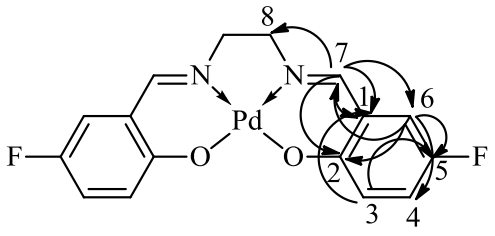

Figure 2. Interactive HMBC (→) of Complex [Pd(5Fsed)] **1a.**

The mass spectrum of Pd(II) complexes showed a peak at 408.9, 667.2 and 667.1 m/z which was assigned for $[M+H]^+$. This result has shown that peak of fragments of ion molecular $[M+H]^+$ (mass m/z ~ M+1) was found in all recorded +MS spectrum with highly frequency (100 %). This show that ligands and their complexes are quite stable in the recorded conditions. Therefore, the result of mass spectrum demonstrate that intended fomula of ligands and their complexes are suitable. This result is suitable with the result of IR spectrum.

The resonance signal of proton on the OH group in the range of 13.15-13.30 ppm is not absent in the ^{1}H-NMR spectrum of complex **1a**; **2a** and **3a**, that indicates the coordination behavior between ligand and Pd(II) via O donor atom.

^{1}H-NMR spectrum of **complex 1a** (Figure 2) showed the proton signals of molecule half. ^{1}H-NMR spectrum gives the signal of 3 aromatic ring protons at δ_H 7.22-7.19 (1H, *d, J* = 2.5, H-6); 7.22-7.19 (1H, *dd, J* = 3.0; 9.0, H-4); 6.84 - 6.81 (1H, *m*, H-3); A signal of olefin proton at δ_H 8.16 (1H, *s*, H-7) and the *singlet* signal of the methylene group at δ_H 3.84 (1H, *s*, H-8). In the ^{1}H-NMR spectrum, the proton signal in the aromatic ring appears as a *doublet* due to H-F coupling.

HSQC spectrum of the complex **1a** shows a resonance signal at H-7 [δ_H 8.16 (1H, *s*)]/ C-7 (δ_C 159.48); H-4 [δ_H 7.22-7.19 (1H, m)]/ C-4 [δ_C 122.18; 121.99 (*d*)]; H-6 [δ_H 7.22-7.19 (1H, m)]/ C-6 [δ_C 116.86; 116.68 (*d*)]; H-3 [δ_H 6.84-6.81 (1H, *m*)]/ C-3 [(δ_C 121.04; 120.98 (*d*)]; H-8 [δ_H 3.84 (3H, s)]/ C-8 (δ_C 59.36).

HMBC spectrum of the complex **1a** shows resonance signal H-7 [δ_H 8.16 (*s*)]/ C-1 [δ_C 119.20, 119.14 (*d*)]; C-2 (δ_C 161.53); C-6 [δ_C 116.86, 116.68 (*d*)]; C-8 (δ_C 59.36); H-3 [δ_H 6.84-6.81 (*m*)]/ C-1 [δ_C 119.20, 119.14 (*d*)]; C-5 [δ_C 152.44, 150.62 (*d*)]; H-6 [δ_H 7.22-7.19 (m)]/ C-7 *(*δ_C 159.48); C-2 (δ_C 161.53); C-5 (δ_C 152.44, 150.62).

^{13}C-NMR spectrum of complex **1a** shows resonance signals of 8 carbons in which 6 carbon atoms in the aromatic ring. The signal of carbon atom in the aromatic ring appears as a *doublet* due to C-F coupling, signals of carbon atoms of the aromatic ring at δ_C 152.44, 150.62 (*d*, C-5); 122.18, 121.99 (*d*, C-4); 121.04, 120.98 (*d*, C-3); 119.20, 119.14 (*d*, C-1); 11.86, 116.68 (*d*, C-6). Signal of carbon atoms olefin and methylene at δ_C 159.48 (C-7) and 59.36 ppm.

^{1}H-NMR spectrum of complex **2a** (Figure 4) shows the proton signals of molecule half, too. The signals of 5 protons in the first aromatic ring and 1 proton conjugated olefin with the aromatic ring at δ_H 7.39-7.36 (3H, *m*, H-7, H-11, H-13); 7.39-7.36 (2H, *m*, H-10, H-14); 7.32-

7.29 (1H, *m*, H-12); 3 protons in the second aromatic ring at δ_H 6.92 (1H, *d*, *J* = 2.5, H-6); 6.81 ppm region (1H, *d*, *J* = 9.0, H-3); 7.27-7.25 (1H, *dd*, *J* = 2.5, 8.5, H-4). Proton H-4 in the aromatic ring interacts to 1 proton meta (H-6) with coupling constant *J* = 2.5 Hz and 1 proton ortho (H-3) with coupling constant *J* = 8.5 Hz. The signal of proton methine containing nitrogen atom at δ_H 6.14 (1H, *q*, *J* = 7.5, H-8). The doublet signal in the spectrum of studied compound at δ_H 1.75 ppm region (3H, *d*, *J* = 6.5, H-15) is assigned of proton in the methyl group. Signals of 9 protons at δ_H 1.22 (9H, *s*, H-17; H-18; H-19) are assigned for 9 protons of three methyl groups**.**

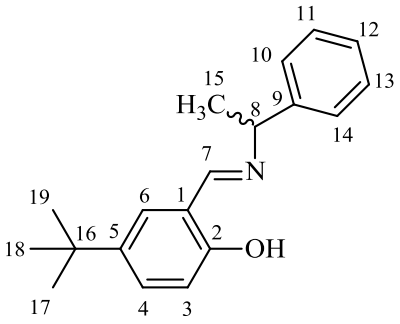

Figure 3: Ligands of NO-donor bidentate Schiff base (*R*)-H5*t*bspa **2** and (*S*)-H5*t*bspa **3**

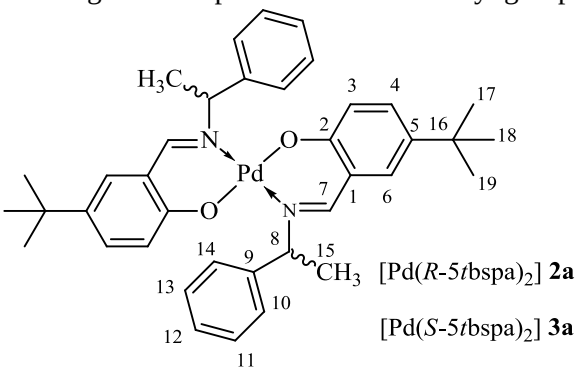

Figure 4: Complexes Pd(II) containing NO-donor bidentate Schiff base ligands

HSQC spectrum of the complex **3a** shows resonance signal at δ_H 7.44 (1H, *d*, *J* = 2.5, H-6)/ C-6 (δ_C 128.08); δ_H 7.39-7.34 (5H, *m*, H-4, H-10, H-11, H-13, H-14)/ C-4 (δ_C 129.44), C-11, C-13 (δ_C 128.54), C-10, C-14 (δ_C 126.26); δ_H 7.24 (1H, *m*, H-12)/ C-12 (δ_C 127.04) và δ_H 6.81 (1H, *d*, *J* = 8.5, H-3)/ C-3 (δ_C 115.89). A *singlet* signal of at δ_H 8.67 (1H, *s*, -C<u>H</u>=N, H-7) is assigned for the proton of the olefin group. The proton of the methylene group is appeared at δ_H 4.64 (1H, *q*, *J* = 7.5, C<u>H</u>-N, H-8) with a*quartet* signal. A *doublet* signal appeared at δ_H 1.55 (3H, *d*, *J* = 7.5, CH_3, H-15) was assigned to protons of the methyl group. A *singlet* signal of the methyl group is appeared at δ_H 1.25 (9H, *s*, CH_3, H-17, H-18, H-19).

HMBC spectrum of the complex **3a** are appeared resonance signal at H-7 (δ_H 8.67, s)/ C-2 (δ_C 158.06), C-6 (δ_C 128.08), C-1 (δ_C 117.92), C-8 (δ_C 66.91), C-15 (δ_C 24.20); at H-6 (δ_H 7.44, *d*, *J* = 2.5 Hz)/ C-7 (δ_C 164.78), C-2 (δ_C 158.06), C-4 (δ_C 129.44), C-16 (δ_C 33.67); at H-4 (δ_H 7.39-7.34, m)/ C-2 (δ_C 158.06), C-6 (δ_C 128.08), C-16 (δ_C 33.67); at H-3 (δ_H 6.81, d, *J* = 8.5 Hz)/ C-2 (δ_C 158.06), C-5 (δ_C 140.85), C-1 (δ_C 117.92); at H-15 (δ_H 1.55, d, *J* = 7.5 Hz)/ C-9 (δ_C 144.04), C-8 (δ_C 66.91). Special resonance signal at H-17, H-18, H-19 (δ_H 1.25, s)/ C-5 (δ_C 140.85) has confirmed the exact position of the *tert*-butyl groups attached to the C-5 position of the aromatic ring.

^{13}CNMR spectrum of the complex **2a, 3a** (Figure 4) shows resonance signals of 19 carbon atoms in which 12 carbon atoms of the aromatic ring at δ_C 161.51, 158.06 (C-2); 142.59; 144.04 (C-9); 137.35, 140.85 (C-5); 132.80, 129.44 (C-4); 129.47, 128.54 (C-11, C-13); 128.60, 128.08 (C-6); 128.12, 127.04 (C-12); 127.35, 126.26 (C-10, C-14); 120.16, 117.92 (C-1); 119.96, 115.89 (C-3). Signal of carbon atoms olefin conjugated the aromatic ring are appeared at δ_C 162.25; 164.78 (C-7); the signal of carbon atom in the methine group containing nitrogen atom are appeared at δ_C 57.07, 66.91 (C-8) and signals of carbon atoms of *tert*-butyl group are appeared at δ_C 33.61, 33.67 (C-16), 21.33, 24.20 (C-15).

4. CONCLUSIONS

Synthesis and characterization of complexes containing tetradentate N_2O_2 and bidentate NO-donor Schiff base ligands have been described in this paper. The spectroscopic data of the complexes give good evidence of proposed structure. The results of IR, ESI - MS, ^{1}H-NMR, ^{13}C-NMR, HMBC and HSQC spectroscopies indicated that the molar ratio of ligand : metal ion in the complex of H_2L ligand is 1: 1 with formula [PdL] in which $(L)^{2-}$ ligand bonds to metal ion via N, N' and two atoms O. The molar ratio of ligand: metal ion in the complexes of HL^n (n: 1 - 2) series are 1: 2 with formula $[PdL_2^n]$, in which $(L^n)^{1-}$ ligands bond to metal ion via N and O.

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