Synthesis, Characterization and antioxidant of new Pd (II) complex of NS donor type Schiff's Base,4-Methyl-N'-(2-(methylthio)benzylidene) benzenesulfonohydrazide

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***Abstract*—A new palladium complex of acyclic bidentate donor type Schiff's base, 4-Methyl-N'-(2-(methylthio) benzylidene) benzenesulfonohydrazide(L1) has been synthesised and characterized by elemental analysis, FT-IR, UV-visible,1H-NMR and 13C{1H}-NMR. The analytical and spectroscopic data revealed that the ligand, L1acts as bidentate donor with the central Pd(II) ion in [Pd(L1) Cl2] which is coordinated through N, S donor atoms. Further, synthesized ligand, L1 and Pd(II) complex [Pd(L1)Cl2] were subjected to antioxidant activity evaluation.**

***Index Terms*—Schiff's base, thioether, hydrazide, palladium, antioxidant.**

I. INTRODUCTION

Schiff base ligands and their transition metal complexes have shown a central role in coordination chemistry. The various inexpensive and effective techniques are also being hired and described for synthesizing Schiff bases and their corresponding metal complexes. Schiff bases have different coordination sites, such as O, N, and S and that form metal ion complexes. Pharmaceutical properties of Schiff base ligands are enhanced by complexation. These synthesized compounds are been highlighting due to their broad range of applications. The utilization of Schiff bases as ligands in metal complexes reveals their potential applications in pharmacology and medicinal chemistry [1-8].

One of the important classes of organic compounds is hydrazide and hydrazone. These synthesized compounds are identified for their potential applications in various fields. In recent years, owing to the multifunctional coordination behaviour of hydrazide greater attention placed, on the synthesis and biological activities of hydrazone-hydrazide ligands and their metal complexes. Hydrazide based metal complexes have been utilized in important biological treatments. Numerous hydrazide Schiff base ligands and their transition metal complexes are reported and evaluated for biological activities, such as antioxidant, antibacterial, antitubercular, antiviral, antifungal, anticonvulsant, anti-inflammatory, and antiprotozoal effects, and have shown effective results [9-13].

Owing to the above facts, newly, we attempt to report the synthesis, characterization and antioxidant evaluation of bidentate N,S donor type Schiff's base ligand,4-Methyl-N'-(2-(methylthio)benzylidene) benz enesulfonohydrazide(L1) and its complex [Pd(L1)Cl2].

II. EXPERIMENTAL

2.1. Materials and analytical methods

2-(Methylthio)benzaldehyde, p-toluene sulfonyl hydrazide and sodium tetrachloropalladate (Na2PdCl4) were purchased from Merck Ind. Pvt. Ltd. All the solvents and other required reagents were procured from different commercial sources. The reactions were monitored by thin-layer chromatography (TLC) using Merck 60 F254 silica gel on pre-coated aluminum sheets. The TLC films were visualized under UV-light and potassium

permanganate stain. Melting points were determined in an open capillary tube and were reported uncorrected. The percentage of carbon (C), hydrogen (H) and nitrogen (N) were determined on semi micro scale by Perkin-Elmer 2400 rapid elemental analyzer (accuracy ± 0.2 %).FT-IR spectra were recorded on the Perkin Elmer Frontier MIR/FIR spectrometer in the range of 400 to 7000 cm-1. 1H and 13C NMR spectra were recorded on an Agilent VNMRS 400 MHz spectrometer. The chemical shift values are given in δ ppm. At the room temperature, the UV-visible spectra were recorded in DMSO of 1.0 × 10-4 M concentration for the wavelength range of 200─800 nm.

2.2. Synthesis of 4-Methyl-N'-(2-(methylthio) benzylidene)benzenesulfonohydrazide (L1)[14]

At room temperature, 2-(Methylthio)benzaldehyde (0.152 g, 1mmol) was magnetically stirred in dry ethanol (20 mL) for 15 minutes. Then a solution of p-toluene sulfonylhydrazide (0.186 g, 1mmol) in dry ethanol (30 mL) was added drop-wise with stirring. Further the reaction mixture was refluxed for 2 h, during which the improvement of the reaction was monitored by TLC. On completion of the reaction, the solvent was completely evaporated on a rotary evaporator to afford L1 as a colourless crystalline solid. The single crystals were developed by the slow evaporation of the methanol solution of L1.

Yield: 0.27 g, 84%; M.P.: 122-124 °C; Anal. Calcd. (found) for C15H16N2O2S2: C 56.22 (56.29), H 5.03 (4.92), N 8.74 (8.61). FT-IR (νmax, ATR/cm-1): 3191 (N-H), 1594 (C=N), 1421 (C=C),1351 (S=O), 1157 (C-N). ^{1}H-NMR (400.31 MHz, DMSO-d6) δ: 2.353 (s, 3H, 10-CH3), 2.42 (s, 3H, S-CH3), 7.16-7.18 (t, 1H, 3-H), 7.320-7.39 (m, 2H, 4-H, 5-H), 7.39-7.42 (d, 2H, 9-H, 11-H), 7.56-7.58 (d, 1H, 2-H), 7.76-7.78 (d, 2H, 8-H, 12-H), 8.27 (s, 1H, CH=N), 11.56 (s, 1H, N-H). ^{13}C-NMR (100.66 MHz; DMSO-d6) δ: 16.07 (S-CH3), 21.44 (C-10), 125.74 (C3), 126.86 (C5), 127.29 (C2), 127.71 (C8, C12), 130.14 (C4), 130.95(C9, C11), 131.53 (C1), 136.47 (C10), 138.43 (C6), 144.03 (C7), 144.27 (CH=N).

2.3. Synthesis of Pd(II) complex, [Pd(L1)Cl2]

A solution of Na2PdCl4 (0.2942 g, 1 mmol) made in (10 m)L of methanol, which was mixed with a solution of L1 (0.320 g, 1 mmol) prepared in methanol (20 mL) under vigorous stirring for 1 h. After complete consumption of the ligand, was monitored by TLC, The solvent was concentrated to 10 mL on a rotary evaporator. Further it was treated with diethylether (15 mL) to afford yellowsolid of [Pd(L1)Cl2], filtered, washed with n-hexane (2x10 mL) and dried.

Yield: 0.38 g, 76%; M.P.: 212–214 °C; Anal. Calcd. (found) for C15H16Cl2N2O2PdS2: C 36.19 (36.28), H 3.24 (3.33), N 5.63 (5.54); λmax(DMSO)/nm: 328, 360 and 411. FT-IR (νmax, ATR/cm-1): 3066 (broad, N-H), 1582 (C=N), 1410 (C=C),1336 (S=O), 1165 (C-N). ^{1}H-NMR (400.31 MHz, DMSO-d6) δ: 2.36 (s, 3H, 10-CH3), 2.463 (s, 3H, S-CH3), 7.174-7.214 (t, 1H, 3-H), 7.331-7.379 (m, 2H, 4-H, 5-H), 7.4-7.42 (d, 2H, 9-H, 11-H), 7.55-7.57 (d, 1H, 2-H), 7.75-7.774 (d, 2H, 8-H, 12-H), 8.289 (s, 1H, CH=N), 11.654 (s, 1H, N-H). ^{13}C-NMR (100.66 MHz; DMSO-d6) δ: 17.05 (S-CH3), 21.46 (C-10), 126 (C3), 126.85 (C5), 127.3 (C2), 127.7 (C8, C12), 130.97 (C9, C11), 130.98 (C4), 131.5 (C1), 136.44 (C10), 140 (C6), 144.06 (C7), 146.87 (CH=N).

2.4. Antioxidant assays

In this study, about three standard methods were determined and measured as per the reported procedure [15]. DPPH activity was performed using 1000 µl of 0.04 mg/ml DPPH solution in methanol. Ligand L1 and its complex [Pd(L1)Cl2] were taken in varying of concentrations of 0 – 1000 µg/ml along with DPPH and incubated in dark for 20 mins. The reduction of DPPH was tabulated by measuring the absorption of the reaction mixture at 517 nm.

Further, ABTS radical was obtained by the reaction of ABTS solution (7 mM) in water taken with 2.45 mM potassium persulfate under 12 h dark condition. The absorbance was adjusted to 0.7±0.02 maintained under ambient temperature at 734 nm. After setting the absorbance, the scavenging potential of L1 and [Pd(L1)Cl2] taken at concentrations of (0 – 1000 µg/ml) was evaluated by taking 10 µl of the compound and incubated for 1 min and absorbance was recorded at the same wavelength. Further, the reaction mixture was incubated for 20 min, the absorbance was re-recorded.

Similarly, superoxide radicals were obtained by taking the reaction mixture containing d 0.1 M phosphate buffer, pH 7.4, 150 µM nitrobluetetrazolium (NBT), 60 µM phenazinemethosulphate, 468 µM NADH. Further,

L1 and [Pd(L1)Cl2] were taken at diverse concentrations (0 – 1000 µg/ml) and incubated at 25° C in dark for a period of 10 min. At 560 nm, the absorbance was measured and recorded.

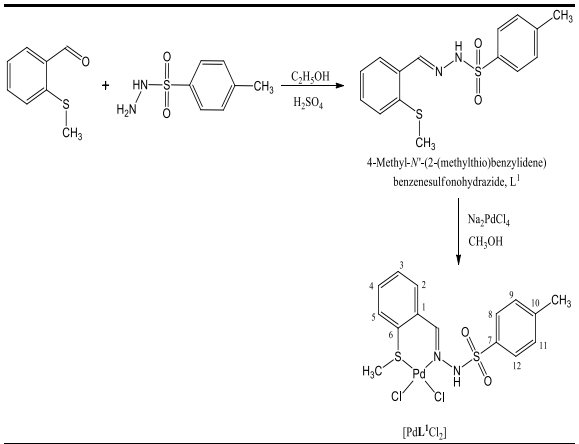
Activities values were expressed as EC50. EC50 says 50% of free, cation and anion radicals scavenged by the L1 and [Pd(L1)Cl2]. The standard antioxidant butylated hydroxyl anisole (BHA) was used as positive control.

III. RESULTS AND DISCUSSION

3.1. Synthesis

The ligand, 4-Methyl-N'-(2-(methylthio) benzylidene) benzenesulfonohydrazide(L1) was synthesized by the reported procedure [14]. The completion of the reaction was observed by TLC using a mixture of methanol and chloroform (1:10). The ligand L1shows a solubility in methanol, ethanol, chloroform, dichloromethane, acetone, DMF, DMSO but insoluble in n-hexane, diethyl ether, THF, toluene, and water.

The product of complex, [Pd(L1)Cl2] was synthesized by a 1:1 stoichiometric reaction betweenL1and Na2PdCl4 at room temperature as per the given reaction in Scheme 1. The solid-state and solution-state of [Pd(L1)Cl2] is stable to air and moisture. The complex [Pd(L1)Cl2] was freely soluble in DMF, DMSO and poorly soluble in methanol, ethanol, chloroform, dichloromethane, acetone. The ligand L1 and complex [Pd(L1)Cl2] were completely characterized by spectroscopic and analytical methods.



Scheme 1 Synthesis of ligand, L1 and itsPd(II) complex, [Pd(L1)Cl2]

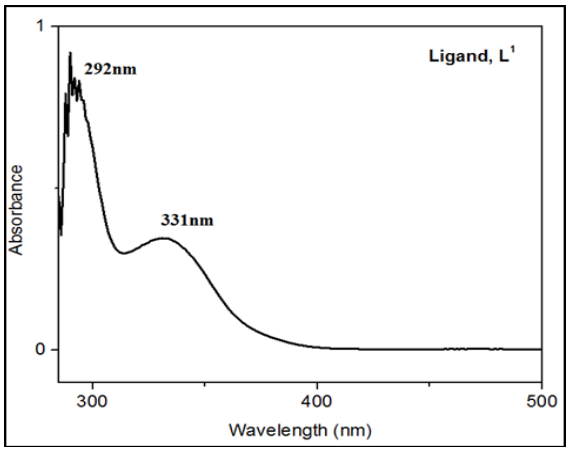
3.2. Spectroscopy [12]

The FT-IR spectra of L1 and [Pd(L1)Cl2]: In the FT-IR spectrum of L1, the N-H stretching band was appeared at ν, 3191 cm-1 which was found at red frequency of about 125 cm-1 in [Pd(L1)Cl2] and appeared at ν, 3066 cm-1.TheC=N stretching band observed at ν, 1594 cm-1, which was found red shift of about 12 cm-1 in [Pd(L1)Cl2] and observed at ν, 1582 cm-1 due to the coordination of imine nitrogen. This indicates that the 'N' atom of imine group (CH=N) was expected to be involved in coordination with central Pd(II) ion.

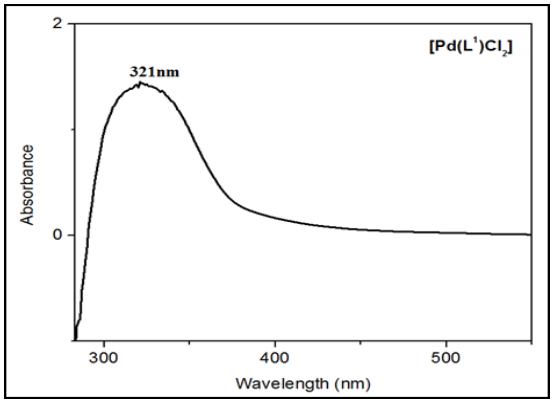
The ^{1}H-NMR spectra of L1and [Pd(L1)Cl2] was recorded in DMSO-d6: In ^{1}H NMR spectrum of L1, the signal for –SCH3 protons observed as singlet at δ, 2.42 ppm, which was found deshielded in [Pd(L1)Cl2], appeared at δ, 2.38 ppm.The azomethine (CH=N) and hydrazide N-H protonsin L1 appeared as a singlet at down field region δ, 8.26 ppm and11.56 ppm respectively. Whereas in [Pd(L1)Cl2], the CH=N and N-H protons appeared at down field region δ, 8.28 ppm and 11.65 ppm respectively. The chemical shifts for other proton of L1 and [Pd(L1)Cl2] were found at characteristic δ ppm values.

The ^{13}C-NMR spectra of L1 and [Pd(L1)Cl2] was recorded in DMSO-d6:. In ^{13}C-NMR spectra of L1, the carbon signal for S–CH3 appeared at δ, 16 ppm whereas in [Pd(L1)Cl2], S–CH3 protons found deshielded and appeared at 17 ppm. The -HC=N (imine) carbon signal observed at about δ, 145ppm whereas in [Pd(L1)Cl2], HC=N carbon signal found deshielded and appeared at 146 ppm. The chemical shifts for the remaining carbons were found less affected by the coordination of donor atoms with Pd(II) ion on coorelation with the ligand L1 and appeared at characteristic δ ppm values.The 1H- and 13C{1H}-NMR spectral data supported that the ligand L1 was coordinated to the central palladium (II) ion as bidentate neutral(N,S) type in [Pd(L1)Cl2].

The UV-Visible spectrum of ligand, L1 and its complex [Pd(L1)Cl2]: The ligand L1 showed two absorption bands at λmax292 nm and λmax331 nm due to π→π* and n→π* transitions respectively. Whereas the complex [Pd(L1)Cl2] shown one strong intense band observed at λmax321 nm is due to the ligand to metal charge transfer (LMCT) and n→π* transition this clearly indicates the existence of coordination of the ligand to central Pd(II) ion.



UV-Visible spectrum of ligand, L1 in DMSO



UV-Visible spectrum of [Pd(L1)Cl2] in DMSO\

3.3 Antioxidant activity

The free radical scavenging capability of L1 and [Pd(L1)Cl2] were examined by a series of in vitro assays viz., results expressed as EC50 values (mg of tests per mL) are summarized in Table 1, revealed that the tested compounds were comparatively lower ($p<0.05$) than standard (positive control).

In all the analysis used in this study, the complex [Pd(L1)Cl2]was effective than the ligand L1 and activities ascended in the order BHA >[Pd(L1)Cl2]> L1. In general, ligand and its Pd complex exhibited a advanced activity in three antioxidant assays. The results revealed that [Pd(L1)Cl2] acquire strong antioxidant ability and significantly lower than the positive control.

Table 1 Antioxidant activity of L1 and [Pd(L1)Cl2]

Compound	EC_{50}*,# (mg/ml)		
	Radical scavenging activities		
	DPPH	ABTS	Superoxide
L^1	3.50 ± 0.32[c]	4.57 ± 1.46[c]	4.50 ± 0.89[c]
$[Pd(L^1)Cl_2]$	2.78 ± 1.53 [b]	3.40 ± 0.27[b]	3.12 ± 0.96[b]
Standard ^	0.65 ± 0.06[a]	0.50 ± 0.04[a]	0.70 ± 0.32[a]

IV. CONCLUSIONS

A new Pd(II) complex of NS donor type hydrazide Schiff's Base, L1, and its Pd(II) complex, [Pd(L1)Cl2] was synthesized and underwent characterization by various spectrochemical techniques. The structures of L1, and its Pd(II) complex, [Pd(L1)Cl2] are supported by UV-VIS, IR, 1HNMR and13CNMR spectroscopic tools. On comparison, the results of the antioxidant activities showed that [Pd(L1)Cl2] performed better than L1 in terms of IC50 values, but less than the standard positive control.

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