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Synthesis and Characterization of Palladium(II) Complexes with Thiosemicarbazones

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Three new complexes *viz.*, $[PdCl_2(H\text{-}aatp)_2]$ (**1**), $[Pd(dmbptz)_2]$ (**2**) and [Pd(btz)] (**3**) have been synthesized by reacting $[PdCl_2(cod)]$ with the ligands H-aatp, H-dmbptz and H_2-btz, respectively (where H-aatp = anisaldene-4-aminothiophenol; H-dmbptz = 2,5-dimethoxybenzyl-4-phenylthiosemicarbazone and H_2-btz = benzil-bisthiosemicarbazone). These have been characterized by various physico-chemical techniques such as FTIR, UV-visible, ^1H and ^{13}C NMR, ESI(+)-mass spectroscopy, *etc*. The complexes were found to be diamagnetic, four coordinated mononuclear neutral molecules with square planar or distorted square planar geometry.

Keywords: Anisaldene-4-aminothiophenol, 2,5-Dimethoxybenzyl-4-phenylthiosemicarbazone, Benzil-bisthiosemicarbazone.

INTRODUCTION

Derivatives of thiosemicarbazones are unique N,S-donors because of their mixed hard-soft character, variable binding modes, flexibility, selectivity and sensitivity towards the central metal atom [1]. These ligands have gained significant attention because of structural similarities with natural biological substances due to the presence of imine group (-N=CH-) which imparts biological activity including antifungal, antibacterial, anti-inflammatory, antiviral, anticonvulsant, antidepressant, anticancer along with good anti-HIV activity and as a result received wide applications in pharmacology and nuclear medicine [2-6]. These ligands can also act as analytical reagents for determining, fixing and entrapping heavy metal ions [7,8]. The transition metal incorporation into thiosemicarbazones leads to an enhancement in their pharmacological activities [9] and the subsequent synergistic effects involving both metal and the thiosemicarbazone leads to the improvement of their biological activities and decreases the cytotoxicity of both the metal ions and ligands [10]. They bind to the transition metal center in a neutral or anionic form. It has been reported that the substituent at the carbon atom of the imine group (-HC=N) can affect the bonding to the metal halides, which determines the formation of mono-, di- and poly-nuclear complexes. Various transition metals such as organotin(IV), iron(II), copper(II), zinc(II), nickel(II), palladium, platinum, ruthenium, *etc*. have been incorporated into thiosemicarbazones and their applications have been studied [11-15]. Palladium(II) derivatives were found to be more preferred for cancer treatment because of their structural analogy with Pt(II) complexes and some complexes show antitumor activity comparable to cisplatin [16]. It has also been reported that pyridoxal thiosemicarbazone ligand is also interesting especially because of the presence of three different existing forms such as (H_2L), singly-deprotonated $(HL)^-$ or doubly-deprotonated $(L)^{2-}$ form [17]. In this note, we wish to report the synthesis and characterization of three new complexes *viz.,* $[PdCl_2(H\text{-}aatp)_2]$, $Pd(dmbptz)_2]$ and [Pd(btz)] from the metal precursor $[PdCl_2(cod)]$ in aerobic condition, which might have potent biological activity.

EXPERIMENTAL

The chemicals used for synthesis and analysis were all of AnalaR grade and procured from Sigma-Aldrich and Fluka. The $PdCl_2$ was purchased from E. Merck. They were used as received without further drying or purification. The metal precursor $[PdCl_2(cod)]$ was synthesized according to literature method [18]. The aluminium-coated TLC (thin-layer chromatography) plates and silica gel used for column chromatography were procured from E. Merck. All the reactions were carried out under aerobic condition.

Physical measurements: The molar conductances of the complexes were measured using digital conductivity bridge (ELICO-CM-180) at room temperature. The melting point of the complexes was determined using a Buchi B450 melting point apparatus. The FTIR spectra (4000-240 cm^{-1}) of the complexes were obtained as KBr disc using Shimadzu Prestige-21 FTIR spectrophotometer. Electronic spectra (800-200 nm) of the complexes were taken by using Shimadzu-Graphicord UV-1700 spectrometer with 1 cm^3 quartz cell. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II FT NMR

spectrometer operating at 400 and 100.62 MHz, respectively using TMS as internal standard. The solvents used were DMSO-d_6 and CD_3CN. The ESI(+) mass spectra of the complexes were recorded on a Water ZQ-4000 mass spectrometer in CH_3CN or $CHCl_3$. Elemental analyses (C, H, N, S) were done by using the Elementer Vario EL III Carlo Erba 1108.

Synthesis

Anisaldene-4-aminothiophenol (H-aatp): To a mixture of anisaldehyde (1.36 g, 10 mmol) and 4-aminothiophenol (1.25 g, 10 mmol) 20 mL methanol was added followed by the addition of few drops of conc. HCl. The mixture was stirred at room temperature for 3 h, which results in the formation of brown coloured precipitate. It was filtered, washed with methanol and then dried over fused $CaCl_2$ in a desiccator. It was soluble in CH_3CN, DCM, DMF, DMSO.

Yield: 77 %; m.p.: 122 °C; m.w. 243 g mol^{-1}, Anal. (%) calcd. for $C_{14}H_{13}NOS$: C, 70.14; H, 5.35; N, 5.66; S, 13.17. Found: C, 69.68; H, 5.12; N, 5.98; S, 12.90. IR (KBr, cm^{-1}): 2575 ν(S-H), 2837 ν(O-CH_3), 1601 ν(C=N), 829 ν(C-S). ^{1}H NMR (300.14 MHz, DMSO-d_6) δ: 8.55 (s, HC=N), 6.87-7.26 (m, 4H, Ph^a-H), 7.51-7.57 (m, 2H, Ph^b-H), 7.87-7.89 (m, 2H, Ph^b-H), 3.84 (s, CH_3), 3.42 (s, S-H). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ: 150.3 (C=N), 114.4 (Ph^a-C^2, Ph^a-C^6), 122.1 (C^{1a}), 128.4 (C^{3a}, C^{5a}), 160.5 (C^{4a}), 127.5 (C^{2b}, C^{6b}), 129.7 (C^{3b}, C^{5b}), 134.3 (C^{1b}), 191.3 (C^{4b}), 55.2 (CH_3).

2,5-Dimethoxybenzaldene-4-phenylthiosemicarbazone (H-dmbptz): To a mixture of 2,5-dimethoxybenzaldehyde (1.66 g, 10 mmol) and 4-phenylthiosemicarbazide (1.65 g, 10 mmol), 25 mL ethanol was added followed by the addition of few drops of glacial acetic acid. The resulting mixture was then refluxed at 65 °C for 2 h to obtain a white solution, which was then allowed to cool to room temperature and a white microcrystalline product was obtained. The solid product was then filtered off, washed with diethyl ether and water and then dried over fused $CaCl_2$ in a desiccator. The crude product was then recrystallized from ethanol for purification. The ligand was soluble in ethanol, DMF and DMSO.

Yield: 82 % m.p.: 220 °C; m.w.: 315 g mol^{-1}. Anal. (%) calcd. for $C_{16}H_{17}N_3O_2S$: C, 60.95; H, 5.40; N, 13.33; S, 10.16. Found: C, 61.12; H, 5.29; N, 13.46; S, 10.37 %. IR (KBr, cm^{-1}): 3319 ν(N-H), 3167 ν(N-H), 2854 ν(O-CH_3), 1606 ν(C=N), 1172 ν(N-N), 830 ν(C=S). ^{1}H NMR (300.14 MHz, DMSO-d_6) δ: 9.80 (s, 1H, N-H), 8.30 (s, HC=N), 9.45 (s, 1H, N-H), 6.96-7.22 (m, 3H, Ph-H), 7.35-7.84 (m, 5H, Ph-H), 3.55, 3.81 (s, CH_3). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ: 177.7 (C=S), 154.8 (C=N), 123.6, 125.7 (C^{6a}), 129.3 (C^{1a}, C^{3a}, C^{4a}), 154.1 (C^{5a}), 139.8 (C^{2a}), 125.3 ($C^{3b,5b}$), 125.7 (C^{2b}, C^{6b}), 129.2 (C^{4b}), 138.8 (C^{1b}), 57.2, 56.5 (CH_3).

Benzil-bisthiosemicarbazone (H_2-btz): To a hot ethanolic solution of thiosemicarbazide (1.82 g, 20 mmol) and benzil (2.1 g, 10 mmol) few drops of conc. HCl were added. The mixture was then refluxed at 65 °C for 3 h. The resulting mixture was then degassed on a rotary evaporator over a water bath, after which it was allowed to cool to get cream-coloured crystals. It was then filtered, washed with cold ethanol and then dried under vacuum. The product was characterized by comparing the physical and spectroscopic data with the literature report [19]. It was soluble in soluble in ethanol, DMF and DMSO.

Yield: 78 % m.p.: 160 °C; m.w.: 356 g mol^{-1}. Anal. (%) calcd. for $C_{16}H_{16}N_6S_2$: C, 53.93; H, 4.49; N, 23.60; S, 17.98. Found: C, 54.46; H, 4.20; N, 23.14; S, 18.27 %. IR (KBr, cm^{-1}): 3420, 3335 ν(N-H), 3142 ν(N-H), 1609 ν(C=N), 1186 ν(N-N), 839 ν(C=S). ^{1}H NMR (300.14 MHz, DMSO-d_6) δ: 10.0, 9.89 (d, N-H), 8.64,8.34 (s, N-H), 7.18-7.89 (m, Ph-H). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ: 179.9 (C=S), 142.4 (C=N), 126.9 (C^4), 125.7 ($C^{2'}$, $C^{6'}$), 127.5 ($C^{2,6}$), 129.6 ($C^{3,5}$), 133.8 (C^1).

Synthesis of [$PdCl_2$(H-aatp)$_2$] (1): To a mixture of [$PdCl_2$(cod)] (0.5 mmol, 0.143 g) and H-aatp (1 mmol, 0.243 g), 20 mL dichloromethane was added. The mixture was stirred in air at room temperature for 3 h to get a reddish brown coloured solution. It was filtered off and then washed with chloroform. The product was dried over fused $CaCl_2$ in a dessicator and then recrystallized from DCM.

Yield: 81 %. m.p.: 147 °C; m.w.: 663 g mol^{-1}, Λ_m: 10 Ω^{-1} cm^2 mol^{-1}. Anal. (%) calcd. for $C_{28}H_{26}O_2N_2S_2PdCl_2$: C, 50.65; H, 3.92; N, 4.22; S, 9.65. Found: C, 50.71; H, 4.11; N, 4.50; S, 9.77 %. IR (KBr, cm^{-1}): 2837.29 ν(O-CH_3), 2594.26 ν(S-H), 1599.06 ν(C=N), 831.32 ν(C-S), 390.12 ν(Pd-S) and 362.68 ν(Pd-Cl). ^{1}H NMR (300.14 MHz, DMSO-d_6) δ: 9.81 (s, 2H, CH), 7.31-7.85 (m, 8H, Ph-H), 6.49-7.23 (m, 8H, Ph-H), 3.67-3.89 (m, 6H, CH_3), 2.49-2.53 (d, 2H, SH). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ: 151.2 (C=N), 115.3 (C^{2a},C^{6a}), 122.8 (C^{1a}), 129.4 (C^{3a},C^{5a}), 161.2 (C^{4a}), 124.7 (C^{2b},C^{6b}), 127.6 (C^{3b},C^{5b}), 131.3 (C^{1b}), 187.5 (C^{4b}), 55.4 (CH_3).

Synthesis of [Pd(dmbptz)$_2$] (2): To a mixture of [$PdCl_2$(cod)] (0.5 mmol, 0.143 g) and H-dmbptz (1 mmol, 0.315 g), 20 mL acetonitrile was added to make a solution. The mixture was stirred in air at room temperature for 3 h to get a bright yellow coloured precipitate, which was washed with acetonitrile and then dried over fused $CaCl_2$ in a desiccator.

Yield: 82 %. m.p.: 166 °C; m.w.: 733 g mol^{-1} Λ_m.:12 Ω^{-1} cm^2 mol^{-1}. Anal. (%) calcd. for $C_{32}H_{32}O_4N_6S_2Pd$: C, 52.43; H, 4.37; N, 11.47; S, 8.74. Found: C, 51.96; H, 4.13; N, 11.70; S, 8.92 %. IR (KBr, cm^{-1}): 3129 ν(N-H), 2834 ν(O-CH_3), 1587 ν(C=N), 1172 ν(N-N), 621 ν(C-S), 449 ν(Pd-N) and 380 ν(Pd-S). ^{1}H NMR (300.14 MHz, DMSO-d_6) δ: 8.13 (s, 2H, CH), 8.73 (s, 2H, NH), 6.63-6.65 (m, 6H, Ph-H), 7.08-7.85 (m, 10H, Ph-H), 3.56 (s, CH_3), 3.81 (s, CH_3). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ: 171.5 (C-S), 150.1 (C=N), 129.3, 130.2, 131.9 ($C^{1a,3a,4a}$), 152.1 (C^{5a}), 140.0 (C^{2a}), 114.4 ($C^{3b,5b}$), 116.7 ($C^{2b,6b}$), 122.0 (C^{4b}), 122.7 (C^{1b}), 55.6 (CH_3).

Synthesis of [Pd(btz)] (3): To a hot solution of the ligand H_2-btz (0.5 mmol, 0.178 g) in 10 mL ethanol [$PdCl_2$(cod)] (0.5 mmol, 0.143 g) solution in 10 mL dichloromethane was added. The mixture was then refluxed at 45 °C in air for 3 h to obtain a reddish brown coloured precipitate. It was filtered off, washed, recrystallized in dichloromethane and then dried over fused $CaCl_2$ in a desiccator.

Yield: 70 %. m.p.: 185 °C; m.w.: 460 g mol^{-1} Λ_m: 18 Ω^{-1} cm^2 mol^{-1}. Anal. (%) calcd. for $C_{16}H_{14}N_6S_2Pd$: C, 41.70; H, 3.48; N, 18.75; S, 13.90. Found: C, 42.26; H, 3.85; N, 18.24; S, 13.52 %. IR (KBr, cm^{-1}): 3130 ν(N-H), 1620 ν(C=N), 1153 ν(N-N), 627 ν(C-S), 467 ν(Pd-N), 393 ν(Pd-S). ^{1}H NMR (300.14 MHz, CD_3CN) δ: 7.62, 7.60 (d, J = 2Hz, 2H, NH), 7.22-7.58 (m, 10H, Ph-H). ^{13}C NMR (100.62 MHz, CD_3CN) δ: 181.2 (C-S), 155.1 (C=N), 129.6 ($C^{4,4'}$), 130.0 ($C^{2,2'}$,$C^{6,6'}$), 130.2 ($C^{3,3'}$, $C^{5,5'}$), 131.9 ($C^{1,1'}$).

RESULTS AND DISCUSSION

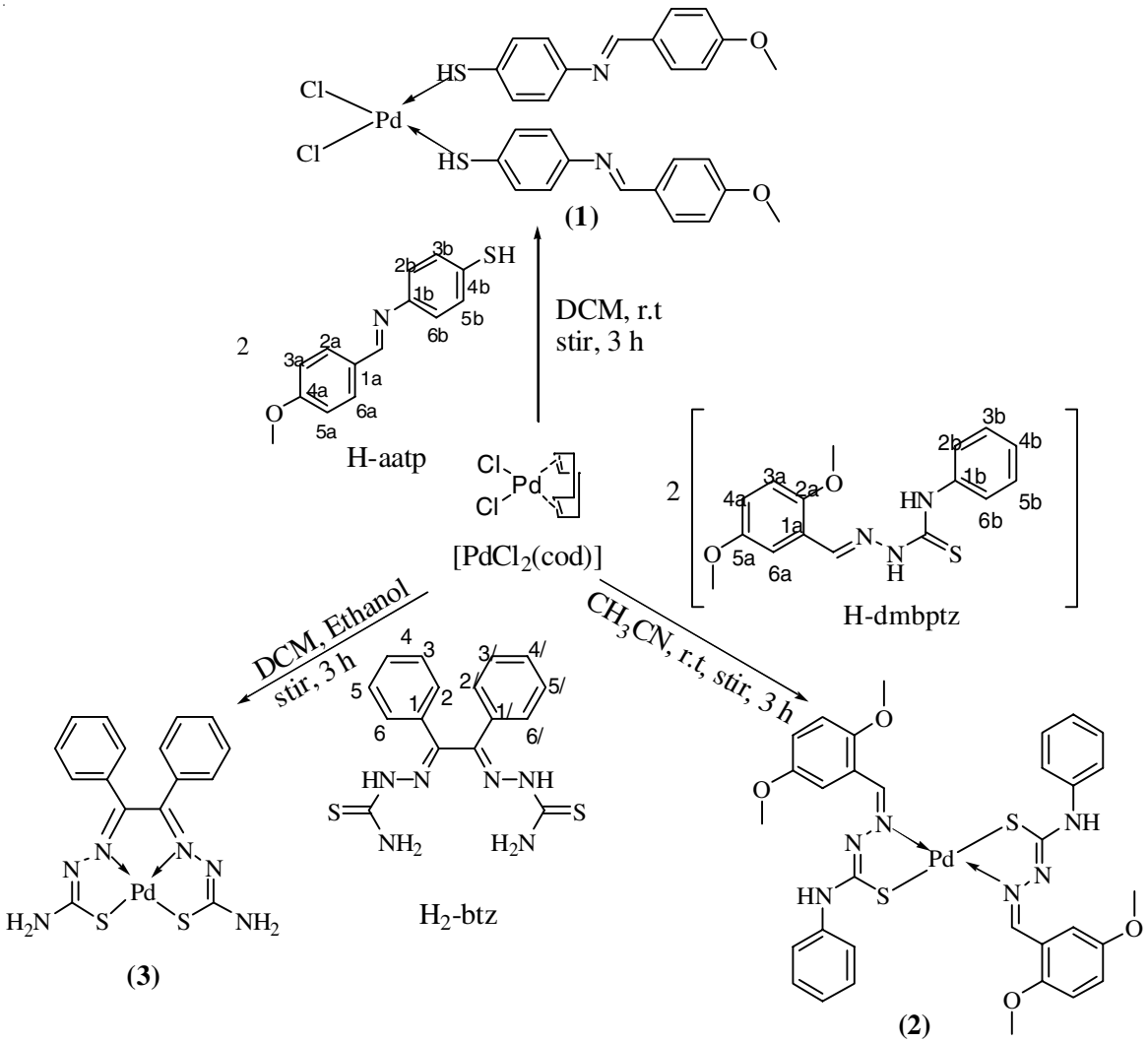
The reaction of $[PdCl_2(cod)]$ with H-aatp in DCM gives reddish brown $[PdCl_2(H\text{-}aatp)_2]$ (**1**), while that with H-dmbptz in acetonitrile gives bright yellow $[Pd(dmbptz)_2]$ (**2**) and that with H_2-btz in hot ethanolic solution yields reddish brown coloured [Pd(btz)] (**3**) complexes (**Scheme-I**). All the complexes were non-electrolyte, thermally stable and soluble in ethanol, acetonitrile, DCM, DMF and DMSO. All the complexes were found to be four coordinated having square-planar or distorted square planar geometry.

The FTIR spectrum of the complex **1** shows a weak absorption at 390 cm^{-1} corresponding to stretching frequency of ν(Pd-S). For the complex **2**, the weak absorptions at 380 and 449 cm^{-1} corresponds to ν(Pd-S) and ν(Pd-N), respectively, while that for the complex **3** at 393 and 467 cm^{-1} corresponds to ν(Pd-S) and ν(Pd-N), respectively. These confirm the complexation of the ligands to the metal centres in all the complexes.

The ESI-mass spectra of all the Pd(II) complexes are in well agreement with the proposed molecular formulations. The complex **1** showed characteristic isotopic ^{35}Cl and ^{37}Cl peaks at *m/z* 507, 509 and at 419, 421 due to the ions $[M\text{-}Cl\text{-}(CH_3O\text{-}Ph\text{-}CH)]^+$ and $[M\text{-}(H\text{-}aatp)]^+$ respectively, whereas the peaks at *m/z* 734 and 590.5 for the complex **2** could be attributed to $[M+1]^+$ and $\{M\text{-}[(CH_3O)_2\text{-}Ph\text{-}CH]+1\}^+$ fragment, respectively. The mass spectrum of complex **3** showed peaks at *m/z* 483 and 428 could be assigned to $[M+23]^+$ and $[M\text{-}S]^+$, respectively.

The electronic spectra of the complexes showed strong bands in the range 300-400 nm attributed to intra-ligand and LMCT transitions. The broad band at 611 nm in the UV-visible spectrum of complex **3** could be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition [10,20]. A typical strong band attributed to intra-ligand $n \rightarrow \pi^*$ transition was observed at 366, 319, 391 nm for the complexes **1**, **2** and **3**, respectively [10,20]. The UV-visible spectrum of the complex **2** is depicted in Fig. 1.

From ^{13}C and ^1H NMR spectra of all the complexes, it has been observed that the complexes **2** and **3** showed coordination induced shift for C=S carbon signal (Δδ = 1.3-7.6 ppm), indicates the coordination of the ligand through thioamide-S. Thiophenol carbon (C-SH) of complex **1** displayed shift of Δδ = 4.3 ppm, representing coordination of the ligand through thiol-SH. The absence of -NH- proton signal in the complexes, **2** and **3** specifies deprotonation of the ligands on coordination and confirms the coordination through the anionic thiolate S-atom of the ligand to Pd(II) ion in these complexes. Complex **1** showed one doublet at 2.49-2.53 ppm (Δδ = 1.91 ppm)



Scheme-I: Synthetic route of the complexes $[PdCl_2(H\text{-}aatp)_2]$ (**1**), $[Pd(dmbptz)_2]$ (**2**) and [Pd(btz)] (**3**) from $[PdCl_2(cod)]$

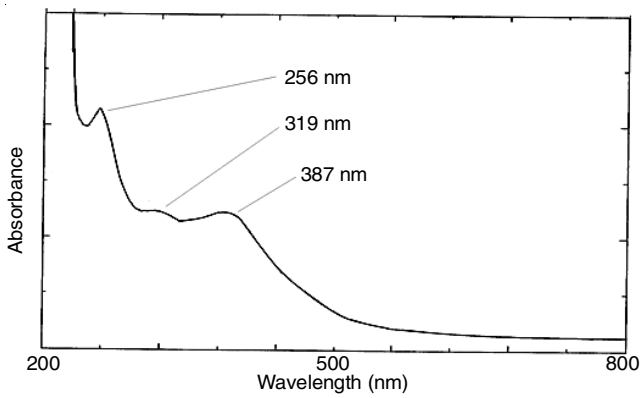


Fig. 1. UV-visible spectrum of complex **2**

corresponding to the proton of thiol group (-SH), suggesting coordination through neutral thiol (-SH) group of the ligand H-aatp to the Pd^{2+} ion (Fig. 2). This complex also exhibited coordination induced shift for all the proton signals. The ^1H NMR spectra of these complexes supported the proposed molecular formulations of the complexes **1**, **2** and **3**.

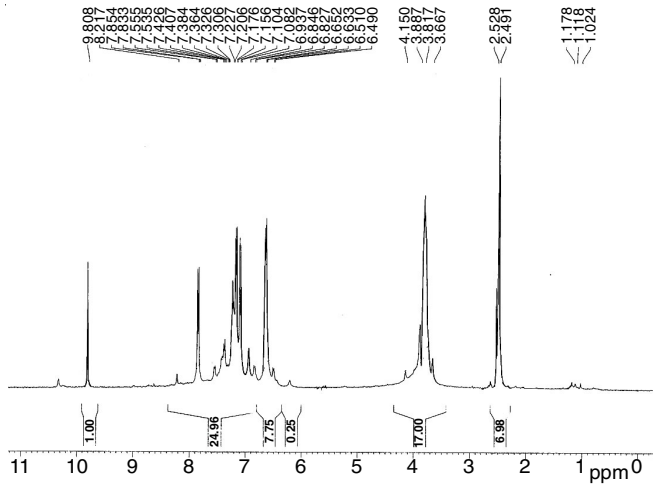


Fig. 2. ^1H NMR spectrum of complex **1**

Conclusion

In summary, this work presents the simple method of synthesizing N, S-donor ligands from readily available and less expensive materials by a simple one-pot condensation reaction. The ligands are found to be air and moisture stable, non-toxic and can easily coordinate to the metal ions. On coordination with metal ions the thiosemicarbazone derived ligands, *viz.,* H-dmbptz and H_2-btz can bond through the azomethine N and thiolate/thione S atom and remain in both the neutral and ionic form. The thiophenol derived ligand H-aatp was found to coordinate to Pd(II) in the neutral form. Though two coordination sites (N and S) were present in the ligand yet chelation was not observed due to the rigid backbone structure and so it preferably bonded to the metal ions *via* the thiol (SH) sulphur atom. These complexes $[PdCl_2(H\text{-}aatp)_2]$ (**1**), $[Pd(dmbptz)_2]$ (**2**) and[Pd(btz)] (**3**) were found to be four coordinated and diamagnetic in nature. On coordination to the Pd(II) centre the ligands get deprotonated confirming complexation through the thiolate S and azomethine N-atom.

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