



## Synthesis and spectroscopic characterization of Pt(II), Pd(II), Ni(II), Co(III) and Cu(II) complexes of *N*-allyl-*N'*-(4-methylthiazol)-2ylthiourea

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### Abstract

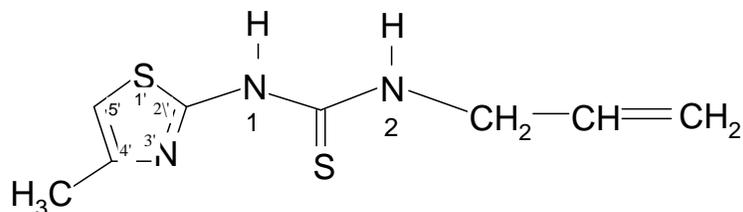
Metal complexes of Co<sup>III</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> with *N*-allyl-*N'*-(4'-methylthiazol)-2ylthiourea (HL) were prepared and characterized by elemental analyses, magnetic susceptibilities, and by I.R., N.M.R., electronic and mass spectral measurements. The i.r. spectra indicate that HL acts as bidentate ligand coordinating *via* the endocyclic imine-nitrogen and thione- or thiol-sulfur atoms. The <sup>1</sup>H- and <sup>13</sup>C-NMR. chemical shifts reveal coordination of endocyclic-imine-N and thiourea-S atoms to the metals. The magnetic moments and electronic spectral data suggest an octahedral geometry for CoL<sub>3</sub>.H<sub>2</sub>O, [Cu(HL)Cl<sub>2</sub>].0.5H<sub>2</sub>O and [Cu(HL)Cl<sub>2</sub>] a square-planar for ML<sub>2</sub> (M = Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup>), [PdL(OAc)(H<sub>2</sub>O)] and [Pd(HL)Cl<sub>2</sub>].

**Keywords:** Metal complexes, HL, elemental analyses, IR, NMR.

### 1. Introduction

Thioureas, having a considerably wide range of applications, are the cousin compounds of ureas in which oxygen has been replaced with sulfur[1]. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen[2]. Thioureas possess broad spectrum of biological activities including antiviral[3]. Antibacterial [4]. antifungal[5]. anti tubercular[6], herbicidal [7], insecticidal [8]. and pharmacological properties [9]. act as corrosion inhibitors, antioxidants and are polymer components [10]. The coordination chemistry of S, N donor ligands has known an increasing interest [11].

Because of their potential application as models for metalloproteins [12]. The complexing ability of thiazoles with borderline acids such as Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> and soft acids as Pd<sup>2+</sup> and Pt<sup>2+</sup> show bonding to the borderline base endocyclic imine nitrogen atom, not to thiazole-thioether sulfur atom [13-16]. In this paper, we report the synthesis and thorough characterization of cobalt(III), nickel(II), copper(II), palladium(II) and platinum(II) with *N*-allyl-*N'*-(4'-methylthiazol)-2ylthiourea (HL), Scheme 1.



**Scheme 1. Structure of *N*-allyl-*N'*-(4'-methylthiazol)-2ylthiourea (HL),**

## 2. Experimental

### 2-1 Measurements

I.r. spectra were recorded as KBr discs on a Perkin Elmer 683 spectrophotometer in the 4000-600  $\text{cm}^{-1}$  range and as CsI discs in *vacuo* in the 600-200  $\text{cm}^{-1}$  range. Electronic spectra were recorded on a Shimadzu -1601 spectrophotometer.  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. spectra were obtained with a Bruker av500 operating at 500MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ , using DMSO- $d_6$  as a solvent with tetramethylsilane as a reference. The mass spectra were recorded on a Shimadzu Qp - 2010 Plus. Magnetic susceptibilities were measured using a Sherwood MK1 balance. Diamagnetic corrections were made using Pascal's constants. Microanalyses of C, H and N were performed by the Microanalytical Center, King Abdul-Aziz University, Jeddah, KSA. Molar conductances in DMF were measured at room temperature using a Welheim WTW.D 8120 conductmeter.

### 2- 2 Synthesis of *N*-allyl-*N'*-(4'-methylthiazol)-2ylthiourea (HL)

The HL ligand was prepared by boiling under reflux an equimolar ratio 4-methyl-2-aminothiazole and allylthiocyanate for 3 hrs in ethanol as a solvent. The reaction product was filtered off, washed with ethanol and recrystallized from ethanol as white crystals of HL (Yield: 24%). The ligand, HL was characterized by elemental analysis (Table 1), by mass,  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. and i.r. spectral measurements as follows: MS:  $m/z$  213( $\text{M}^+$ , molecular ion peak) and  $m/z$  114(base peak), 198, 179 and 157 assignable to cations  $\text{MeTzNH}_2^+$ ,  $\text{AllMeTzTu} - \text{CH}_3^+$ ,

$\text{AllMeTzTu}^+$  and  $\text{AllMeTzTu} - \text{AllN}^+$ , respectively.  $^1\text{H}$ -n.m.r. ( $d_6$ -DMSO): / p.p.m. = 11.60 (1H, N1H, s), 9.85 (1H,N2H, s), 6.23 (1H, H(5'), s), 5.93(1H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ , m), 5.21, 5.14(2H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ , dd), 3.56 (2H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ , d,  $J_{\text{H-H}} = 9$  Hz) and 2.21(3H,  $\text{CH}_3$ -Tz, s). 146.0(C(4')), 134.3(C(5')), 116.3, 106.5 and 46.6 (three carbons of the allyl group). I.r.(KBr disc,  $\text{cm}^{-1}$ ): 3173 ( $\text{N}^1\text{-H}$ ), 3022 ( $\text{N}^2\text{-H}$ ), 1563 and 1533 (Tz ring vibs.) and 823 (C=S).

### 2-3 Synthesis of cobalt(III), nickel(II) and copper(II) complexes

$[\text{CoL}_3]\cdot\text{H}_2\text{O}$ ,  $[\text{NiL}_2]$  and  $[\text{CuL}_2(\text{H}_2\text{O})_2]$  were prepared according to the following procedure [17- 18]. A hot aqueous solution of the metallic acetate was added dropwise to a hot ethanol solution of the ligand, HL, in a 1: 2 (M: HL) molar ratio for nickel and copper and 1:3 ratio for cobalt. The reaction mixture was stirred under reflux at 70  $^\circ\text{C}$  for 3 hrs and then concentrated by rotary evaporation under reduced pressure until the onset of the precipitation of the products. The resulting solids obtained were filtered, washed successively with  $\text{H}_2\text{O}$ , warm EtOH and  $\text{Et}_2\text{O}$  and dried in *vacuo*. The green  $[\text{Cu}(\text{HL})\text{Cl}_2]\cdot 0.5\text{H}_2\text{O}$  was synthesized similarly, but the ethanol solution of the ligand was added to the aqueous solution of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  in 1:1 molar ratio.

### 2-4 Synthesis of palladium(II) and platinum(II) complexes

Palladium(II) and platinum(II) complexes were prepared by the methods described previously[19,20]. Elemental analyses and some physical properties of the complexes formed are given in Table 1.

**Table 1.** Colours, yields, melting points, molar conductivities and elemental analyses of AllMeTzTu and its metal complexes

Compound	colour	M.P (°C)	Yield (%)	Found (Calcd) %			M	$\mu_{\text{eff}}$ (B.M.)
				C	H	N		
AllMeTzTu (HL) C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> S <sub>2</sub> (213)	White	183	24	44.96 (45.07)	4.9 (5.16)	19.38 (19.72)	-	-
[NiL <sub>2</sub> ] C <sub>16</sub> H <sub>20</sub> N <sub>6</sub> S <sub>4</sub> N (482.7)	Brown	161	59.59	39.53 (39.77)	4.04 (4.14)	17.36 (17.40)	5	Diamag.
[CoL <sub>3</sub> ].H <sub>2</sub> O C <sub>24</sub> H <sub>32</sub> N <sub>9</sub> S <sub>6</sub> OCo (712.9)	Pale purple	142	25.81	40.13 (40.40)	4.28 (4.49)	17.46 (17.67)	6	Diamag.
[Cu(HL)Cl <sub>2</sub> ].0.5H <sub>2</sub> O C <sub>16</sub> H <sub>24</sub> N <sub>6</sub> S <sub>4</sub> O <sub>2</sub> Cu (523.5)	Green	196	28.00	27.44 (26.93)	3.22 (3.34)	12.03 (11.78)	10	1.69
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub> Cu (347.5)	Green	212	59.52	36.76 (36.68)	4.25 (4.58)	15.63 (16.05)	9	1.72
[Pd(HL)Cl <sub>2</sub> ] C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> S <sub>2</sub> Cl <sub>2</sub> Pd (390.4)	Orange	230	88.24	24.36 (24.59)	2.78 (2.82)	10.47 (10.76)	7	Diamag.
[PdL(OAc)(H <sub>2</sub> O)] C <sub>10</sub> H <sub>15</sub> N <sub>3</sub> S <sub>2</sub> O <sub>3</sub> Pd (395.4)	Brown	195	54.48	30.23 (30.35)	3.78 (3.79)	10.47 (10.62)	8	Diamag.
[Pd(HL) <sub>2</sub> ]Cl <sub>2</sub> C <sub>16</sub> H <sub>22</sub> N <sub>6</sub> S <sub>4</sub> Cl <sub>2</sub> Pd (602.4)	Brown	212	34.02	31.78 (31.88)	3.00 (3.65)	13.40 (13.94)	123	Diamag.
[PdL <sub>2</sub> ] C <sub>16</sub> H <sub>20</sub> N <sub>6</sub> S <sub>4</sub> Pd (530.4)	Orange	210	54.24	36.20 (36.01)	3.53 (3.77)	16.24 (15.88)	5	Diamag.
[PtL <sub>2</sub> ] C <sub>16</sub> H <sub>20</sub> N <sub>6</sub> S <sub>4</sub> Pt (619.01)	Yellow	195	26.22	31.12 (31.02)	2.32(2.52)	12.93 (13.57)	4	Diamag.

### 3. Results and Discussion

The reaction between allylthiocyanate and 2-amino-4-methylthiazole in ethanol under refluxing conditions yields the ligand AllMeTzTu, HL, Scheme I. The elemental analysis and <sup>1</sup>H- and <sup>13</sup>C NMR assignments as well as the appearance of the highest ion peak at m/z 213 in E.I. mass spectrum confirm the preparation of HL. HL exists in the thione (thio keto) form in DMSO solution as revealed by the appearance of a <sup>13</sup>C NMR signal assigned to the carbon of C=S group. Interaction of the divalent metal salts with HL in aqueous ethanol in 1:1 and 1:2 (M: HL) for

platinum, palladium, nickel and copper; 1:3 molar ratio for cobalt produced complexes listed in Table 1 along with their analytical data and some physical properties. All the prepared metal complexes are colored, nonhygroscopic, partially soluble in most organic solvents but entirely soluble in DMF and DMSO. The molar conductance values in 10<sup>-3</sup> M DMF solution fall in 4-12 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup> range indicating the nonelectrolytic nature of these complexes, with exception [Pd(HL)<sub>2</sub>].Cl<sub>2</sub> which showed a molar conductance of 123 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup> indicating a 1:2 electrolyte [21].

### 3-1 Infrared spectra

The infrared spectrum of HL (Table 2) shows N1H and N2H stretching vibrations at 3173 and 3022  $\text{cm}^{-1}$ , respectively [22,23], which are shifted to higher wave numbers in the spectra of the complexes but the N1H band disappears in  $\text{ML}_2$  and  $\text{CoL}_3 \cdot (\text{H}_2\text{O})$  and replaced by a broad band due to lattice water molecule in the latter complex. HL also shows CS stretching band at 823  $\text{cm}^{-1}$  which is lowered by 70 -100  $\text{cm}^{-1}$  in its complexes. This indicates coordination of sulfur-thiourea moiety to metal ions in the form of thione or thiol [24-30]. The disappearance of N1H stretch as well as the signal of proton of N1H in the  $^1\text{H}$  NMR spectra (*vide infra*) of  $\text{ML}_2$  and  $\text{CoL}_3 \cdot \text{H}_2\text{O}$  indicates coordination of thio-S with the formation of imine

linkage. The C=N stretch of imine probably overlapped with C=N stretch of thiazole-imine. A downward shift of the thiazole ring vibrations from 1563 and 1533  $\text{cm}^{-1}$  in the spectrum of HL to 1551-1558 and 1526-1530  $\text{cm}^{-1}$  in the spectra of the complexes indicates that either thiazole-S or -N atoms are coordinated to metal ions. Coordination of thiazole-N atom has been reported in many metal complexes [31] and has proven in our laboratory currently by solving X-ray structure of  $\text{Pt}(\text{EtMeTzTu})_2$ . The coordination of the acetato and chloro ligands is indicated by the appearance of (COO) at 1560  $\text{cm}^{-1}$  in  $[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$ ; (Pd-Cl) and (Cu-Cl) at 326 and 345  $\text{cm}^{-1}$  in  $[\text{Pd}(\text{HL})\text{Cl}_2]$  and  $[\text{Cu}(\text{HL})\text{Cl}_2]$ , respectively [32].

**Table 2. Important IR spectral bands (  $\text{cm}^{-1}$  ) of AllMeTzTu and its metal complexes**

Compound	(N1H) or (OH)	(N2H)	Thiazole ring vibs.	(CS)
HL	3173(m)	3022(m)	1563(vs), 1501(vs) 1533(vs)	823(m)
$[\text{NiL}_2]$	-	3019(m)	1551(vs), 1530(vs), 1529(vs)	754(m)
$[\text{CoL}_3] \cdot \text{H}_2\text{O}$	-	3079(w)	1558(m), 1526(sh), 1528(vs,b)	743(m)
$[\text{Cu}(\text{HL})\text{Cl}_2] \cdot 0.5\text{H}_2\text{O}$	3461(b)	3117(m)	1557(vs), 1528(vs), 1526(s)	726(m)
$[\text{CuL}_2(\text{H}_2\text{O})_2]$	-	3090w, 3140(m)	1556(vs), 1527(s)	750(s)
$[\text{Pd}(\text{HL})\text{Cl}_2]$	3193(w)	3093(w)	1558(sh), 127(vs)	755(sh)
$[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$	3400(b)	3065(w)	1560(sh)	713(m)
$[\text{Pd}(\text{HL})_2]\text{Cl}_2$	-	3079(w)	1551(m), 1530(vs,b)	729(m)
$[\text{PdL}_2]$	-	3075(w)	1551(m), 1528(vs,b)	729(m)
$[\text{PtL}_2]$	-	3080(w)	1551(m,b)	728(m)

### 3-2 Magnetic moments and electronic spectra

Magnetic data are consistent with  $d^9$  mononuclear copper(II) ( $\mu_{\text{eff}} = 1.78$  B.M./Cu atom), a square-planar geometry for a  $d^8$  platinum, palladium and nickel complexes and a complete oxidation of Co(II) to Co(III) in  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$  and that the latter complex is of a low-spin octahedral type.

The electronic spectrum of HL in DMF (Table 3) shows unsymmetrical broad band at  $\lambda_{\text{max}} = 299$  nm due to  $d-d$  and  $n \rightarrow \pi^*$  transitions. This band seems to be influenced by the complexation and type of metallic cations as revealed by its small red shifts in nickel(II),  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$  and copper(II) complexes but to slightly shorter wavelengths with splitting in platinum(II) and palladium(II) complexes. This may be attributed to the extensive delocalization of  $\pi$  system by the significant  $\pi$ -back bonding M-L between the soft

platinum(II) and palladium(II) ions and both thiourea-S and thiazole-N atoms. The new band appeared in  $\text{NiL}_2$  at 401 nm ( $\lambda = 23,081$ ), in platinum(II) and palladium(II) complexes at 305 -322 nm ( $\lambda > 500$ ), and tailing out of the intraligand bands of copper(II) complexes and  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$  to the visible region are due to superimposed of L-M charge transfer or  $\pi \rightarrow \pi^*$  transitions involving metal and ligand orbitals [33]. In the visible region,  $\text{NiL}_2$  shows two bands at 514 and 640 nm, characteristic of square-planar geometry of nickel(II) complexes containing  $\text{NiN}_2\text{S}_2$  chromophore [34];  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$  exhibits two transitions at 469 and 623 nm, assignable to  $^1A_{1g} \rightarrow ^1T_{1g}(1)$  and  $^1A_{1g} \rightarrow ^1T_{2g}(2)$  transitions, respectively, for low-spin octahedral cobalt(III) complexes containing  $\text{CoS}_3\text{N}_3$  chromophore [35];  $[\text{CuL}_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}(\text{HL})\text{Cl}_2]$  exhibit relatively broad bands at  $\lambda_{\text{max}} = 491$  and 475 nm with shoulders at 590 and 585 nm, respectively.

This band could be considered as a composite of charge-transfer transitions and some d-d transitions. Shoulders could be assigned to  ${}^3B_{1g} \rightarrow {}^3A_{1g}$  transition, similarly to distorted octahedral copper(II) complexes [36]. This is indicative of joining two DMF ligands to

the copper(II) cation in  $[\text{Cu}(\text{HL})\text{Cl}_2]$ , thus completing the 4 + 2 coordination sphere. Platinum(II) and palladium(II) complexes show charge transfer bands at 305 -325 nm, the tails of which obscure the weaker d-d transitions [37].

**Table 3: Electronic spectra  $\lambda_{\text{max}}$ (nm) AllTzTu and its complexes**

Compound	Intraligand and charge transfer band ( $\lambda_{\text{max}}$ / $\text{Lmol}^{-1}\text{cm}^{-1}$ )	d-d band ( $\lambda_{\text{max}}$ / $\text{Lmol}^{-1}\text{cm}^{-1}$ )
AllMeTzTu	299(1443)	-
$[\text{NiL}_2]$	315(1742), 401(23491)	514(50), 640(15)
$[\text{CoL}_3] \cdot \text{H}_2\text{O}$	313(1233) rbr	469(396), 623(43)
$[\text{Cu}(\text{HL})\text{Cl}_2] \cdot 0.5\text{H}_2\text{O}$	303(1077) rbr	475(402)br, 585(190)sh
$[\text{CuL}_2(\text{H}_2\text{O})]$	318(1589)rbr	491(408)vbr, 800(390)vbr
$[\text{Pd}(\text{HL})\text{Cl}_2]$	278(280), 286(370) 305(662) tailed to 540 nm	Over lapped with CT band
$[\text{PdL}(\text{OAc})\text{H}_2\text{O}]$	295(1579) 325(1729) tailed to 520 nm	Over lapped with CT band
$[\text{Pd}(\text{HL})_2\text{Cl}_2]$	291(1558) 321(1674) tailed to 520 nm	Over lapped with CT band
$[\text{PdL}_2]$	298(1551) 322(2251) tailed to 520 nm	Over lapped with CT band
$[\text{PtL}_2]$	267(1354), 305(1833) 350 sh (833) tailed to 500 nm	Over lapped with CT band

### 3-3 ${}^1\text{H-N.M.R.}$ spectra

The  ${}^1\text{HNMR}$  data of the complexes (table 4) when compared with those of the free HL point to the following: (i) One  ${}^1\text{HNMR}$  signal corresponding to N2H proton is appreciably upfield-shifted from 10.85 ppm to 9.91-8.22 ppm in the complexes, whereas the N1H signal is slightly upfield-shifted by 0.18 ppm in  $[\text{Pd}(\text{HL})\text{Cl}_2]$  but disappeared in all complexes containing the monoanion, L. This indicates coordination of thiono-S atom to palladium(II) in  $[\text{Pd}(\text{HL})\text{Cl}_2]$  and thio-S to metal ions in  $\text{ML}_2$  and  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$ , resulting in reduced electron density around NH's protons by the withdrawing effect of the metal ions through  $\pi$ -bonding which is opposed unequally by the delocalized  $\pi$ -bonding as a result of participation of the soft metal ions in back  $\pi$ -bonding with sulfur atom or decreased the anisotropic effect of CS on NH's protons as a result of reducing  $\pi$ -electron character and/ or decreasing the number of unshared electrons from two to one upon coordination in  $[\text{Pd}(\text{HL})\text{Cl}_2]$  and  $[\text{Pd}(\text{HL})_2\text{Cl}_2]$  [19,20]. (ii) Small

shifts occur for thiazole proton H(5') from 6.63 ppm in HL to 6.87- 6.61 ppm. This is an evidence for coordination of thiazole -N atom, not thiazole -S atom to metal ions, since the prominent withdrawing effect of the metal through  $\pi$ -bonding on proton H(5') would be the prominent factor in case of the borderline acids  $\text{Ni}^{\text{II}}$  and  $\text{Co}^{\text{III}}$ , but through the distance-independent extensive delocalized  $\pi$ -system as due to the participation of the soft acids  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  with the exocyclic imine in back  $\pi$ -p bonding. The signal of the thiazole-methyl protons show the same trend, where the methyl protons signal is shifted from 2.21 ppm. in HL to 2.15 and 2.23 ppm in  $[\text{NiL}_2]$  and  $[\text{CoL}_3] \cdot \text{H}_2\text{O}$ , respectively, but in the  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  complexes the methyl protons signal show significant upfield shift to 1.95 -1.70 ppm, probably due to the hyperconjugation of methyl group which is facilitated with soft acids. The allyl protons in the complexes are almost at same chemical shifts as in HL, indicating the nonparticipation of the allyl group in organometallic bond.

Table 4. <sup>1</sup>H -N.M.R. spectral data (p.p.m.) of HL and its meal complexes

Compound	CH <sub>3</sub>	Allyl			H(5')	N1H	N2H
		-CH=	=CH <sub>2</sub>	-CH <sub>2</sub> -			
HL	2.21	5.92	5.21 5.15	4.20	6.63	11.62	10.85
[NiL <sub>2</sub> ]	2.15	5.87	5.12	4.18	6.61	-	9.91
[CoL <sub>3</sub> ].H <sub>2</sub> O	2.23	5.94	5.17	4.21	6.69	-	8.40
[Pd(HL)Cl <sub>2</sub> ]	1.85	5.90	5.18 5.08	3.68	6.84	11.44	8.86
[PdL(OAc)(H <sub>2</sub> O)]	1.92 2.38	5.92	5.29 5.12	3.92	6.67	-	8.43
[Pd(HL) <sub>2</sub> ].Cl <sub>2</sub>	1.70	5.73	5.05 4.96	3.77	6.87	-	8.23
[PdL <sub>2</sub> ]	1.70	5.73	5.04 4.96	3.77	6.66	-	8.22
[PtL <sub>2</sub> ]	1.70	5.17	5.09	3.35	6.82	-	8.48

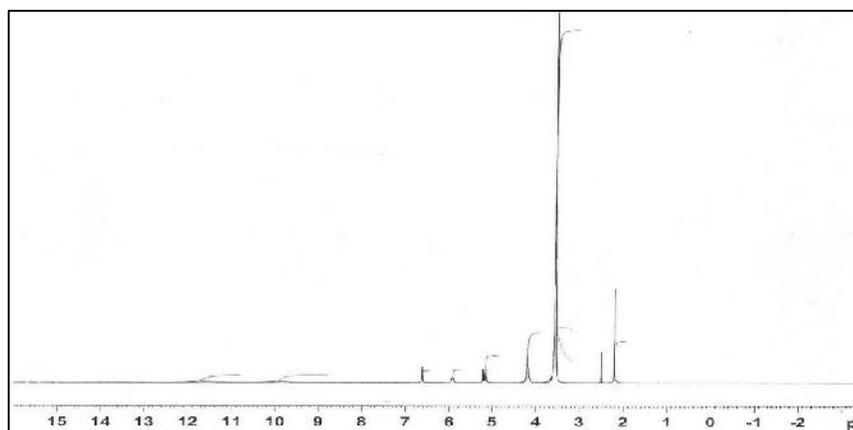


Fig. 1. <sup>1</sup>H-N.M.R. spectrum of HL in d<sup>6</sup>-DMSO.

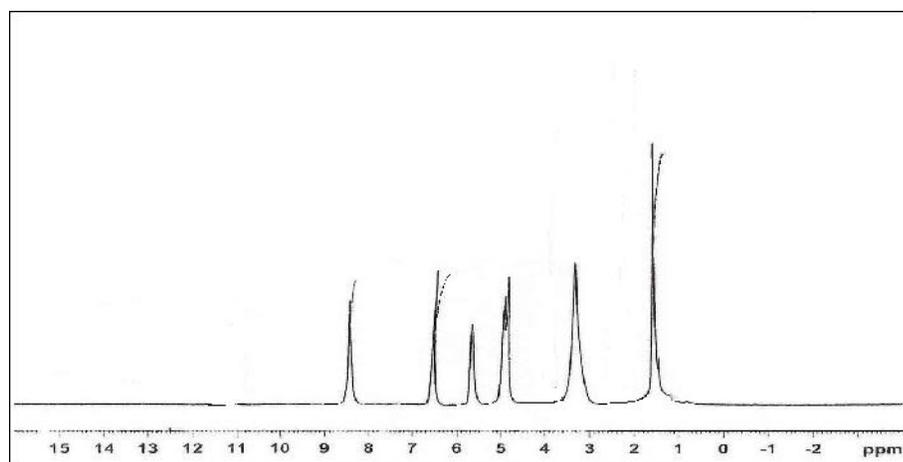


Fig. 2. <sup>1</sup>H-N.M.R. spectrum of [PdL<sub>2</sub>] in d<sup>6</sup>-DMSO.

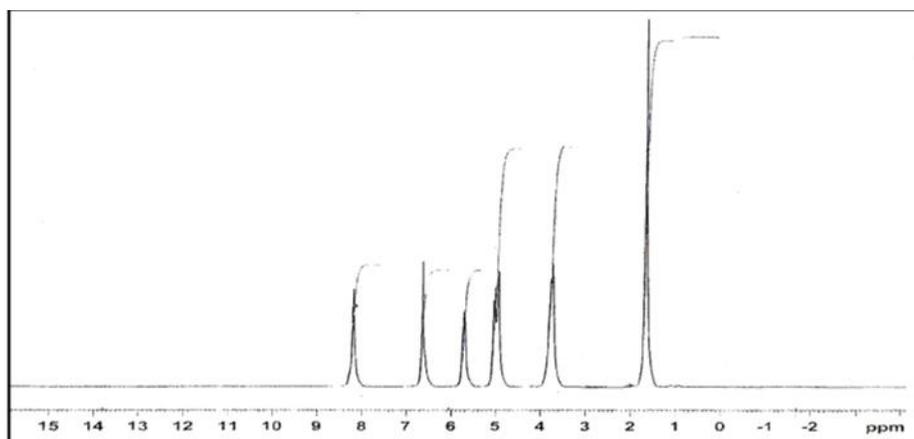


Fig. 3.  $^1\text{H-N.M.R.}$  spectrum of  $[\text{PtL}_2]$  in  $\text{d}^6\text{-DMSO}$ .

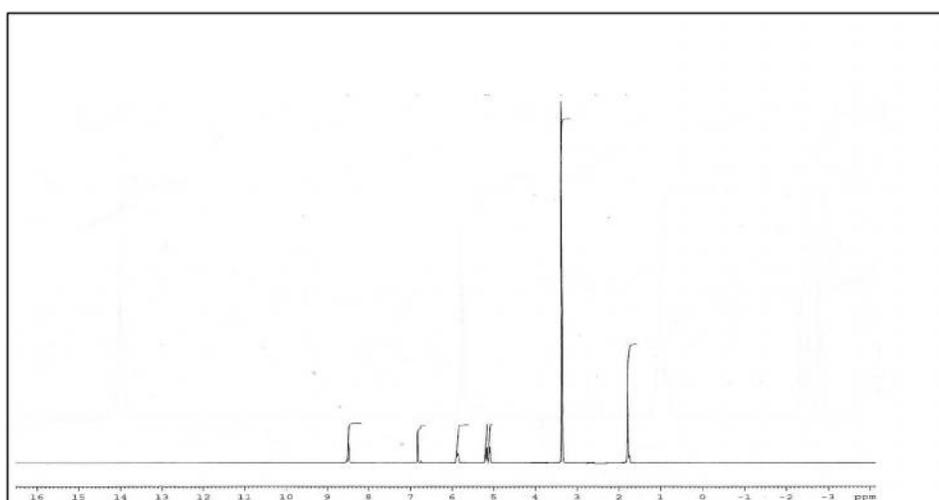


Fig. 4.  $^1\text{H-N.M.R.}$  spectrum of  $[\text{PtL}_2]$  in  $\text{d}^6\text{-DMSO}$ .

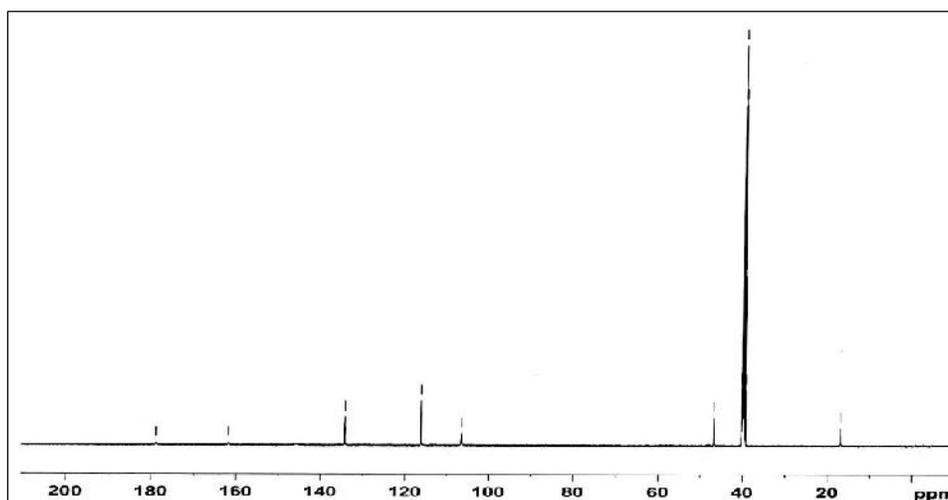
### 3- 4 $^{13}\text{C-N.M.R.}$ spectra

The  $^{13}\text{C-n.m.r.}$  spectra of the complexes in  $\text{DMSO-d}_6$  as a solvent (table 5) showed signals for all carbons of allyl, thiazole, thiocarbonyl and methyl groups, and on comparing their chemical shift values with those of the free HL, the following points can be deduced. (i) An upfield shift for thiocarbonyl carbon from 179.0 ppm. in the free HL to 176.2 -175.0 ppm. in complexes containing the neutral HL ligand; to 172.7-171.1 ppm. in ones containing the monoanion L. This

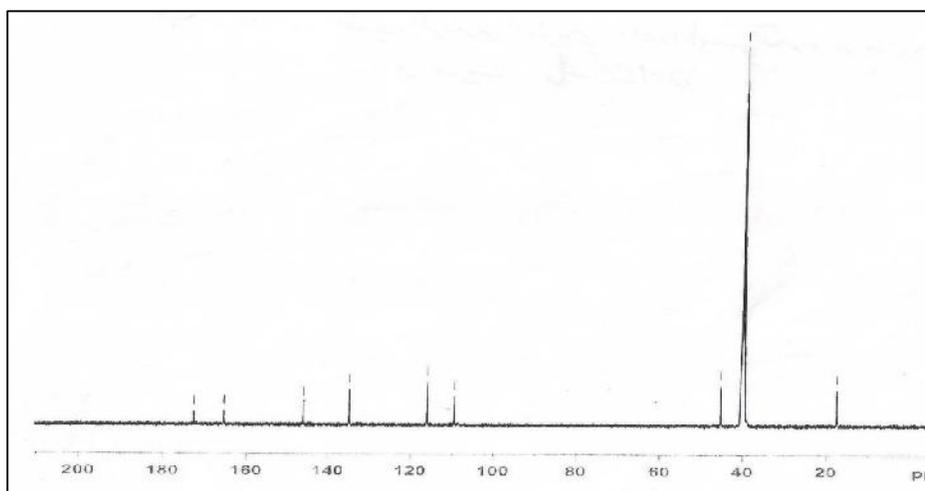
indicates coordination of thio-S atom to  $\text{Pd}^{\text{II}}$  in  $[\text{Pd}(\text{HL})\text{Cl}_2]$  and  $[\text{Pd}(\text{HL})_2]\text{Cl}_2$ ; thio-S atom to metals in  $[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$ ,  $[\text{ML}_2]$  and  $[\text{CoL}_3]\cdot\text{H}_2\text{O}$ . (ii) A downfield shift the methyl-carbon bearing thiazole from 16.9 ppm. in the HL to 17.5- 16.9 ppm. (iii) No clear trend in shifts of signals of thiazole ring carbons C(2'), C(4') and C(5'). This could be attributed to the two opposing effects of  $\pi$ -electron withdrawing and  $\sigma$ -bonding on the electron density around those carbons which are influenced by the metallic cations [19,20].

**Table 5.**  $^{13}\text{C}$ -N.M.R. spectral data (p.p.m.) of HL and its meal complexes

Compound	$\underline{\text{C}}\text{H}_3$	Allyl			CS	C(5')	C(4')	C(2')
		$-\underline{\text{C}}\text{H}=\text{}$	$=\underline{\text{C}}\text{H}_2$	$-\underline{\text{C}}\text{H}_2$				
HL	16.87	116.32	106.5	46.65	179.1	134.3	146.0	162.0
[NiL <sub>2</sub> ]	16.95	116.24	106.6	46.8	170.1	134.4	134.96	161.9
[CoL <sub>3</sub> ].H <sub>2</sub> O	17.86	116.82	109.1	45.9	172.0	134.2	146.12	163.3
[Pd(HL)Cl <sub>2</sub> ]	19.72	116.49	109.5	45.5	176.2	134.8	145.70	161.7
[PdL(OAc)(H <sub>2</sub> O)]	17.5 23.9	116.5	109.6	45.3	172.7	135.2	146.20	165.5
[Pd(HL) <sub>2</sub> ].Cl <sub>2</sub>	17.51	116.15	109.6	45.3	172.7	135.15	146.22	165.0
[PdL <sub>2</sub> ]	17.51	116.15	109.6	45.3	172.7	135.1	146.20	165.5
[PtL <sub>2</sub> ]	16.99	115.74	108.8	44.8	172.6	135.00	146.16	163.4



**Fig. 5.**  $^{13}\text{C}$ -N.M.R. spectrum of HL in  $\text{d}^6$ -DMSO.



**Fig. 6.**  $^{13}\text{C}$ -N.M.R. spectrum of [Pd(HL)<sub>2</sub>]Cl<sub>2</sub> in  $\text{d}^6$ -DMSO.

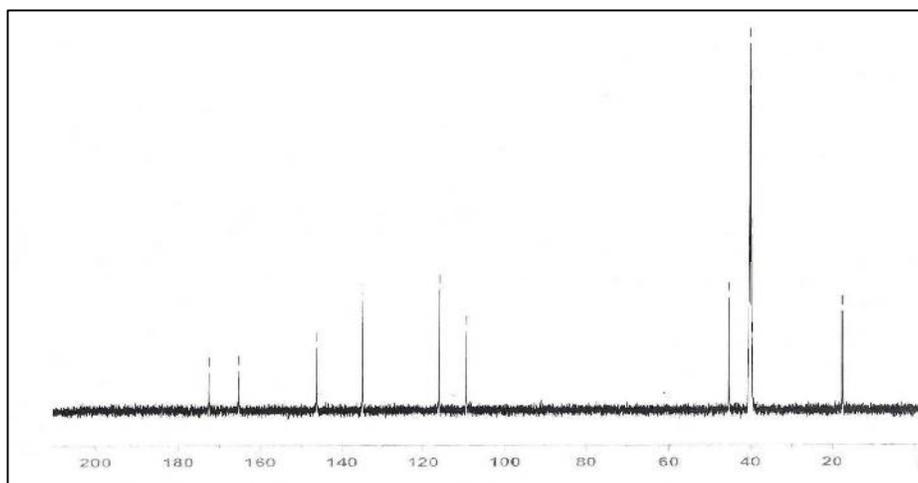


Fig. 7.  $^{13}\text{C}$ -N.M.R. spectrum of  $[\text{PdL}_2]$  in  $\text{d}^6$ -DMSO.

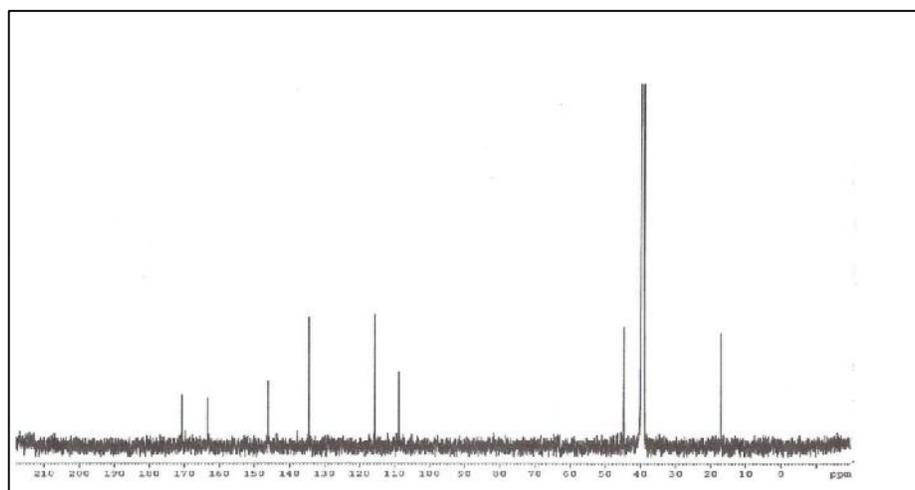


Fig. 8.  $^{13}\text{C}$ -N.M.R. spectrum of  $[\text{PtL}_2]$  in  $\text{d}^6$ -DMSO.

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