



Synthesis and characterization of Ni(II), Pd(II), Pt(II) complexes of *N*-allyl-*N'*-(4-methylthiazol-2-yl)thiourea

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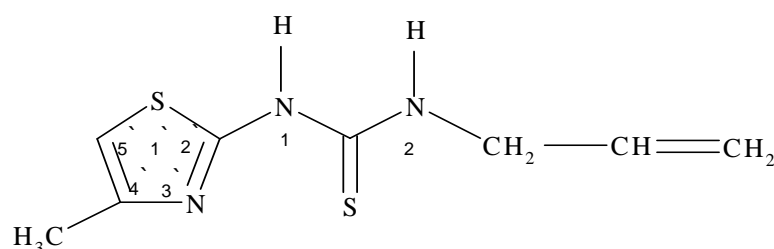
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Abstract

Metal complexes of Ni(II), Pd(II), and Pt(II) with *N*-allyl-*N'*-(4'-methylthiazol-2-yl)thiourea (HL) were prepared and characterized by elemental analyses, magnetic susceptibilities, IR, NMR electronic and mass spectral measurements. The IR spectra indicate that HL acts as bidentate ligand coordinating *via* the endocyclic imine-N thione- or thiol-S atoms. The ¹H and ¹³C NMR chemical shifts reveal coordination of endocyclic-imine-N and thiourea-S atoms to the metals. The magnetic moments and electronic spectral data suggest a square- planar for ML₂ (M = Ni(II), Pd(II) and Pt(II)), [Pd(L)(OAc)(H₂O)] and [Pd(HL)Cl₂].

1. Introduction

Thioureas containing the N, S-heterocyclic ring, thiazole, are multidentate nitrogen- sulfur donors. Such ligands and their metal complexes are promising to possess remarkable biological activities[1-3]. Thiazole and its derivatives occur as structural unit in biologically active products asvitamin B1, bacitracin, penicillins and luciferin and in numerous synthetic drugs, fungicides, dyes and industrial chemicals [4-12]. The complexing ability of thiazoles with borderline acids such as Ni²⁺ and soft acids as Pd²⁺ and Pt²⁺ 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 characterization of Ni(II), Pd(II) and Pt(II) with *N*-allyl-*N'*-(4'-methylthiazol-2-yl)thiourea HL, (Scheme 1).



Scheme 1. Structure of *N*-allyl-*N'*-(4-methylthiazol-yl)thiourea (HL).

2. Experimental

Synthesis of N-allyl-N'-(4'-methylthiazol-2-yl)thiourea (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 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, ¹H and ¹³C NMR and IR spectral.

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

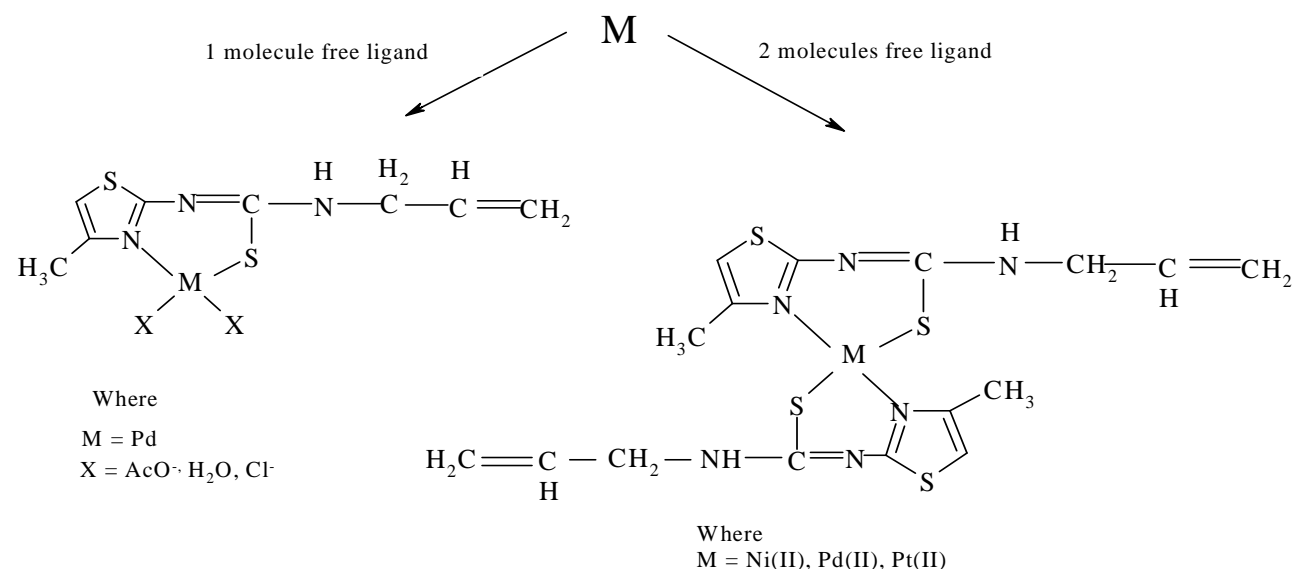
Compound	colour	M.P (°C)	Yield (%)	Found (Calcd) %			Λ_M^b	μ_{eff} (B.M.)
				C	H	N		
AllMeTzTu (HL) C ₈ H ₁₁ N ₃ S ₂ (213)	White	183	24	44.96 (45.07)	4.9 (5.16)	19.38 (19.72)	-	-
[NiL ₂] C ₁₆ H ₂₀ N ₆ S ₄ N (482.7)	Brown	161	59.59	39.53 (39.77)	4.04 (4.14)	17.36 (17.40)	5	Diamag.
[Pd (HL)Cl ₂] C ₈ H ₁₁ N ₃ S ₂ Cl ₂ Pd (390.4)	Orange	230	88.24	24.36 (24.59)	2.78 (2.82)	10.47 (10.76)	7	Diamag.
[Pd(L) (OAc)(H ₂ O)] C ₁₀ H ₁₅ N ₃ S ₂ O ₃ Pd (395.4)	Brown	195	54.48	30.23 (30.35)	3.78 (3.79)	10.47 (10.62)	8	Diamag.
[Pd(HL) ₂]Cl ₂ C ₁₆ H ₂₂ N ₆ S ₄ Cl ₂ Pd (602.4)	Brown	212	34.02	31.78 (31.88)	3.00 (3.65)	13.40 (13.94)	123	Diamag.
[PdL ₂] C ₁₆ H ₂₀ N ₆ S ₄ Pd (530.4)	Orange	210	54.24	36.20 (36.01)	3.53 (3.77)	16.24 (15.88)	5	Diamag.
[PtL ₂] C ₁₆ H ₂₀ N ₆ S ₄ Pt (619.01)	Yellow	195	26.22	31.12 (31.02)	2.32 (2.52)	12.93 (13.57)	4	Diamag.

^an-allyl-N'-(4'-methylthiazol-2yl)thiourea.
^b $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

The measurements as follows: MS: m/z 213(M⁺, molecular ion peak) and m/z 114 (base peak), 198, 179 and 157 assignable to cations MeTzNH²⁺, AllMeTzTu - CH³⁺, AllMeTzTu⁺ and AllMeTzTu - AllN⁺, respectively. ¹H NMR (d⁶-DMSO): ppm =11.60 (s, 1H, N1H), 9.85 (1H,N2H, s), 6.23 (1H, H(5'), s), 5.93 (1H, -CH₂-CH=CH₂, m), 5.21, 5.14 (2H,-CH₂-CH=CH₂, dd), 3.56 (2H, -CH₂-CH=CH₂, d, JH-H = 9 Hz) and 2.21 (3H, CH₃-Tz, s). 146.0 (C(4')), 134.3 (C(5')), 116.3, 106.5 and 46.6 (three carbons of the allyl group) IR (KBr disc, cm⁻¹): 3173 v (N1-H), 3022 v (N2-H), 1563 and 1533 (Tzringvibs.) and 823 v (C=S).

Synthesis of nickel(II) complex

The [NiL₂] complexes were prepared according to the following procedure (Scheme 2) [17, 18]. Drops of hot aqueous solution of metallic acetate were added to ligand solution in a ratio of 1 : 2 ((M : HL)). Their action mixture was stirred under reflux at 70 °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 H₂O, warm EtOH and Et₂O and dried in *vacuo*.



Scheme 2. Synthesis of complexes of HL

Synthesis of palladium(II) and platinum(II) complexes

Pd(II) and Pt(II) complexes were prepared by the methods described previously (Scheme 2)[19, 20]. Elemental analyses and some physical properties of the complexes formed are given in (Table 1).

Measurements

IR spectra were recorded as KBr discs on a Perkin Elmer 683 spectrophotometer in the 4000- 600 cm^{-1} range and as CsI discs in *vacuo* in the 600- 200 cm^{-1} range. Electronic spectra were recorded on a Shimadzu- 1601 spectrophotometer. ^1H - and ^{13}C NMR spectra were obtained with a Bruker av 500 operating at 500 MHz for ^1H and 125 MHz for ^{13}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.

3. Results and discussion

The reaction between allylthiocyanate and 2-amino- 4- methylthiazole in ethanol under refluxing conditions yields the ligand HL, (Scheme 1). The elemental analysis and ^1H and ^{13}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 (thioketo) form in DMSO solution as revealed by the appearance of a ^{13}C NMR signal assigned to the carbon of $\text{C}=\text{S}$ group. Interaction of the divalent metal salts with HL in aqueous ethanol in 1:1 and 1:2 (M: HL) for platinum, palladium and nickel 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^{-3} M DMF solution fall in 4- 12 $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ range indicating the nonelectrolytic nature of these complexes, with exception $[\text{Pd}(\text{HL})_2]\cdot\text{Cl}_2$ which showed a molar conductance of 123 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating a 1:2 electrolyte [21].

Infrared spectra

The infrared spectrum of HL (Table 2) shows N1H and N2H stretching vibrations at 3173 and 3022 cm^{-1} , respectively [22, 23], which are shifted to higher wave numbers in the spectra of the complexes but the N1H band disappears in ML_2 and replaced by a broad band due to lattice water molecule in the latter complex. HL also shows CS stretching band at 823 cm^{-1} which is lowered by 70- 100 cm^{-1} in its complexes. This indicates coordination of sulfur-thiourea moiety to metal ions in the form of thione or thiol [24- 30].

Table 2: Important IR spectral bands ν, cm^{-1} of HL and its metal complexes

Compound	ν (N1H) or ν (OH)	ν (N2H)	Thiazole ring vibs.	ν (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)
$[\text{Pd}(\text{HL})\text{Cl}_2]$	3193 (w)	3093 (w)	1558 (sh), 1 27 (vs)	755 (sh)
$[\text{Pd}(\text{L}) (\text{OAc})(\text{H}_2\text{O})]$	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)

The disappearance of N1H stretch as well as the signal of proton of N1H in the ^1H NMR spectra (*vide infra*) of ML_2 indicates coordination of thio-S with the formation of imine linkage. The $\text{C}=\text{N}$ stretch of imine probably overlapped with $\text{C}=\text{N}$ stretch of thiazole-imine. A downward shift of the thiazole ring vibrations from 1563 and 1533 cm^{-1} in the spectrum of HL to 1551- 1558 and 1526- 1530 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 $\text{Pt}(\text{EtMeTzTu})_2$ where Tz= thiazole, Tu= thiourea. The coordination of the

acetato and chloro ligands is indicated by the appearance of $\nu(\text{COO})$ at 1560 cm^{-1} in $[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$; $\nu(\text{Pd-Cl})$ at 326 cm^{-1} in $[\text{Pd}(\text{HL})\text{Cl}_2]$ [32].

Magnetic moments and electronic spectra

Magnetic data are consistent, a square- planar geometry for a d^8 platinum, palladium and nickel complexes 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 $\lambda_{\text{max}} = 299 \text{ nm}$ due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Table 3. Electronic spectra $\lambda_{\text{max}}(\text{nm})$ for HL and its complexes

Compound	Intraligand and charge transfer bands ($\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$)	d-d bands ($\epsilon/\text{Lmol}^{-1}\text{cm}^{-1}$)
HL	299 (1443)	-
$[\text{NiL}_2]$	315 (1742), 410 (24018)	514 (50), 640 (15)
$[\text{Pd}(\text{HL})\text{Cl}_2]$	278 (280) 286 (370) 305 (662) tailed to 540 nm	Over lapped with CTband
$[\text{Pd}(\text{L})(\text{OAc})(\text{H}_2\text{O})]$	295 (1579) 325 (1729) tailed to 520 nm	Over lapped with CTband
$[\text{Pd}(\text{HL})_2]\text{Cl}_2$	291 (1558) 321 (1674) tailed to 520 nm	Over lapped with CTband
$[\text{PdL}_2]$	298 (1551) 322 (2251) tailed to 520 nm	Over lapped with CTband
$[\text{PtL}_2]$	267 (1354), 305 (1833) 350sh (833) tailed to 500 nm	Over lapped with CTband

This band seems to be influenced by the complexation and type of metallic cations as revealed by its small red shifts in nickel(II), but to slightly shorter wave lengths with splitting in Pt(II) and Pd(II) complexes. This may be attributed to the extensive delocalization of π system by the significant π -back bonding $\text{M} \rightarrow \text{L}$ between the soft Pt(II) and Pd(II) ions and both thiourea-S and thiazole-N atoms. The new band appeared in NiL_2 at 401 nm ($\epsilon = 23,081$), in Pt(II) and Pd(II) complexes at 305- 322 nm ($\epsilon < 500$), to the visible region are due to superimposed of $\text{L} \rightarrow \text{M}$ charge transfer or $\pi \rightarrow \pi^*$ transitions involving metal and ligand orbitals [33]. In the visible region, NiL_2 shows two bands at 514 and 640 nm, characteristic of square- planar geometry of Ni(II) complexes containing NiN_2S_2 chromophore [34,35]. This band could be considered as a composite of charge- transfer transitions and some $d \rightarrow d$ transitions. Shoulders could be assigned to ${}^3B_{1g} \rightarrow {}^3A_{1g}$ transition [36]. Pt(II) and Pd(II) complexes show charge transfer bands at 305- 325 nm, the tails of which obscure the weaker $d-d$ transitions [37].

${}^1\text{H}$ NMR spectra

The ${}^1\text{H}$ NMR data of the free ligand and the complexes (Figures 1- 4 , Table 4) when compared with those of the free HL point to the following: (i) One ${}^1\text{H}$ NMR 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 Pd(II), $[\text{Pd}(\text{HL})\text{Cl}_2]$ and thio-S to metal ions in ML_2 , resulting in reduced electron density around NH's protons by the withdrawing effect of the metal ions through σ -bonding which is opposed unequally by the delocalized π -bonding as a result of participation of the soft metal ions in back π -bonding with sulfur atom or decreased the anisotropic effect of CS on NH's protons as a result of reducing π -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 σ -bonding on proton H(5') would be the prominent factor in case of the borderline acids Ni(II), but through the distance-independent extensive delocalized π -system as due to the participation of the soft acids Pd(II) and Pt(II) with the exocyclic imine in back $d\pi$ - π bonding.

Table 4: ^1H and ^{13}C NMR spectral data (ppm) of HL and its metal complexes

Compound	CH ₃	Allyl			H(5')	N1H	N2H	CH ₃	Allyl			CS	C(5')	C(4')	C(2')
		-CH=	=CH ₂	-CH ₂ -					-CH=	=CH ₂	-CH ₂ -				
HL	2.21	5.92	5.21 5.15	4.20	6.63	11.62	10.85	16.87	116.32	106.5	46.65	179.1	134.3	146.0	162.0
[NiL ₂]	2.15	5.87	5.12	4.18	6.61	-	9.91	16.95	116.24	106.6	46.8	170.1	134.4	134.96	161.9
[Pd(HL)Cl ₂]	1.85	5.90	5.18 5.08	3.68	6.84	11.44	8.86	19.72	116.49	109.5	45.5	176.2	134.8	145.70	161.7
[Pd(L)(OAc) H ₂ O]	1.92 2.38	5.92	5.29 5.12	3.92	6.67	-	8.43	17.5 23.9	116.5	109.6	45.3	172.7	135.2	146.20	165.5
[Pd(HL) ₂].Cl ₂	1.70	5.73	5.05 4.96	3.77	6.87	-	8.23	17.51	116.15	109.6	45.3	172.7	135.15	146.22	165.0
[PdL ₂]	1.70	5.73	5.04 4.96	3.77	6.66	-	8.22	17.51	116.15	109.6	45.3	172.7	135.1	146.20	165.5
[PtL ₂]	1.70	5.17	5.09	3.35	6.82	-	8.48	16.99	115.74	108.8	44.8	172.6	135.00	146.16	163.4

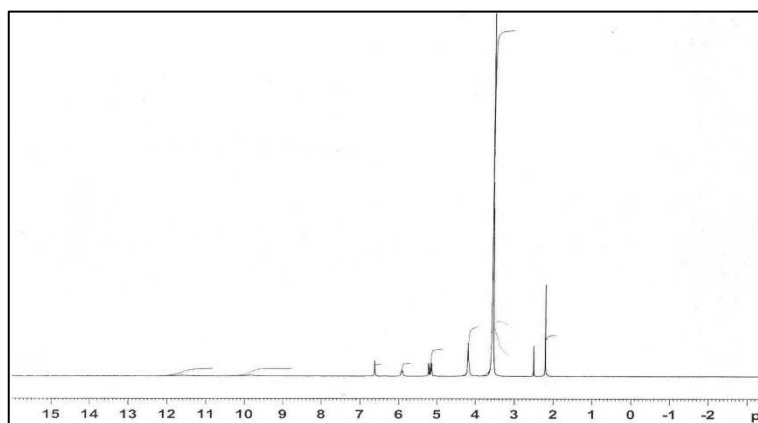


Fig. 1. ^1H NMR spectrum of HL in DMSO- d₆.

The signal of the thiazole- methyl protons show the same trend, where the methyl proton signal is shifted from 2.21 ppm. in HL to 2.15 ppm in [NiL₂], but in the Pd(II) and Pt(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.

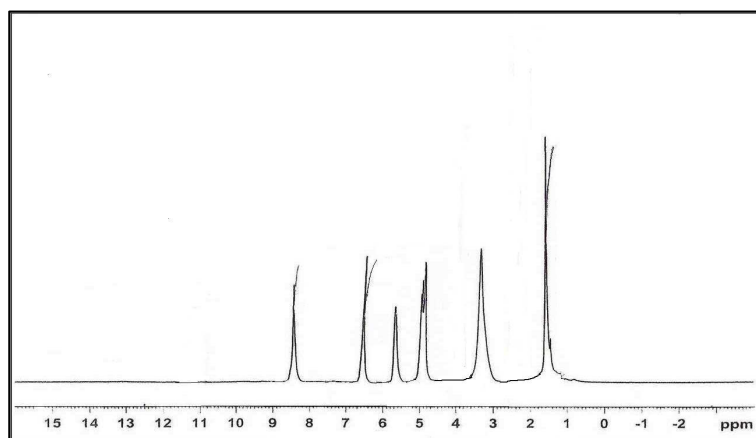


Fig. 2. ^1H NMR spectrum of [Pd(HL)₂]Cl₂ in DMSO- d₆.

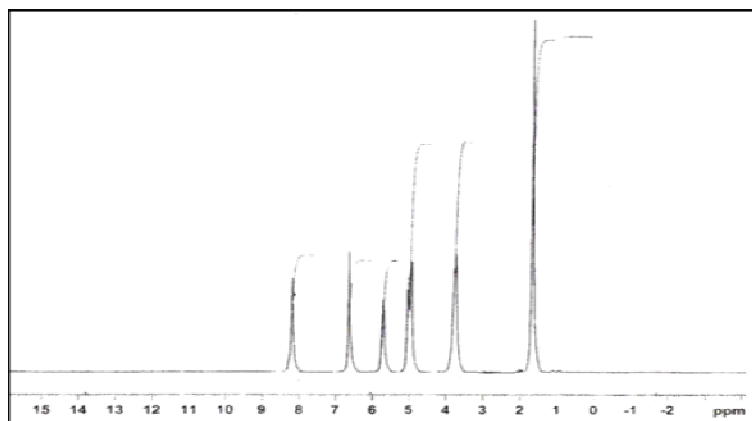


Fig. 3. ^1H NMR spectrum of $[\text{PdL}_2]$ in DMSO-d_6 .

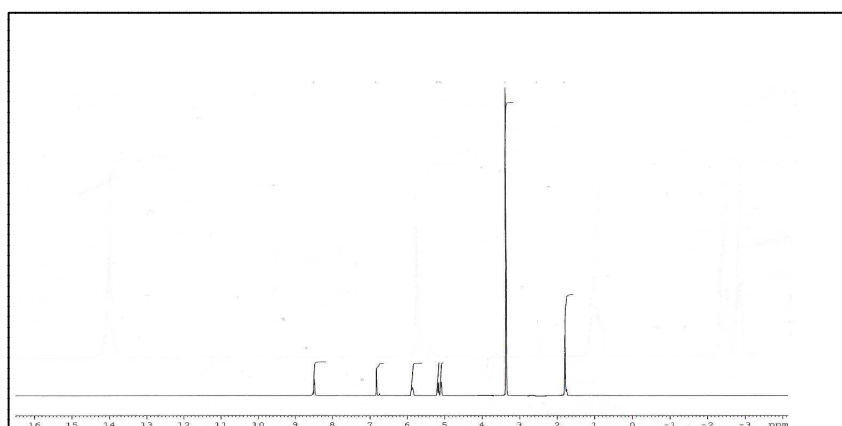


Fig. 4. ^1H NMR spectrum of $[\text{PtL}_2]$ in DMSO-d_6 .

^{13}C NMR

The ^{13}C NMR spectra of the complexes in DMSO-d_6 as a solvent (Figures 5- 8, Table 4) show 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 Pd(II) in $[\text{Pd}(\text{HL})\text{Cl}_2]$ and $[\text{Pd}(\text{HL})_2]\text{Cl}_2$; thio-S atom to metals in $[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$, $[\text{ML}_2]$. (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 σ - electron withdrawing and π -bonding on the electron density around those carbons which are influenced by the metallic cations [19, 20].

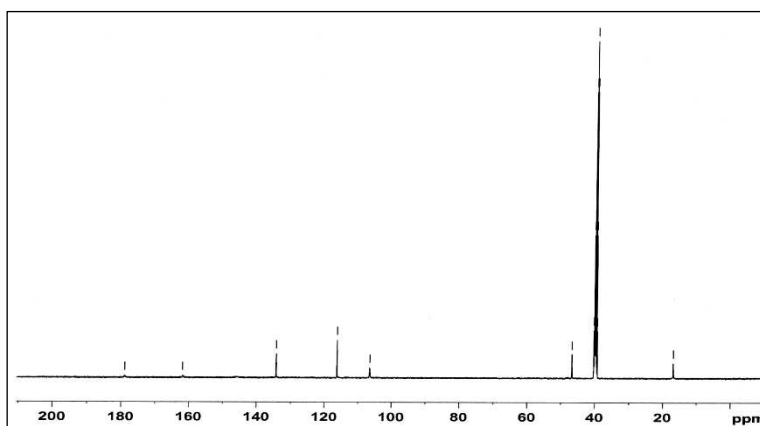


Fig. 5. ¹³C NMR spectrum of HL in DMSO- d6

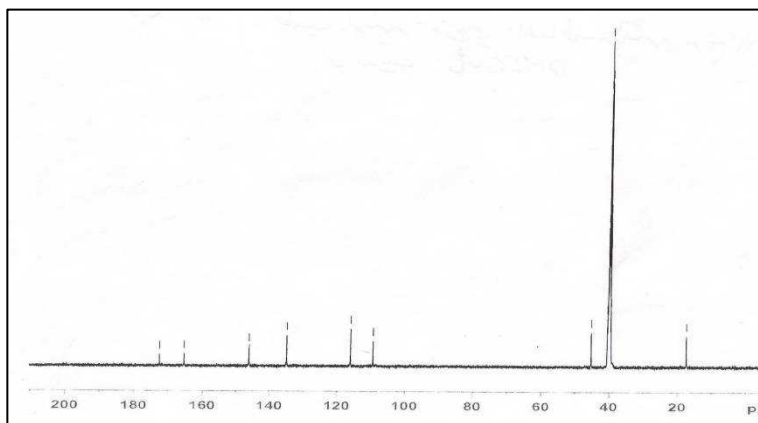


Fig. 6. ¹³C NMR spectrum of [Pd(HL)₂]Cl₂ in DMSO- d6

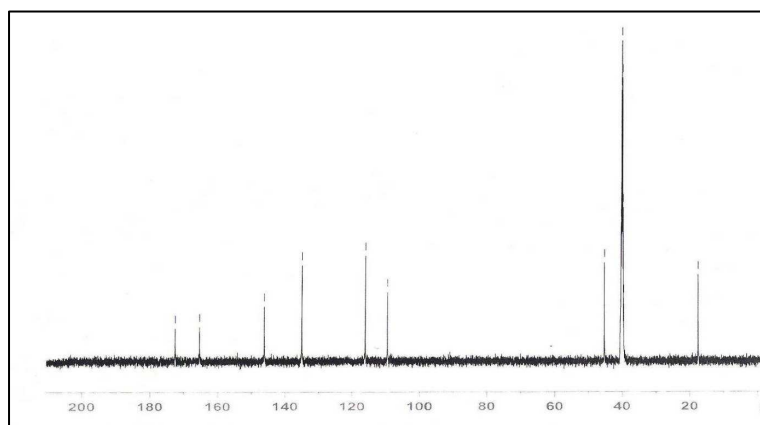


Fig. 7. ¹³C NMR spectrum of [PdL₂] in DMSO- d6 .

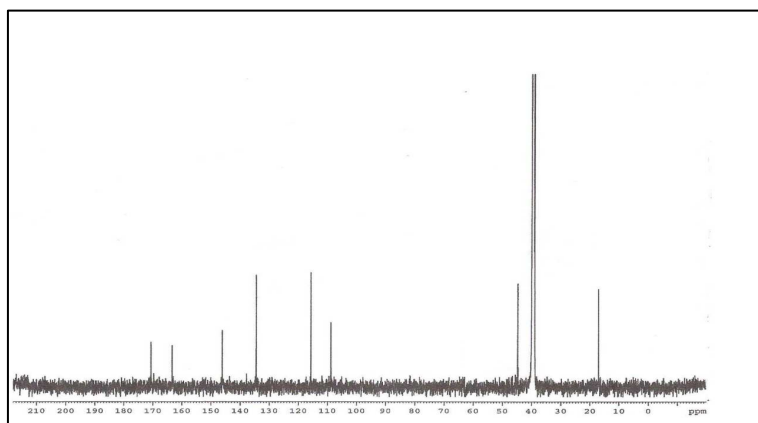


Fig. 8. ^{13}C NMR spectrum of $[\text{PtL}_2]$ in DMSO-d_6 .

Mass spectra of the complexes

The mass spectra of the Pd(II) and Pt(II) complexes (Figures 9- 11), under EI condition, using GC/ EIMS technique showed the highest peaks for $[\text{PdL}(\text{OAc})(\text{H}_2\text{O})]$, $[\text{Pd}(\text{HL})_2]\text{Cl}_2$ and PtL_2 (Scheme 3- 5) at m/z 353, 607 and 619 corresponding to the molecular weights $[\text{M}-\text{Allyl}]^+$, $[\text{M}+1]^+$ and $[\text{M}]^+$, respectively. These assignments are based on the atomic weights of Pd-106, Pt-195 and Cl-35 isotopes; besides another peaks containing another isotope distribution of the metal and Cl. Figure 11 represents the mass spectrum of PtL_2 and fragmentation pattern (Scheme 5- b) as an illustrative example for the complexes under electron impact conditions. The spectrum shows a peak at m/z 619 corresponding to the molecular formula of the complex among several molecular weights calculated based on the isotope distribution of Pt. The relatively high intensity of the parent ion suggests the high thermal stability of PtL_2 in the vapour state. This molecular ion (A) Scheme 5 loses $\text{HN-CH}_2\text{-CH=CH}_2$ radical, forming Pt(II) complex (B); with m/z 563. The spectrum also shows isotope cluster peaks at m/z 407 (highest int.), 408, 409 and 406 corresponding to the molecular cation (C), resulting from removal of AlImeTzTu molecule from the parent ion. A fragmentation pathway is also traced for the removal of methyl groups from the parent ion, giving molecular cations (D) and (E).

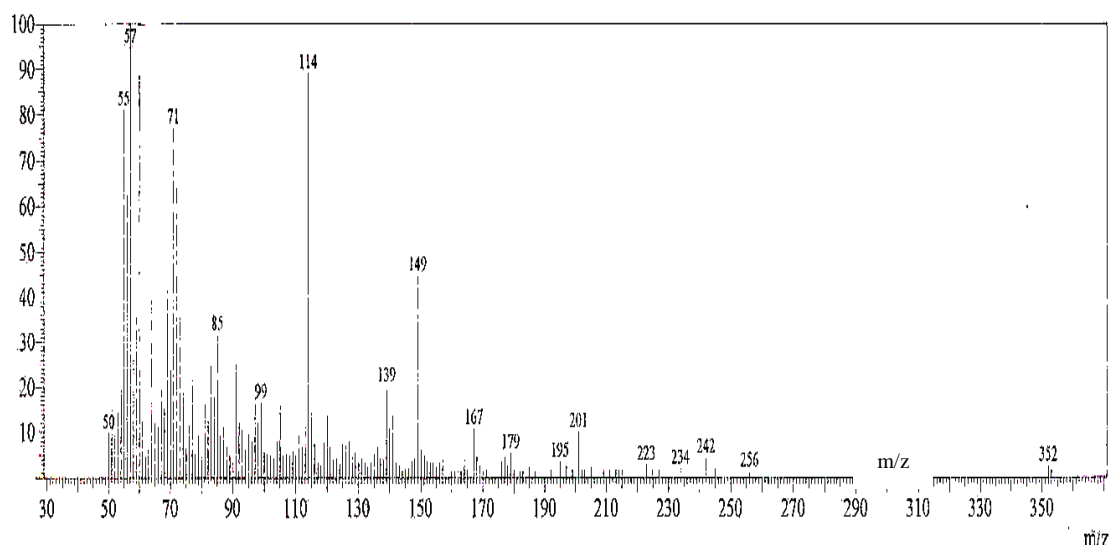


Fig. 9. Electronic impact mass spectrum of $[\text{Pd}(\text{L})(\text{OAc})(\text{H}_2\text{O})]$.

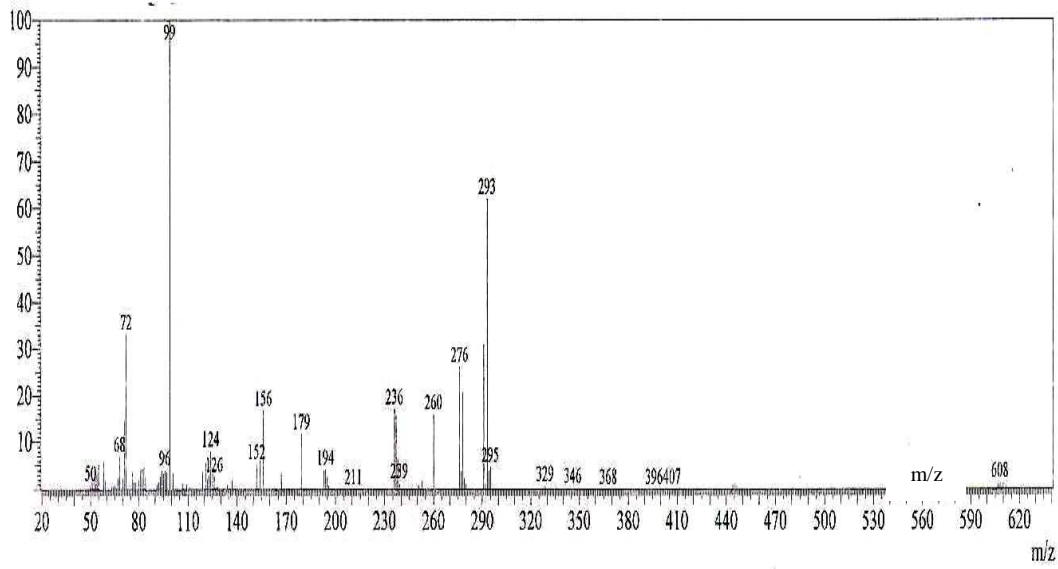


Fig. 10. Electronic impact mass spectrum of $[\text{Pd}(\text{HL})_2]\text{Cl}_2$

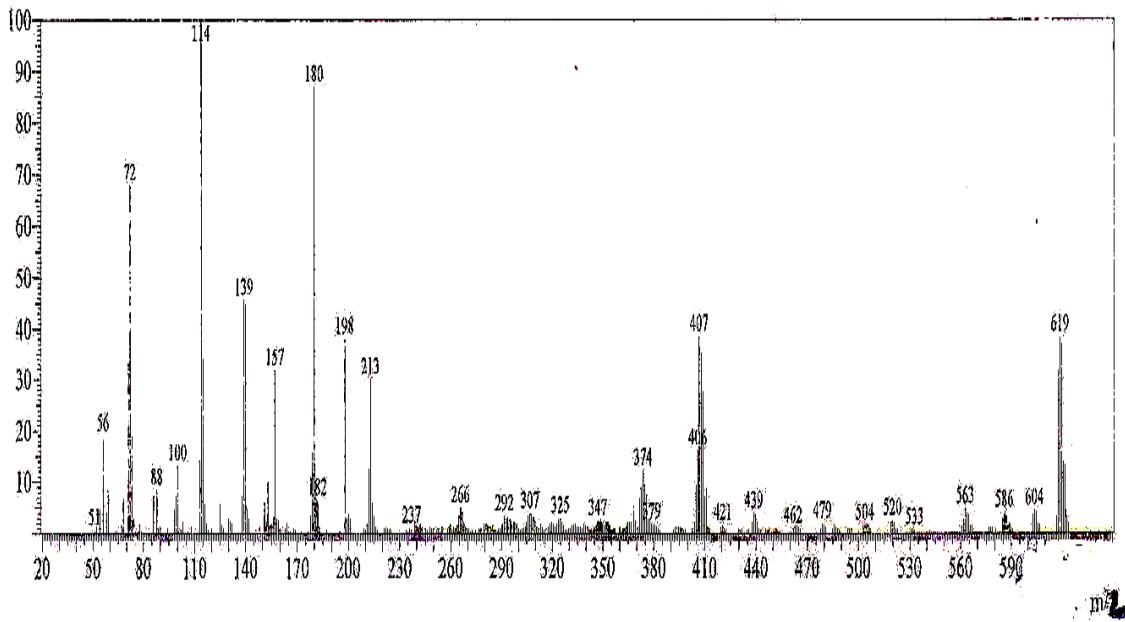
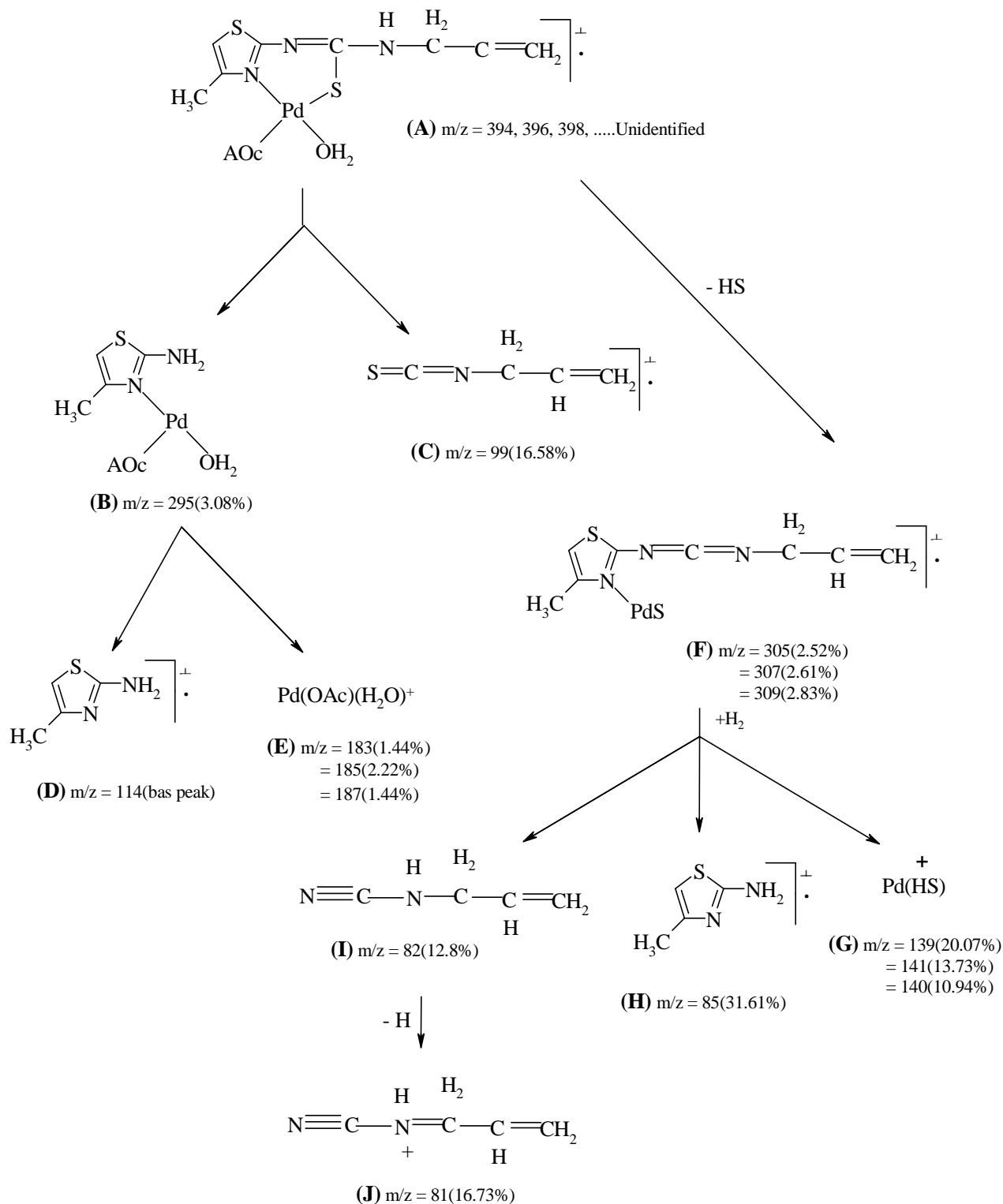
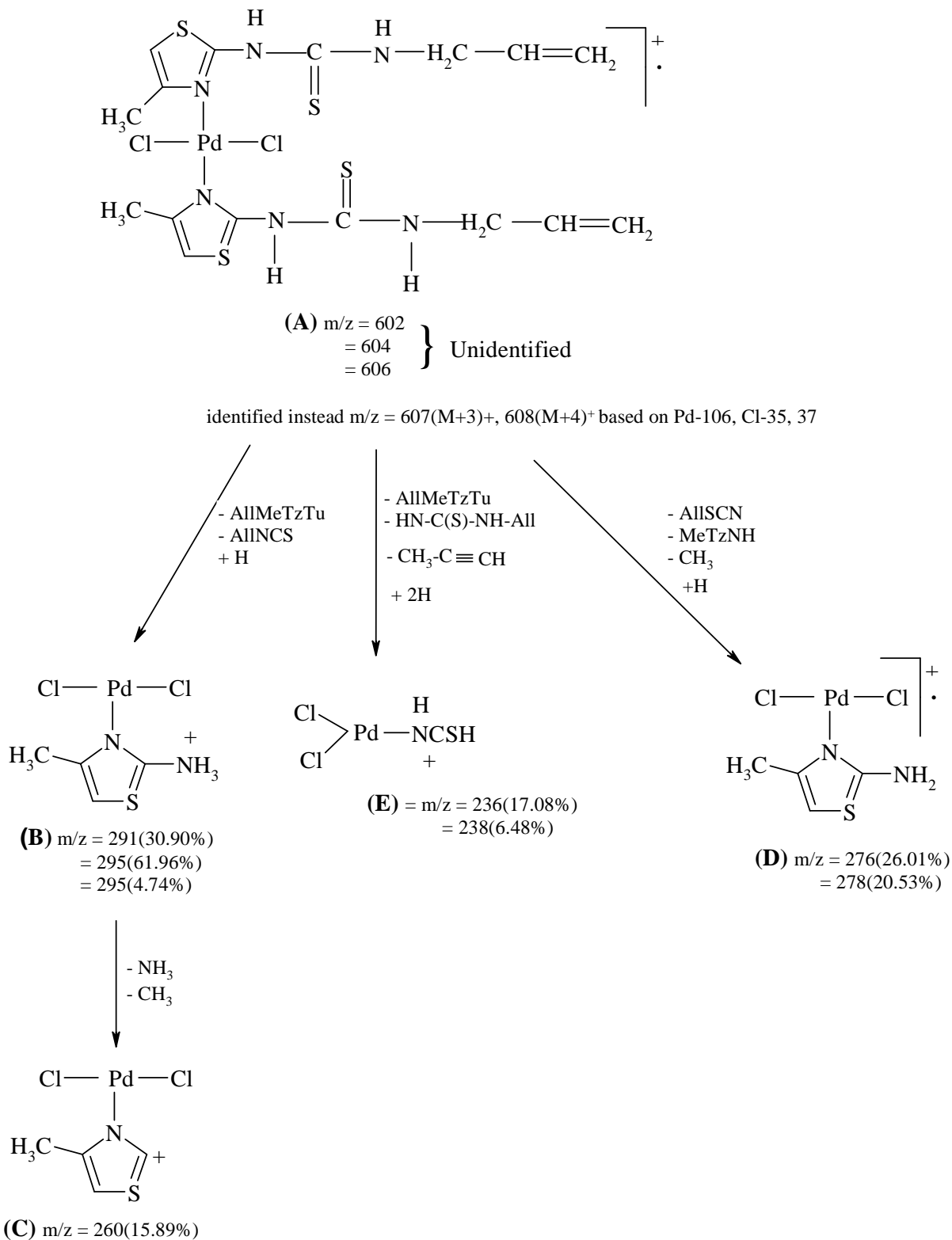


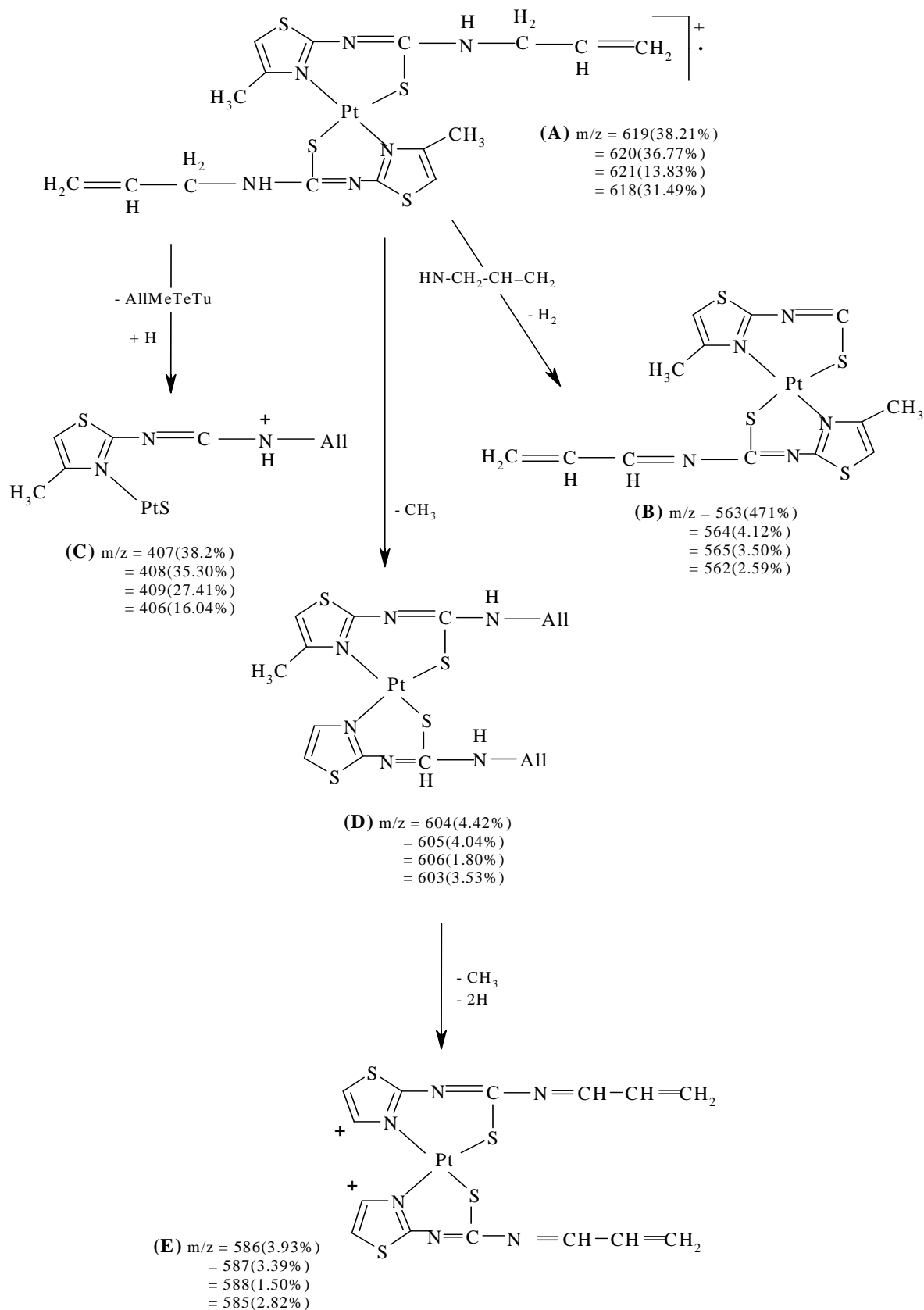
Fig. 11. Electronic impact mass spectrum of $[\text{PtL}_2]$



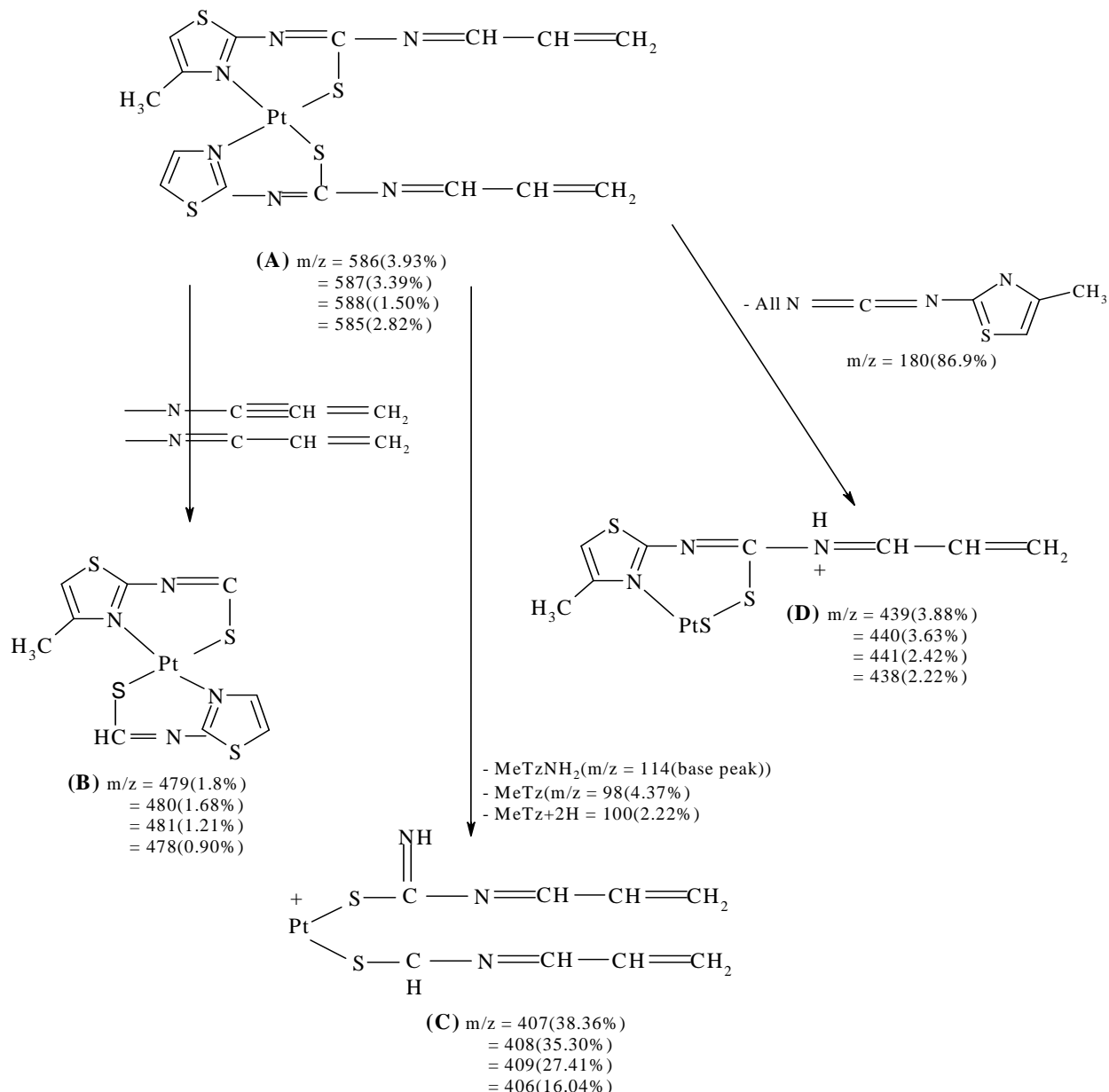
Scheme 3. Fragmentation pathway of $[Pd(L)(OAc)(H_2O)]$.



Scheme 4. Fragmentation pathways of [Pd(HL)₂] Cl₂ .



Scheme 5- a. Fragmentation pathways of $[PtL_2]^+$



Scheme 5-b. Fragmentation pathway of [PtL₂]

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