

Spectroscopic and Thermal Studies of Palladium (II) Complex of *N*-(5-methylpyridin-2-ylcarbamothiol) Cinnamamide Ligand

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Abstract

N-(5-methylpyridin-2-ylcarbamothiol) cinnamamide ligand (L1) and dichloro (*N*-(5-methylpyridine-2-yl-carbamothiol) cinnamamide – $\kappa^2 O,S$) palladium (II) (ML1) were successfully synthesised and characterized by several typical spectroscopic and analytical techniques namely Infra-Red (IR) Spectroscopy, ¹H and ¹³C Nuclear Magnetic Resonance and Thermogravimetric Analysis (TGA). The Infrared spectrum for L1 shows four bands of interest namely $\nu(N-H)$, $\nu(C=O)$, $\nu(C-N)$, $\nu(C=N)$ and $\nu(C=S)$ which can be observed at 3247cm⁻¹, 1682cm⁻¹, 1473cm⁻¹, 1541cm⁻¹ and 764cm⁻¹ respectively while for the designated metal complex, ML1 the values fall at 3227cm⁻¹, 1689cm⁻¹, 1492cm⁻¹, 1542cm⁻¹ and 774cm⁻¹ respectively. In ¹H NMR spectra for the compound L1 and ML1 show protons for N-H which can be observed at δ_H 10.11ppm, 13.02ppm and δ_H 8.71ppm, 8.99ppm while the ¹³C NMR spectra for these compounds, the signal of C=O and C=S can be observed at δ_C 177ppm, 164ppm and δ_C 173ppm, 166ppm. Whilst, in thermogravimetric analysis, compounds L1 and ML1 started to degrade at temperature 162.14°C (80% weight of sample) and 186.15°C (74 % weight of sample) respectively.

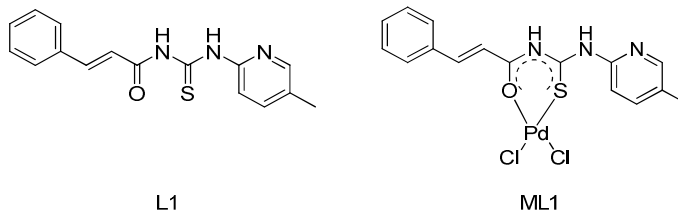
Keywords: Thiourea, palladium complex, and spectroscopic studies.

Introduction

Thiourea and its derivatives have been introduced in early 1873¹. Since then, there are many findings have been reported on the applications of thiourea and its derivatives such as in pharmaceutical industry^{2,3}, as catalysts^{3,4} in chemical reactions and for extraction of toxic metals using a solid supported liquid membrane system^{3,5}. Thiourea is a versatile ligand which has unique properties as it is able to coordinate to a range of metal centres as neutral ligand, monoanions or dianions⁶⁻⁸. Besides thiocyanate, thiourea and its derivatives are also an ambidentate ligand which can coordinate to a metal either by the S or N atom⁵. Isothiocyanates is widely used as intermediates in organic chemistry due to their tendency to undergo nucleophilic additions and cycloadditions reactions⁹. In addition, these derivatives have been proven to have a potential as an antimalarial¹⁰, anti-HIV¹¹, antibacterial¹² agents in addition to pose as anticonvulsant activity¹³. Recently thiourea also been

applied as single molecule solar cell where it is an energy saving technology¹⁴⁻¹⁸.

Furthermore, thiourea itself play a role as catalyst after undergoes complexation with transition metal such as palladium¹⁹. Palladium-catalysed coupling reactions have shown widespread application as versatile tools for carbon-carbon bond forming process due to their potential in the synthesis of complex structure such as in Suzuki, Heck and Sonogashira cross-coupling reaction²¹⁻²⁴. In this study, a new ligand (L1) and its metal complex (ML1) has been synthesised and characterized. The molecular structure of ligand, namely *N*-(5-methylpyridin-2-ylcarbamothiol) cinnamamide(L1) and its palladium complex, dichloro (*N*-(5-methylpyridine-2-yl-carbamothiol) cinnamamide – $\kappa^2 O,S$) palladium (II) (ML1) are shown in figure 1.

**Figure-1**

The molecular structure of *N*-(5-methylpyridin-2-ylcarbamothiol) cinnamamide ligand (L1) and dichloro (*N*-(5-methylpyridine-2-yl-carbamothiol) cinnamamide – $\kappa^2 O,S$) palladium (II) (ML1)

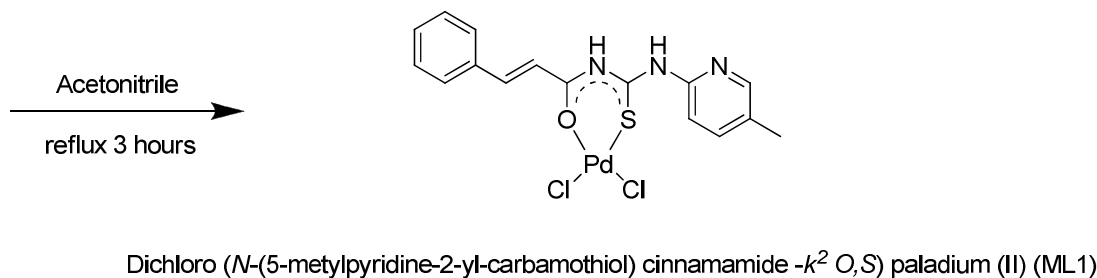
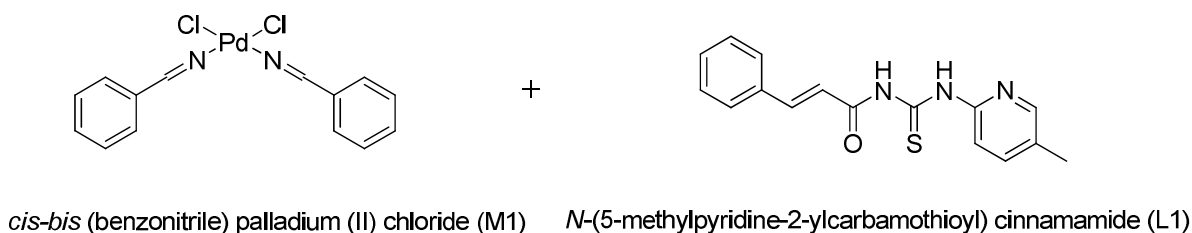
Material and Methods

Materials: All reactions were carried out under an ambient atmosphere and no special precautions were taken to exclude air or moisture during work-up⁶. The infrared (IR) spectra were recorded on a Fourier Transform-Infrared Spectrophotometer, Perkin Elmer Spectrum 100 in the range of 4000-400 cm^{-1} using potassium bromide (KBr) pellets. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded in deuterated chloroform (CDCl_3) and deuterated dimethyl sulphoxide ($\text{DMSO-}d_6$) on a BrukerAvance 400 MHz Spectrometer. The chemical shift values were given in parts per million (ppm) relative to solvent resonances as internal standard. Analytical thin-layer chromatography (TLC) was carried out on precoated plate of TLC Silica Gel 60 F254 (Merck) with solvent system hexane:dichloromethane (4:1), and spots were visualized with ultraviolet light. The melting point was measured in the range 20°C-360°C by Stuart Scientific model SMP3. The CHNS-OAnalyzerFlashea 1112 series was used to determine the experimental percentage of C, H, N and S elements of the synthesized compounds. The stability of the compound was analysed by using Perkin-Elmer TGA Analyzer from 0°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

Preparation of *N*-(5-methyl-2ylcarbamothiol) cinnamamide as a ligand (L1): A solution of cinnamoyl chloride (5.00g, 1mol) in 50ml acetone was added dropwise into a solution of ammonium thiocyanate (2.29g, 1mol) in 50ml acetone. The reaction mixture was put at reflux with continuous stirring for *ca.* 2 hours in a two-necked 250ml round-bottomed flask. A solution of 2-amino-5-picoline (3.25g, 1mol) in 50ml acetone

was added dropwise to the mixture. The reaction mixture was put at reflux with continuous stirring for *ca.* 5 hours. The progress of the reaction was monitored using Thin Layer Chromatography (TLC) (hexane: dichloromethane: 1:4). When the reaction has completed, the reaction mixture was cooled to room temperature after which it was filtered. The off-yellow precipitate was removed and the filtrate was added to three ice cubes, which was then filtered to obtain the light yellow precipitate. The precipitate was then recrystallized from hot acetone to afford the title compound (L1) as white crystalline solid.

Preparation of dichloro (*N*-(5-methylpyridine-2-yl-carbamothiol) cinnamamide – $\kappa^2 O,S$) palladium (II) (ML1): The ligand *N*-(5-methyl-2ylcarbamothiol) cinnamamide (L1) (0.1g, 0.03mmol) was dissolved in 5ml of acetonitrile in a 100ml three necked round bottom flask. Whilst, *cis-bis* (benzonitrile) palladium (II) chloride (M1) (0.30 g, 0.79 mmol) was also dissolved separately in 5ml acetonitrile. Then, the metallic solution was added dropwise into the flask containing a ligand solution. The content was stirred and put at reflux under nitrogen atmosphere for *ca.* 3 hours. The colour of the reaction mixture changed from light orange to orange colour with the formation of an orange precipitate. When the reaction has completed, the reaction mixture was cooled to room temperature after which it was filtered to give an orange solid of the title compound ML1. The general experimental procedure of palladium thiourea complex (ML1) is shown in scheme 1 below. Physical properties and analytical data of the synthesised compounds are shown in table 1.



Scheme-1
The preparation of palladium thiourea complex (ML1)

Results and Discussion

Infrared Spectroscopy Analysis: IR spectra of the synthesised ligand (L1) and the metal complex (ML1) show five bands of interest namely $\nu(\text{N-H})$, $\nu(\text{C=O})$, $\nu(\text{C=N})$, $\nu(\text{C-N})$ and $\nu(\text{C=S})$. The IR spectrum of L1 shows two bands at 3247cm^{-1} and 3011cm^{-1} which represent the asymmetric and symmetric stretching vibration in the secondary thioamide group for $\nu(\text{N-H})$ and $\nu(\text{N'H})$ respectively. These are consistent with earlier studies that $\nu(\text{N-H})$ and $\nu(\text{N'H})$ can be seen at above 3200cm^{-1} and 3000cm^{-1} due to the existence of intramolecular hydrogen bonding^{5,6}. The *trans-cis* conformation of L1 compound is related to the N-H stretching frequencies range which depends on the position -NHC(S)NHC(O)- group vibrations and stabilized by hydrogen bonding⁵. Meanwhile, the $\nu(\text{N-H})$ vibration of the ML1 spectrum was shifted to lower wavenumber on the formation of the metal-thiourea complex at 3227cm^{-1} . The formation of S→M bond was expected to increase the contribution of the highly polar structure to the thiourea molecule, which result in the increase of the double bond nature of the C-N bond and a greater single bond character for the carbon-to-sulphur bond²⁵.

The carbonyl band $\nu(\text{C=O})$ for both L1 and ML1 can be observed at 1682cm^{-1} and 1689cm^{-1} respectively with medium intensity. There is only a small difference between the wave number of the L1 and the ML1 due to the resonance effect with the phenyl rings and the existence of intermolecular hydrogen bonding with thiocarbonyl and carbonyl group respectively which effect the experimental and calculated $\nu(\text{N-H})$ stretching mode^{5,6}. Besides, this can be attributed to the stabilization of thiocarbonyl and carbonyl bond in the palladium (II) chloride due to the metal-to-ligand π -back bonding. The delocalization of thiocarbonyl and carbonyl moiety gives rise to the reduction in N-H bond length in the complex compared to the ligand²⁶.

A strong band attributed to the $\nu(\text{C=N})$ for L1 and ML1 can be seen at around 1541cm^{-1} and 1542cm^{-1} respectively. The $\nu(\text{C=N})$ band of picoline is a combination band containing certain contribution from the $\nu(\text{C-N})$ and $\nu(\text{N-H})$ motion which is connected to the thioureido band²⁷. However, the $\nu(\text{C-N})$ modes can be observed at around 1473cm^{-1} as a medium to strong band. The C-N absorption occurs at higher frequency at around 1350cm^{-1} to 1250cm^{-1} because resonance raises the double bond character between the ring and the attached nitrogen²⁸. This band was shifted to 1492cm^{-1} in IR spectrum of ML1 due to the intermolecular bonding between the carbon atom and nitrogen atom become weak to supply the electron to the oxygen atom and tend to form bonding with palladium metal. The vibration of (C=S) indicate some double bond character which can be observed at 764cm^{-1} and 774cm^{-1} with medium intensity for the L1 and ML1 spectrum. The C=S group is less polar than C=O group and has considerably weaker bond. In consequence, the bond is not intense, and it falls at lower frequencies, where it is much more susceptible to coupling effects and due to the greater mass of sulphur^{29,30}. Table 2 shows the comparison of FTIR absorption results of L1 and ML1.

NMR Spectroscopy Analysis: The chemical shifts of methyl protons for L1 appear at around δ_{H} 2.34ppm show a smaller deshielding effect as it usually can be seen at around δ_{H} 0.7. The large shift of methylene hydrogens are due to the electronegativity of the attached nitrogen in the picoline ring due to the increased in the π densities in the methyl compound^{28,29}. The vinyl protons resonances for L1 can be observed at δ_{H} 7.94-7.86ppm and δ_{H} 6.48-6.44ppm with coupling constant³ $J_{\text{HH}} = 16\text{Hz}$ respectively which indicate *trans* conformation. While for *cis* conformation the coupling constant is around³ $J_{\text{HH}} = 5-15\text{Hz}$. The splitting patterns of vinyl protons may be complicated by the fact that they may not be equivalent even when located on the same carbon of the double bond²⁸.

Table-1
The physical properties and analytical data of the synthesised compounds

Compound	Products colour and state	Yield (%)	Melting point (°C)	Element (%)			
				C	H	N	S
L1	White crystalline solid	40	188.6-189.5	64.88 (64.95)	4.88 (4.87)	14.27 (14.54)	16.73 (16.03)
ML1	Orange powdered solid	83	252.8-253.1	37.01 (40.47)	37.01 (40.47)	7.96 (8.85)	9.33 (6.75)

*In bracket: theoretical percentage of element.

Table-2
The comparison of FTIR absorption results of L1 and ML1

Compound	IR Absorption bands (cm^{-1})				
	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\nu(\text{C=S})$
L1	3247.13 (m)	1682.64 (m)	1541.08 (s)	1473.52 (m)	764.23 (w)
ML1	3227.84 (m)	1689.82 (m)	1542.98 (s)	1492.49 (s)	774.95 (m)

Phenyl and heteroatom peaks can be observed at around δ_H 8.65 to 7.44ppm (L1). Hydrogen attached to an aromatic ring has large chemical shift, usually near δ_H 7.0ppm. They are deshielded by the large anisotropic produced by the electrons in the ring's π system²⁸. L1 shows two single peaks at δ_H 13.01 and 8.73ppm which refer to the NHC=O and NHC=S respectively. Protons on nitrogen atom of an amine salt exchange at a moderate rate, they are seen as a broad peak between δ_H 8.0 to 6.0 ppm and they are coupled to protons on adjacent carbon atom³¹. The peak for NHC=O is much deshielded compared to the NHC=S due to the higher electronegativity of oxygen than sulphur atom.

In ^{13}C NMR analysis, the methyl groups of L1 can be found at δ_C 17.98ppm. Meanwhile, the vinyl carbons, phenyl and heteroatom carbon, C=S and C=O can be seen at around δ_C 149.01, 115.88, 118.20-148.68, 164.99 and 177.05 ppm respectively.

Based on ^1H NMR spectrum of ML1, the methyl protons can be seen at around δ_H 2.30ppm. The vinyl protons for the metal

complex can be observed at δ_H 7.90-7.92ppm, 6.96-7.00ppm with coupling constant $^3J_{HH} = 16\text{Hz}$. At δ_H 7.83-7.05ppm the peak for phenyl and heteroatom can be observed. Meanwhile for the ML1, the NHC=O and NHC=S protons can be observed at δ_H 9.0 and 8.7ppm.

For the ^{13}C NMR analysis of ML1, the chemical shift of vinyl carbon of the ML1 can be found at around δ_C 37-44ppm. The chemical shift for the methyl carbon can be seen at δ_C 17.17ppm. The C=O and C=S signal can be observed at δ_C 173.20ppm and 166.71ppm respectively. Table 3 shows the chemical shift of ^1H NMR and ^{13}C NMR analysis of the ligand (L1) and metal complex (ML1). Figure 3 depicts the numbering scheme for ^1H and ^{13}C NMR spectral assignment of ligand (L1) and metal complex (ML1) and table 3 shows the chemical shift of ^1H NMR and ^{13}C NMR analysis of the ligand (L1) and metal complex (ML1). In addition, Figure 2 states the numbering scheme for ^1H and ^{13}C NMR spectral assignment of ligand (L1) and metal complex (ML1).

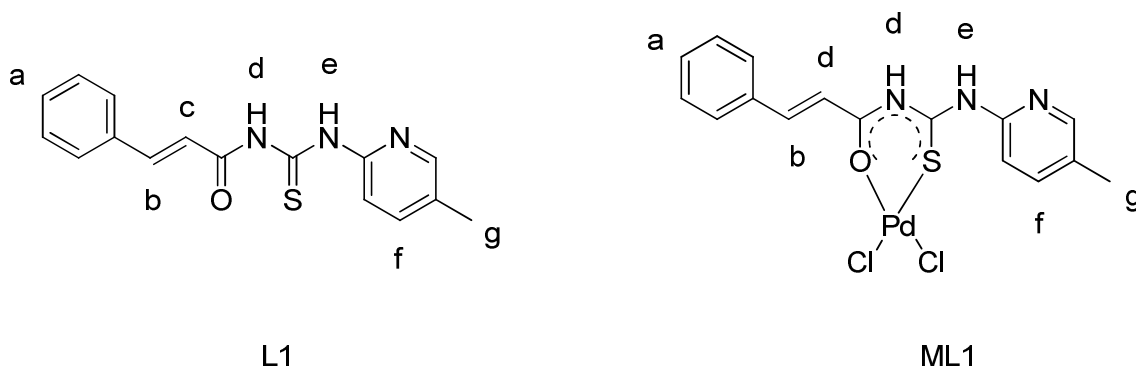


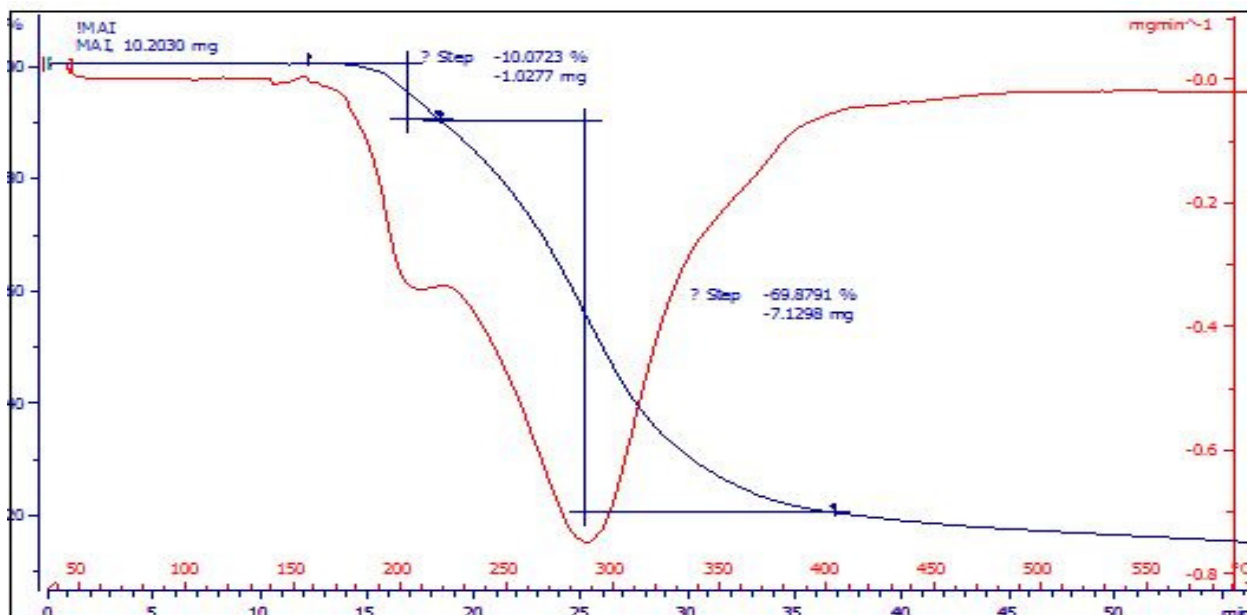
Figure-2
Numbering scheme for ^1H and ^{13}C NMR spectral assignment of ligand (L1) and metal complex (ML1)

Table-3
The chemical shift of ^1H NMR and ^{13}C NMR analysis of the ligand (L1) and metal complex (ML1)

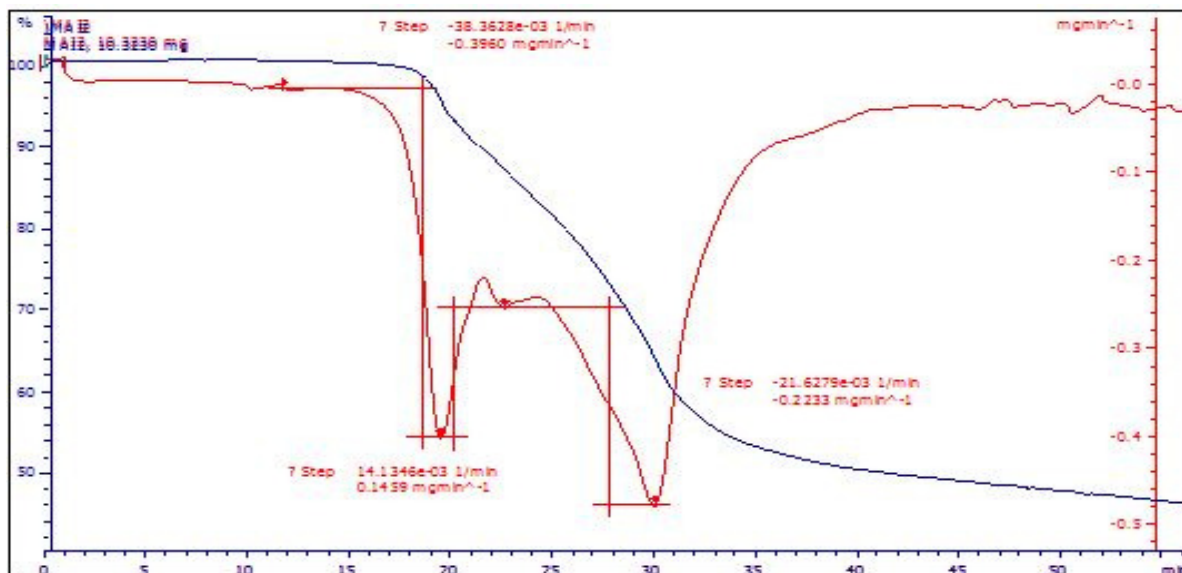
Compound	^1H NMR / δ_H (ppm)	^{13}C NMR / δ_C (ppm)
L1 (CDCl_3)	2.37 (s, 3H, CH_3) 6.49-6.53 (d, $^3J_{HH} = 16\text{Hz}$, 1H, CH(b)) 7.44-7.45 (pseudo-d, $^3J_{HH} = 6\text{ Hz}$, 3H, $\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 7.57-7.59 (pseudo-d, $^3J_{HH} = 6\text{ Hz}$, 2H, $\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 8.63 - 8.66 (d, $^3J_{HH} = 16\text{ Hz}$, 1H, CH(c)) 8.27 (s, 1H, C_5H_3) 10.11(s, 1H, NH(e)) 13.02 (s, 1H, NH(d))	17.98 (CH_3) 149.01, 115.88 (2x CH) 118.20-146.81 ($\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 148.68 (C_5H_3) 164.99 (C=S) 177.05 (C=O)
ML1 ($\text{DMSO}-d_6$)	2.30 (s, 3H, CH_3), 6.96-7.00 (d, $^3J_{HH} = 16\text{Hz}$, 1H, CH(b)) 7.44-7.49(pseudo-d, $^3J_{HH} = 9\text{ Hz}$, 3H, $\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 7.61-7.68(pseudo-d, $^3J_{HH} = 9\text{ Hz}$, 2H, $\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 7.79-7.83 (d, $^3J_{HH} = 16\text{ Hz}$, 1H, CH(c)) 7.92 (s, 1H, C_5H_3) 8.71 (s, 1H, NH(e)) 8.99 (s, 1H, NH(d))	17.17 (CH_3) 104.70, 152.61 (2x CH) 118.79-146.77 ($\text{C}_6\text{H}_5 + \text{C}_5\text{H}_3$) 146.77 (C_5H_3) 166.71 (C=S) 173.20 (C=O)

Thermogravimetric Analysis: The degradation process of L1 is illustrated in figure 4 which shows the stages of degradation process. The decomposition of L1 starts around 210°C which shows that the compound was stable until at that temperature and produces sharp weight loss of 10.07% which is followed by another weight loss at about 69.89% at 285°C. Table 4 shows the thermogravimetry analysis data for L1 and ML1. Based on the thermogram data above, there is no weight loss under 210°C, therefore it is confirm that the crystal does not contains water in it^{30,32-34}. Meanwhile, the degradation process of ML1 shows three stages of decomposition. Initially, the compound was stable up to 230°C with 38.36% of weight loss. While at the

second stage, ML1 was degraded at around 275°C (14.13% weight loss) and lastly for ML1 the weight loss of about 21.69% at around 335°C. When the heating rate is increase, the weight loss and temperature of decomposition also increases³⁵. The thermal stability of the compound rises as the temperature of degradation increases due to the increase in molecular weight. Therefore, it can be concluded that, the synthesised compounds show high thermal stability at high temperature and they have great potential to act as catalyst. Figure 4 shows the thermogram of L1 and ML1 and in detail, Table 4 explains the thermogravimetric analysis data for L1 and ML1.



L1



ML1

Figure-4

The thermogram of L1 (a) and ML1 (b)

Table-4
Thermalgravimetry analysis data for L1 and ML1

Compound	Onset temperature(°C)	Offset temperature (°C)	Temperature (°C), Weight loss (%)	Moiety
L1	235	345	Stage 1: 210°C, 10.07% Stage 2: 285°C, 69.89%	2x N-H 2-amino-5-picoline, benzene, S
ML1	200	345	Stage 1: 230°C, 38.36% Stage 2: 275°C, 14.13% Stage 3: 335°C, 21.69%	benzene, 2x N-H, 2x Cl C=O, S, N-H C=S, C=O, 2x N-H

Conclusion

In conclusion, *N*-(5-methyl-2ylcarbamothiol) cinnamamide (L1) and its palladium complex, dichloro (*N*-(5-methylpyridine-2-yl-carbamothiol) cinnamamide – $\kappa^2 O,S$) palladium (II) (ML1) have been successfully synthesised and characterized via FT-IR, ¹H and ¹³C NMR, TGA and CHNS Elemental Analysis. The Infrared spectra show several important functional groups in L1 namely $\nu(N-H)$, $\nu(C=O)$, $\nu(C=N)$, $\nu(C-N)$ and $\nu(C=S)$ which can be seen at 3247 cm⁻¹, 1682 cm⁻¹, 1541 cm⁻¹, 1473 cm⁻¹ and 764 cm⁻¹ respectively. While, ML1 shows the largest shifted at NH moiety which can be seen at 3227.84 cm⁻¹ compared to L1 due to the nitrogen atom is believed to donate certain amount of electrons to the oxygen and sulphur atoms and it contributes electrons to the palladium (II) chloride. Besides, in the NMR spectroscopy, the N-H-C=O moiety shows the most shifted atom in the metal complex spectrum compared to the ligand spectrum. This is due to the formation of bond between the C=O and the palladium as palladium is an electropositive atom as it attract electron from C=O moiety. Thus, it is confirmed that the molecular structure for the ligand and its metal complex.

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References

- Binzet G., Emen F.M., Flörke U., Ilkaynak T., Külcü N. and Arslan H., 4-Chloro-N-[N-(6-methyl-2-pyridyl) carbamothiol] benzamide, *Acta Cryst.*, **65**, 081-082 (2009)
- Abbasi S., Khani, H., Hosseinzadeh, L and Safari, Z. Determination of thiourea in fruit juice by a kinetic spectrophotometric method, *Journal of Hazardous Materials*, **174**, 257–262 (2010)
- Tadjarodi A., Adhami F., Hanifehpour Y., Yazdi M., Moghaddamfard Z. and Kickekbeck G., Structural characterization of a copper(II) complex containing oxidative cyclization of N-2-(4-picoly)-N'-(4-methoxyphenyl)thiourea, new ligands of 4-picolythiourea derivatives and the precursor molecular structure of oxidative cyclization of N-(2-pyridyl)-N'-(4-methoxyphenyl) thiourea, *Polyhedron*, **26**, 4609–4618 (2007)
- Ahmad A., Rashid H.M. and Kassim K., Copper Supported On Functionalised Mcm41 Containing Thiourea Ligand As An Catalyst In Oxidation Of Cyclohexene With Hydrogen Peroxide, *The Malaysian Journal of Analytical Sciences*, **16**, 62-70 (2012)
- Tadjarodi, A., Adhami, F., Hanifehpour. Y., Yazdi.M., Moghaddamfard, Z. & Kickekbeck. G. Structural characterization of a copper (II) complex containing oxidative cyclization of N-2-(4-picoly)-N0-(4-methoxyphenyl)thiourea, new ligands of 4-picolythiourea derivatives and the precursor molecular structure of oxidative cyclization of N-(2-pyridyl)-N'-(4-methoxyphenyl) thiourea, *Polyhedron.*, **26**, 4609–4618 (2007)
- Yusof M.S.M., Jusoh R.H., Khairul W.M. and Yamin B.M., Synthesis and Characterization of Series of N-(3, 4-Dichlorophenyl)-N'(2,3 and 4-methylbenzoyl)thiourea Derivatives, *Journal of Molecular Structure*, **975**, 280–284 (2010)

7. Arslan H., Monsuroglu D.S., Vanderveer D. and Binzet G., The molecular structure and vibrational spectra of N-(2,2-diphenylacetyl)-N'-(naphthalen-1yl)-thiourea by Hartree-Fock and density functional methods, *Spectrochimica Acta Part A.*, **72**, 561-571 (2009)
8. Henderson W., Nicholson B.K. and Rickard C.E.F., Platinum(II) complexes of chelating and monodentate thiouremonoanions incorporating chiral, fluorescent or chromophoric groups, *Inorganica Chimica Acta.*, **320**, 101-109 (2001)
9. Shusheng Z., Tianrong Z., Kun C., Youfeng X. and Bo Y., Simple and efficient synthesis of novel glycosylthiourea derivatives as potential antitumor agents, *European Journal of Medicinal Chemistry*, **43**, 2778-2783 (2008)
10. Sunduru N., Srivastava K., Rajakumar S., Puri S.K., Saxena J.K., Chauhan P.M.S., Synthesis of novel thiourea, thiazolidinedione and thioparabanic acid derivatives of 4-aminoquinoline as potent antimalarials, *Bioorganic & Medicinal Chemistry Letters*, **19**, 2570-2573 (2009)
11. D'Cruz O.J. and Uckun F.M., Discovery of 2,5-dimethoxy-substituted 5-bromopyridyl thiourea (PHI-236) as a potent broad-spectrum anti-human immunodeficiency virus microbicide, *Molecular Human Reproduction*, **11**, 767-777 (2005)
12. Nitulescu G.M., Draghici C., Chifiriuc M.C. and Missir A.V., Synthesis of Isomeric N-(1-Methyl-1Hpyrazole-4-Carbonyl)-N'-(Xylyl)-Thiourea and Their Antimicrobial Evaluation, *Farmacia.*, **57**:5 (2009)
13. Celen A.O., Kaymakçioğlu B., Gumru S., Toklu H.Z and Arıcıoğlu F., Synthesis and anticonvulsant activity of substituted thiourea derivatives. *Marmara Pharmaceutical Journal.*, **15**, 43-47 (2011)
14. Adli H.K., Khairul W.M. and Salleh H., Synthesis, Characterization and Electrochemical Properties of Single Layer Thin Film of N-Octyloxyphenyl-N'-(4-Chlorobenzoyl) Thiourea-Chlorophyll As Potential Organic Photovoltaic Cells, *Int. J. Electrochem. Sci.*, **7**, 499 (2012)
15. Adli H.K., Khairul W.M. and Salleh H., Linear Nonyloxy-Substituted Thiourea-Chlorophyll Thin Film As Potential Single Layer Photovoltaic Cells, *International Journal of Advanced Chemical Technology.*, **1**, 1 (2011)
16. Rahamathulla R., Khairul W.M., Salleh H., Adli H.K., Isa M.I.N. and Tay M.G., Synthesis, Characterization and Electrochemical Analysis of V-Shaped Disubstituted Thiourea-Chlorophyll Thin Film as Active Layer in Organic Solar Cells, *Int. J. Electrochem. Sci.*, **8**, 3333-3348 (2013)
17. Mahesh D. and Rajesh J., TiO₂ Microstructure, Fabrication of Thin Film Solar Cells and Introduction to Dye Sensitized Solar Cells, *Research Journal of Recent Sciences*, **2**, 25-29 (2012)
18. Rasool F.K. and Samaneh P., Photovoltaic Device Modeling and Effect of its Parameters, *Research Journal of Recent Sciences*, **2**, 59-64 (2013)
19. Birinci E., Gulfen M. and Aydin A.O., Separation and recovery of palladium (II) from base metal ions by melamine-formaldehyde-thiourea (MFT) chelating resin, *Hydrometallurgy*, **95**, 15-21 (2009)
20. Saluste C.G., Whitby R.J. and Furber M., Palladium-catalysed synthesis of imidates, thioimidates and amidines from aryl halides, *Tetrahedron Letters*, **42**, 6191-6194 (2001)
21. Jung E., Park K., Kim J., Jung H., Oh I. and Lee S., Palladium-catalyzed Mizoroki-Heck coupling reactions using sterically bulky phosphite ligand, *Inorganic Chemistry Communications*, **13**, 1329-1331 (2010)
22. Fairlamb I.J.S., Lee A.F., Loe Mie F.E.M., Niemela E.H., O'Brien C.T. and Whitwood A.C., Halogenated-2-pyrones in Sonogashira cross-coupling: limitations, optimisation and consequences for GC analysis of Pd-mediated reactions, *Tetrahedron*, **61**, 9827-9838 (2005)
23. Alonso F., Beleskaya I.P. and Yus M., Non-conventional methodologies for transition-metal catalysed carbon-carbon coupling: a critical overview, Part 1: The Heck reaction, *Tetrahedron*, **61**, 11771-11835 (2005)
24. Dawood K.M., Microwave-assisted Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions of aryl chlorides and bromides in water using stable benzothiazole-based palladium(II) precatalysts, *Tetrahedron*, **63**, 9642-9651 (2007)
25. El-Bahy G.M.S, El-Sayed B.A. and Shabana A.A., Vibrational and electronic studies on some metal thiourea complexes, *Vibrational Spectroscopy*, **31**, 101-107 (2003)
26. Philip, V. Structural and Spectral Investigations of Transition Metal Complexes of Di-2-pyridyl ketone N(4), N(4)-Disubstituted Thiosemicarbazones, Submitted Doctor of Philosophy Thesis (2004)
27. Estévez-Hernández, O., Otazo-Sánchez, E., J.L. Hidalgo-Hidalgo de Cisneros., Naranjo-Rodríguez, I & Reguera, E. A Raman and infrared study of 1-furoyl-3 monosubstituted and 3,3-disubstituted thioureas. *Spectrochimica Acta Part A.*, **62**, 964-971 (2005)
28. Pavia D.L., Lampman G.M. and Kriz G.S., *Introduction to Spectroscopy*, 3rd Ed. Washington. Brooks/Cole Thomson Learning (2009)
29. Abraham R.J. and Reid M., ¹H chemical shifts in NMR. Part 18. Ring currents and π-electron effects in heteroaromatics, *J. Chem. Soc., Perkin Trans.*, **2**, 1081-1091 (2002)
30. Raja C.R., Vijayabhaskaran B., Vijayan N. and Paramasivam P., Synthesis, growth and characterization

- analysis of nickel mercury thiocyanate crystal (NMTC), *Materials Letters*, **62**, 2737-2739 (2008)
31. Silverstein R.M., Webster F.X. and KIemle D.J., *Spectrometric Identification of Organic Compounds*, 7th edition, John Wiley & Sons, Inc (2005)
32. Kumar S.M.R., Selvakumar S., Kiruba S., Tholkappian M. and Sagayaraj P., Nucleation, growth and characterization of Bis(thiourea) cadmium formate NLO sigle crystals, *International Journal of Science and Technology* (2011)
33. Mudlgoudra B.S. and Chougale R.B., Thermal Behavior of Poly (vinyl alcohol)/ Poly (vinyl pyrrolidone)/ Chitosan Ternary Polymer Blend Films, *Research Journal of Recent Sciences*, **1**, 83-86 (2012)
34. Morteza M., Reza M.S.A. and Shiva J., Synthesize, Characterization and Thermal behaviour of some New Mercury and Cadmium halides Coordination compounds of Recently synthesized Schiff base, *Research Journal of Resent Sciences*, **1**, 9-15 (2012)
35. Singh R.K., Bijayani B. and Sachin K., Determination of Activation Energy from Pyrolysis of Paper Cup Waste Using Thermogravimetric Analysis, *Research Journal of Recent Sciences*, **2**, 177-182 (2013)