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Neutral half-sandwich arene Ru(II) complexes bearing a bulky N-((2,6-diisopropylphenyl) carbamothioyl) acetamide (L) ligand: Synthesis, spectral and biological studies.

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Abstract

Neutral half-sandwich arene Ru(II) complexes are coordination compounds containing a ruthenium(II) metal center coordinated to an arene ligand and other neutral ligands. These complexes are commonly used in various fields such as catalysis, medicinal chemistry, and material science due to the unique properties of ruthenium. So, herein, we report a bulky N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L) ligand which was synthesized by the reaction between 2,6-diisopropylamine, acetyl chloride, and potassium thiocyanate which was subsequently used to prepare half-sandwich *p*-cymene Ru(II) and benzene Ru(II) complexes. Halide bridged precursors such as $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and $[Ru(\eta^6\text{-benzene})Cl_2]_2$ on reaction with (L) afforded neutral complexes having formula $[Ru(\eta^6\text{-}p\text{-cymene})(L)\kappa^1{}_{(S)}Cl_2]$ (**1**) and $[Ru(\eta^6\text{-benzene})(L)\kappa^1{}_{(S)}Cl_2]$ (**2**). All these compounds were characterized by various spectroscopic studies which confirmed that the ligand coordination to ruthenium was primarily through the thione sulfur as evidenced by IR and NMR studies. The complexes (**1-2**) were screened for In vitro antibacterial activities against S. aureus and showed moderate antibacterial activity with MIC values, 55 µg/mL, and 58 µg/mL, respectively.

Keywords: Ru(II) complexes, half-sandwich arene ruthenium complexes, thiourea ligands.

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Introduction:

In the field of organometallic chemistry, half-sandwich arene ruthenium complexes represent one of the most important metal-based compounds having diverse applications in various arenas [1, 2]. These compounds are very special in terms of developing metal therapeutic agents and as metal-based drug candidates [3]. Arene Ru complexes have opened a platform for researchers and it has been widely studied and examined the bioactivity of these complexes [4, 5]. Chelating ligands having nitrogen and oxygen donor ligands have been utilized for synthesizing arene ruthenium complexes and which has also been explored for their various bioactivity anti-tumor, anti-malarial, anti-fungal, and also catalytic activity [6-10]. Arene ruthenium complexes of heterocyclic thiourea ligands and their anti-cancer activity were first reported in 2012 by Samuelson *et al* [11]. Owing to the diverse coordination modes of these thiourea-based ligands numerous arene metal complexes based on these ligands are reported in which the most common coordination mode was through the thione sulfur (-S) atom despite having several other possible modes of coordination [12]. Also, Batista *et al*. showed that different reaction conditions in the synthetic route allowed distinct coordination of acyl thiourea ligands towards Ru(II) complexes monodentate through S as well as bidentate *via* O, S. Although most reported arene ruthenium complexes bear monodentate sulfur coordination to ruthenium however insertion of an appropriate donor group such as pyridine also allowed the NS coordination [14]. Interestingly it was reported by Grgurić-Šipka *et al*. that Ru(II) arene complexes with benzoyl thiourea derivatives changed in coordination from monodentate sulfur to bidentate NS coordination during crystallization [15]. Kavembu and co-workers have reported several *p*-cymene Ru(II) and benzene Ru(II) complexes with various acyl, aryl, and alkyl thiourea derivatives and also explored its anti-tumor as well as catalytic activity [12].

Analogs of urea are a class of organic compounds well known as thiourea where the oxygen atom is replaced by sulfur. The amino hydrogens in thiourea when replaced by alkyl or aryl groups provide a platform for the synthesis of heterocyclic thiourea derivatives which are bio-active organic compounds [16, 17]. These thiourea derivates have been widely explored for their various applications such as anti-bacterial, anti-fungal, anti-oxidant, anti-inflammatory, anti-cancer, and anti-fungal properties [18-20]. The basic skeleton of the alkyl/aryl thiourea fragment is shown in Figure 1 and we can see that it has a rich source of donor atoms which makes it a diverse ligand possessing interesting properties and having the ability to coordinate various metal ions in mono or bi-dentate ligands through its oxygen, sulfur, or nitrogen donor atoms. The presence of C=O and C=S functional groups in thiourea derivatives makes it a useful chelating ligand and thus can coordinate metal ions in a diversified manner [21]. Various metal complexes of thiourea derivatives have been explored over many years and these are found to exhibit a wide range of bio-activity such as anti-fungal, anti-oxidant, anti-bacterial, herbicidal, and plant growth regulators [22-24]. Also, various research groups have explored the thermal properties and ionization constants of some of the thiourea-derived ligands and their corresponding metal complexes [25, 26].

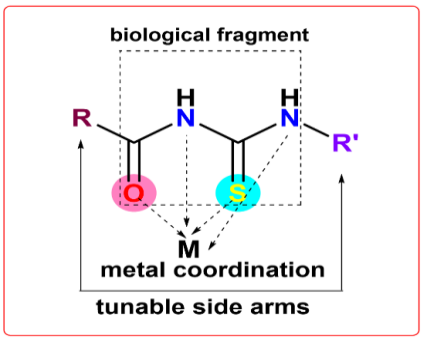
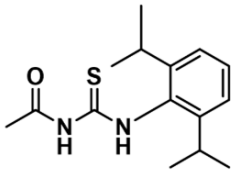


Figure 1: Pictogram of acyl thiourea fragment

Because of the existing and interesting coordination modes of the thiourea ligands towards metal ions, it prompted us to explore the chemistry of thiourea ligands by incorporating a bulky amino group in the side arms along with an acetyl group. Thus herein we report the synthesis, of a bulky thiourea ligand N-((2,6-diisopropylphenyl) carbamothioyl) acetamide (L) and its *p*-cymene Ru(II) and benzene Ru(II) complexes The ligand used in this study is shown in (Figure 2).



N-((2,6)diisopropylphenyl)carbamothioyl)acetamide
(White powder)
(L)

Figure 2: Ligand (L) used in the present study.

Materials and Methods:

All the chemicals and reagents used were of commercial quality and were used without further purification. $RuCl_3.nH_2O$, α-phellandrene, 1,3-cyclohexadine, 2,6-diisopropyl aniline were purchased from Sigma-Aldrich and acetyl chloride and potassium thiocyanate were purchased from Alfa-Aesar. The ruthenium precursors, namely $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and $[Ru(\eta^6\text{-benzene})Cl_2]_2$ required for the preparation of these complexes, were prepared according to the published procedures [27, 28]. All the NMR spectra were recorded in deuterated solvent ($CDCl_3$) on a Bruker Advance II (^1H: 400 MHz), spectrometer at room temperature which was internally referenced to TMS (tetramethylsilane). Chemical shift values, δ, are reported in ppm (parts per million), and coupling constants (J) in Hertz. The abbreviations for the peak multiplicities are as under: (singlet, s), (doublet, d), (triplet, t), and (multiplet, m) respectively. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer using (KBr pellets; 400-4000 cm^{-1}). Absorption spectra are recorded on a Perkin-Elmer Lambda 25 UV/Visible spectrophotometer in the range of 200-800 nm at room temperature in acetonitrile. Mass spectra were recorded with Q-Tof ESI-MS instrument (model HAB 273) using acetonitrile as solvent.

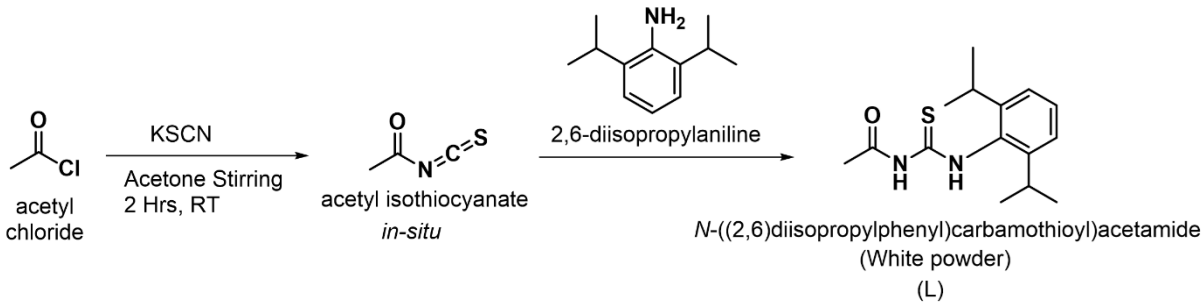
Antibacterial activity assay:

By using the broth microdilution technique, all of these recently synthesized complexes were checked for their potential in vitro antibacterial activity against S. aureus. To find the MICs, each test drug was dissolved in DMSO and serially diluted in a range of concentrations at a 2-fold dilution (250, 90, 60, 30, 15, 7.5 μg/mL). The overall percentage of DMSO was kept to 5 % while testing the sample. The reference standard was the antibiotic ciprofloxacin.5%). The pH 8 TBE buffer was used to run the gel electrophoresis at 70 mV for 1 hour. The band was evaluated with a U-Vis light.

Result and Discussion:

Synthesis of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

(5 mmol) of acetyl chloride was dissolved in anhydrous acetone (5 mL) which was added dropwise to a stirred solution of potassium thiocyanate KSCN (5 mmol) in anhydrous acetone (5 mL). Within a few minutes, precipitation of potassium chloride was observed which was further continued stirring for 1 hour, then (5 mmol) of 2,6-dimethyl aniline was added in-situ to the formed acetyl isothiocyanate and this solution was further stirred for 1 hour and the reaction mixture was poured in ice-cold water 100 mL whereupon white solid of thiourea precipitated out which was filtered in Bücher funnel, yielding the desired ligand as a white powder in good yields which was used for the preparation of ruthenium complexes in next step without further purification (Scheme-1).



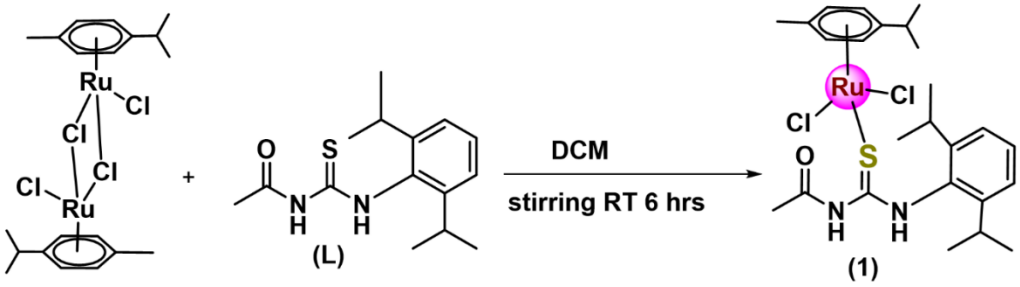
Scheme-1: Synthesis of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

Color: White powder; Yield 80 %; FT-IR (KBr, cm^{-1}): 3430, 3345, 3241, 1648, 1230, 1180(m); ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 11.80 (s, 1H, thioamide, N-H), 10.37 (s, 1H, amide, N-H), 7.43 (t, 1H, J = 8 Hz, $CH_{(aromatic)}$), 7.26 (d, 2H, J = 8 Hz, $CH_{(aromatic)}$), 3.04-3.10 (m, 2H, $CH_{(aliphatic)}$), 2.24 (s, 3H, $CH_{(aliphatic)}$), 1.33 (d, 6H, $CH_{(aliphatic)}$), 1.20 (d, 6H, $CH_{(aliphatic)}$); ^{13}C (100 MHz, $CDCl_3$-d): 181.47 (C=S), 172.11 (C=O), 145.50, 132.46, 129.14, 128.77, 123.92, 123.80 ($C_{(aromatic)}$), 28.84, 28.73, 24.35, 24.31, 23.96, 23.09 ($C_{(aliphatic)}$); ESI-MS (*m/z*) [found (calcd)]: 279.1655 (279.1526) {$[M + H^+]^+ = [C_{15}H_{23}N_2OS]^+$}; UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 274 (0.69), 320 (0.05).

Synthesis of Dichloro(*p*-cymene)[N-((2,6-diisopropylphenyl)carbamothioyl)acetamide]ruthenium(II) (**1**)

$[(p\text{-cymene})RuCl_2]_2$ dimers (30 mg, 0.049 mmol, 1 eq) were added to a vigorously stirred solution of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L) (27.25 mg, 0.09 mmol, 2 eq) in dichloromethane 5 mL resulting in an orange-red colored solution which was stirred for 6 hours and then after the desired time excess hexane was added to the solution which resulted in the formation of a red precipitate which was collected on a frit funnel and washed with cold methanol (2 mL) and diethyl ether (10 mL) and dried in vacuum.

Yield: (65 %); FT-IR (KBr, cm^{-1}): 3430, 3316, 3261, 1645, 1158, 1020; ^{1}H-NMR (400 MHz, $CDCl_3$-d): δ (ppm) = 11.66 (s, 1H, thioamide, NH), 11.18 (s, 1H, amide, NH), 7.33 (t, 1H, J = 8 Hz, $CH_{(aromatic)}$), 7.17 (d, 2H, J = 8 Hz, $CH_{(aromatic)}$), 2.88-2.95 (m, 2H, $CH_{(aliphatic)}$), 2.77-2.84 (m, 1H, $CH_{(p\text{-}cym)}$) 2.14 (s, 3H, $CH_{3(aromatic)}$), 2.12 (s, 3H, $CH_{(p\text{-}cym)}$), 1.21 (d, J = 8 Hz, 6H, $CH_{(aliphatic)}$), 1.15 (d, J = 8 Hz, 6H, $CH_{(aliphatic)}$), 1.04 (d, J = 8 Hz, 6H, $CH_{(p\text{-}cym)}$); ESI-MS (*m/z*) [found (calcd)]: 513.1474 (513.1508) {$[M - 2H^+ - 2Cl^- + H^+]^+ = [C_{25}H_{35}N_2ORuS]^+$}; UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 275 (0.51), 442 (0.017).

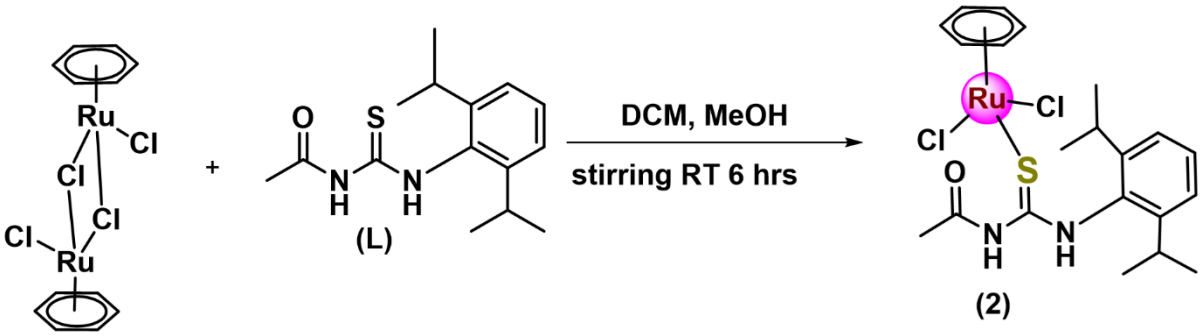


Scheme-2: Synthesis of $[(p\text{-cymene})Ru(L)\kappa^1_{(S)}Cl_2]$(**1**)

***Synthesis of* Dichloro(benzene)[N-((2,6-diisopropylphenyl) carbamothioyl)acetamide]ruthenium(II) (2)**

[(benzene)$RuCl_2$]$_2$ dimers (30 mg, 0.049 mmol, 1 eq) were added to a vigorously stirred solution of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L) (27.25 mg, 0.09 mmol, 2 eq) in a mixture of solvent dichloromethane 5 mL and methanol 5 mL resulting in a brown-red colored solution which was stirred for 6 hours and then after the desired time excess hexane was added to the solution which resulted in the formation of a brownish red precipitate which was collected on a frit funnel and washed with cold methanol (2 mL) and diethyl ether (10 mL) and dried in vacuum.

Yield: (72 %); FT-IR (KBr, cm^{-1}): 3427, 3310, 3200, 1648, 1160, 1020; ^{1}H-NMR (400 MHz, $CDCl_3$-d): δ (ppm) = 11.71 (s, 1H, thioamide, NH), 11.21 (s, 1H, amide, NH), 7.34 (t, 1H, J = 8 Hz, $CH_{(aromatic)}$), 7.25 (d, 1H, J = 4 Hz, $CH_{(aromatic)}$), 7.09-7.11 (m, 1H, $CH_{(aromatic)}$), 5.52 (s, 6H, $CH_{(benzene)}$), 2.88-2.96 (m, 2H, $CH_{(aliphatic)}$), 2.15 (s, 3H, $CH_{(aliphatic)}$), 1.23 (d, J = 8 Hz, 6H, $CH_{(aliphatic)}$), 1.06 (d, J = 8 Hz, 6H, $CH_{(aliphatic)}$); ESI-MS (*m/z*) [found (calcd)]: 457.0816 (457.0882) {$[M - 2H^+ - 2Cl^- + H^+]^+$ =$[C_{21}H_{27}N_2ORuS]^+$}; UV–Vis {Acetonitrile, λ_{max}, nm ($\varepsilon/10^{-4}$ M^{-1} cm^{-1})}: 276 (0.53), 445 (0.012).



Scheme-3: Synthesis of [(benzene)Ru(L)$\kappa^1_{(S)}Cl_2$](**2**)

Synthesis of ligand and p-cymene Ru(II) and benzene Ru(II) complexes

The thiourea-based ligand was synthesized by the reaction between acetyl chloride and potassium thiocyanate resulting in-situ formation of acetyl isothiocyanate in which 2,6-diisopropylamine was successively added which resulted in the formation of the ligand as white precipitate upon addition of this reaction mixture to ice cold water. This ligand was used in the next step for reaction with metal precursors without any purification. The ruthenium complexes were synthesized by the reaction between (L) and ruthenium precursors such as [Ru(η^6-*p*-cymene)Cl_2]$_2$ and [Ru(η^6-benzene)Cl_2]$_2$ in dichloromethane resulting in a red colored solution which on the addition of excess hexane after 6 hours resulted in the formation of the complexes as a reddish powder. These complexes were found to be very stable in the air non-hygroscopic in nature and soluble in methanol, acetone, dichloromethane, etc. The outline for the synthetic scheme of ligand and ruthenium complexes are shown in Scheme-1 and 2 respectively. These compounds were isolated as a reddish powder in yields > 70% and are neutral complexes. Both the ligand and the Ru compounds were characterized by spectroscopic methods such as IR, UV-Vis, NMR, and ESI-MS studies the details of which are explained as under.

Spectroscopic analysis of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

The FT-IR spectra of the thiourea ligand exhibited bands in the region 2961-3151, 1697, and 1240 cm^{-1} for $\nu_{(N-H)}$ and $\nu_{(C-H)}$,

$\nu_{(C=O)}$ and $\nu_{(C=S)}$ respectively (Figure 1). The ^{1}H spectrum of (L) is displayed in (Figure 2). The thioamide proton was observed as a singlet at 11.80 ppm whereas the amide N-H was observed singlet at 10.37 ppm. Also, the aromatic protons of the ligand exhibited a doublet at 7.26 ppm and a triplet at 7.40-7.43 ppm respectively. The methine and methyl protons of the ligand were observed as a multiplet between 3.04-3.10 ppm and as a singlet at 2.24 ppm. The isopropyl group protons exhibited two distinct doublets at 1.33 and 1.20 ppm indicating that they are chemically non-equivalent.

The mass spectral analysis of the ligand showed a prominent ion peak as $[M+H]^+$ at *m/z* 279.1655 (Figure 3).

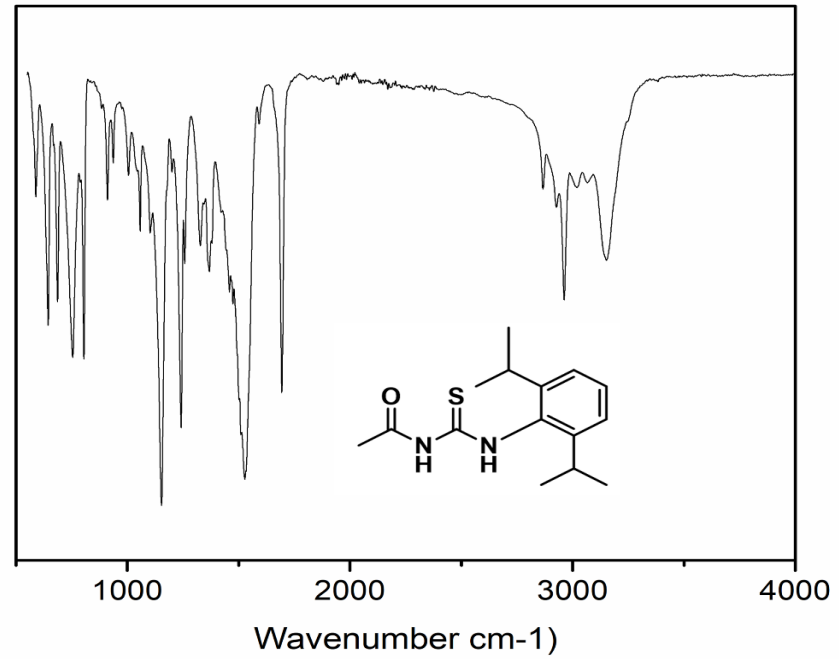


Figure :1 IR spectra of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

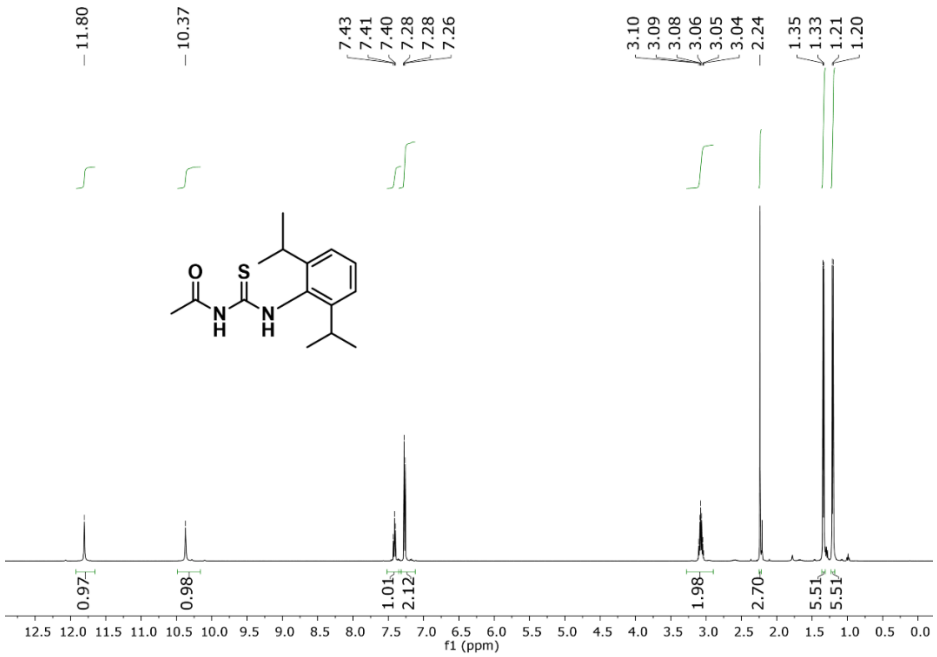


Figure 2: ^{1}H NMR spectra of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

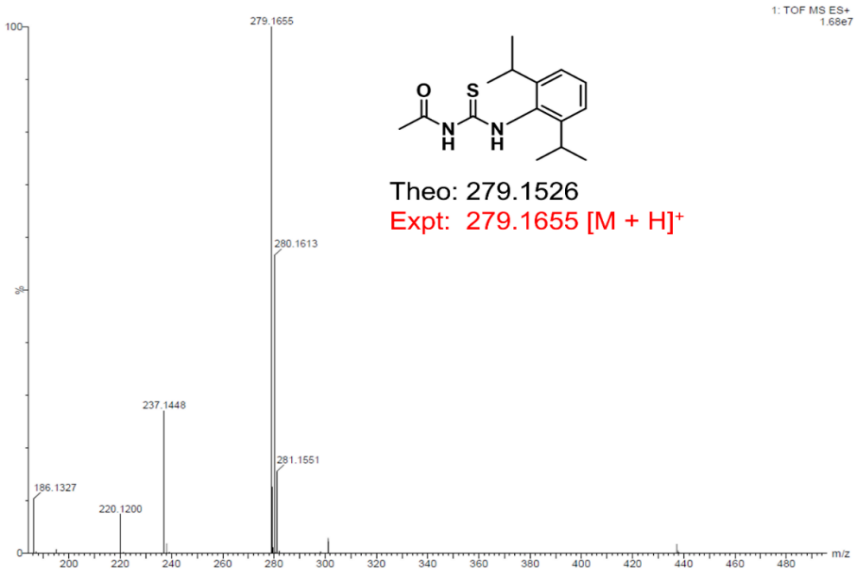


Figure 3: ESI-MS spectra of N-((2,6-diisopropylphenyl)carbamothioyl)acetamide (L)

IR studies of p-cymene Ru(II) and benzene Ru(II) complexes

Preliminary IR studies of the ruthenium compounds suggested the formation of the complexes where the frequencies due to $\nu_{(N-H)}$ and $\nu_{(C-H)}$ were observed around 2961-3150 cm^{-1} and for $\nu_{(C=O)}$ it was present around 1698–1699 cm^{-1} whereas for thioamidic $\nu_{(C=S)}$ it was observed around 1213–1218 cm^{-1} respectively. The presence of $\nu_{(N-H)}$ band confirms that it is not involved in coordination with the ruthenium ion which is further confirmed by ^{1}H-NMR analysis. As it can be seen the band due to $\nu_{(C=O)}$ was almost unaltered but the band corresponding to $\nu_{(C=S)}$ stretching frequencies decreased and was observed in the region 1213-1218 cm^{-1}. This decrease of (C=S) stretching frequency and the presence of an unaltered C=O band suggest the coordination of the sulfur atom to the ruthenium ion [24]. The IR spectra of the complexes are shown in (Figures 4 and 5).

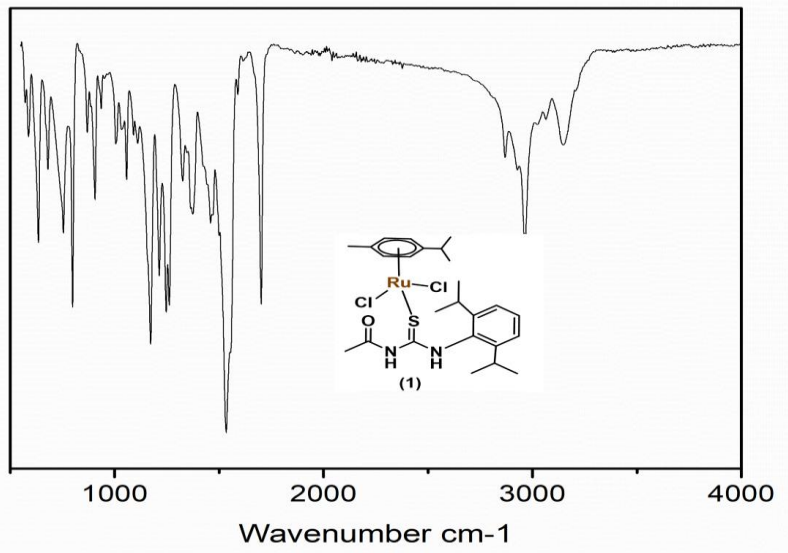


Figure 4: IR spectra of complex (**1**)

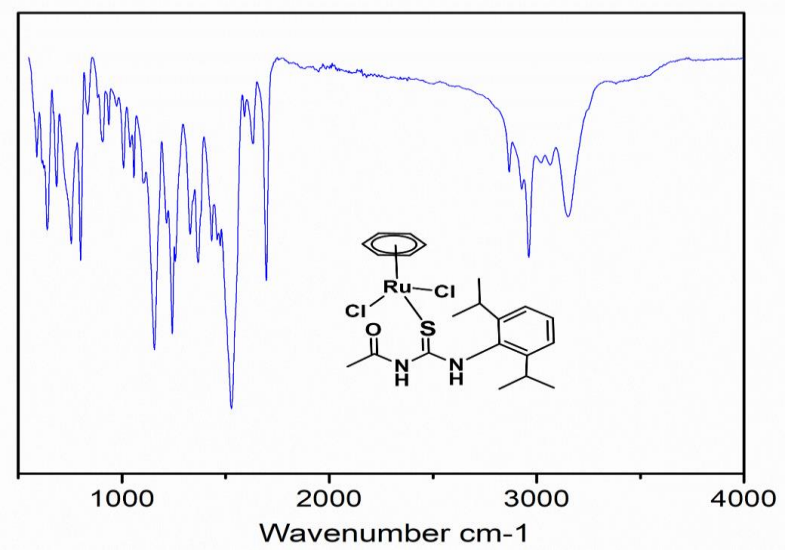


Figure 5: IR spectra of complex (**2**)

[1]H-NMR studies of p-cymene Ru(II) and benzene Ru(II) complexes

NMR studies of the ruthenium complexes further ascertained the coordination of the ligand to the ruthenium ion where the proton signals from the *p*-cymene ligand, coordinated benzene as well as the ligand protons were observed. In these complexes the thioamide and amide N-H protons signals were observed as a singlet between 11.18-11.71 ppm and the appearance of these signals confirms that these are not involved in bonding to ruthenium and are in good agreement with the IR studies which confirmed the presence of N-H stretching frequency, also the amide signal is observed at downfield region indicating the coordination of sulfur to metal [30]. The aromatic proton signals were almost unaltered as compared to the ligand and were observed as a doublet, triplet, and multiplet in the region around 7.09-7.44 ppm. A multiplet was observed in the region between 2.88-2.96 ppm for the methine protons of the iso-propyl group of the ligand and a singlet for the methyl protons of the ligand around 2.14-2.15 ppm. And the methyl protons of the iso-propyl group were observed as two distinct doublets for both these complexes in the region around 1.06-1.23 ppm. Also, signals associated with the aromatic protons of the *p*-cymene ring in complex (**1**) were observed as two doublets at 5.08 and 5.23 ppm [29-31]. And the methine and methyl proton resonances of the *p*-cymene group were observed as multiplet in the region 2.77-2.84 ppm and as a singlet at 2.12 ppm. In benzene Ru(II) complexes in addition to ligand proton signals the presence of a peak at 5.52 ppm is due to the protons of the coordinated benzene ring. Overall, the NMR studies confirm the coordination of the ligand and formation of the complexes which are shown in (Figures 6 and 7).

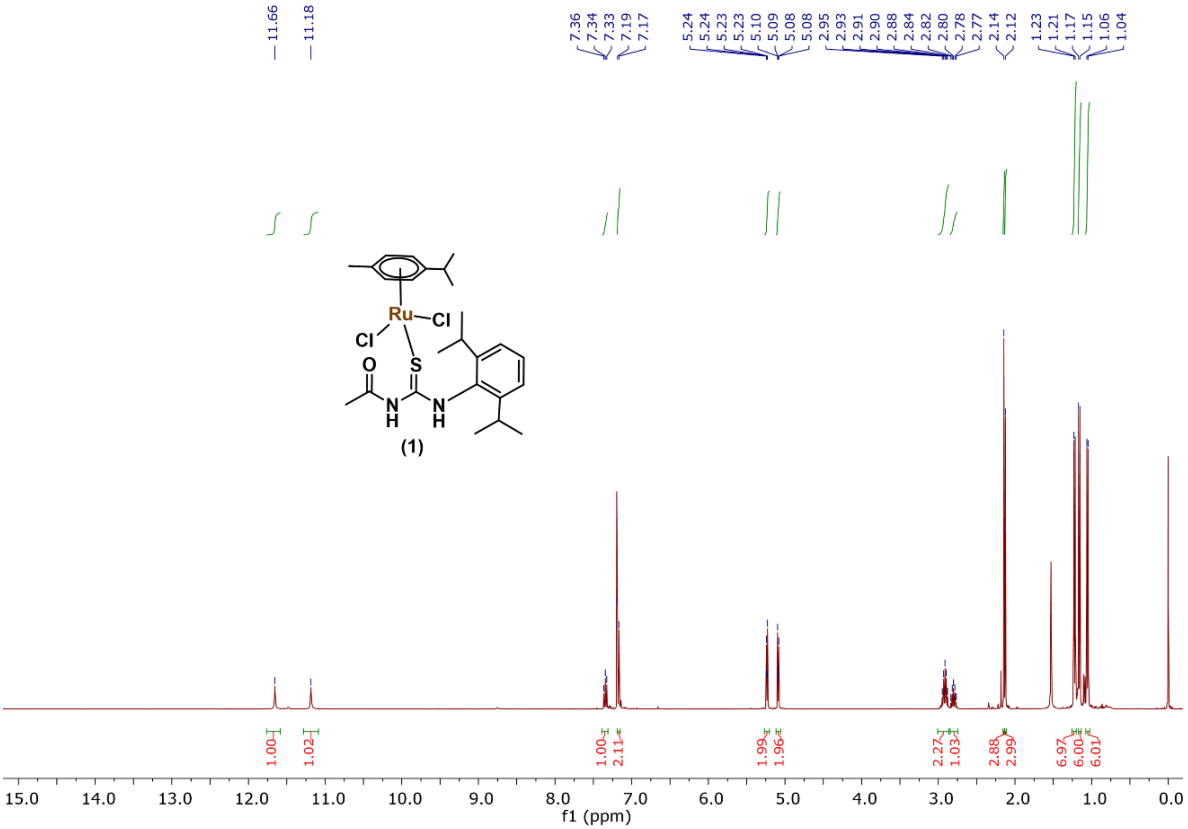


Figure 6: ^{1}H NMR spectra of complex (**1**)

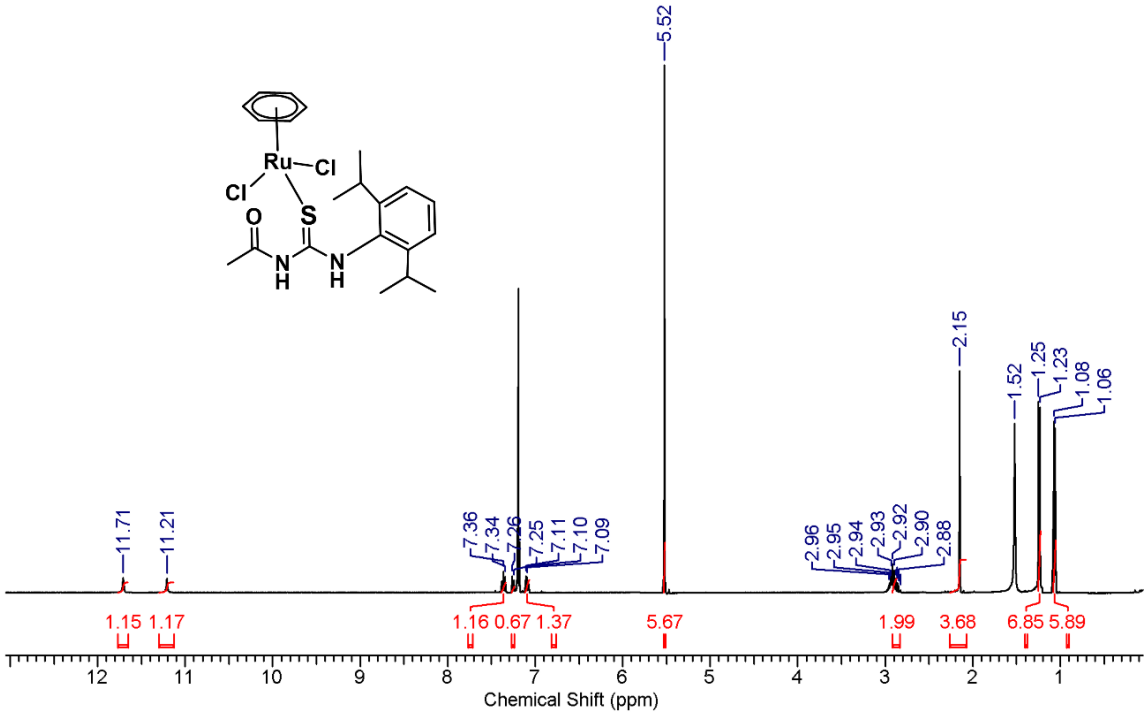


Figure 7: ^{1}H NMR spectra of complex (**2**)

Mass spectra of complexes

The ESI-MS analysis of the complexes also confirmed the composition and formation of the complexes. In general, most arene Ru(II) complexes having monodentate thiourea derivatives coordination show the common ion peak formed after the loss of two (N-H) hydrogens and two chlorides from the molecule which was also observed in these complexes. The ESI-MS spectra of complex (**1**) showed a molecular ion peak at *m/z* value 513.1474 and for complex (2) it showed a peak at *m/z* 457.0816 corresponding to $[M-2H^{+}-2Cl^{-}+H^{+}]^{+}$ fragment as shown in (Figures 8 and 9)

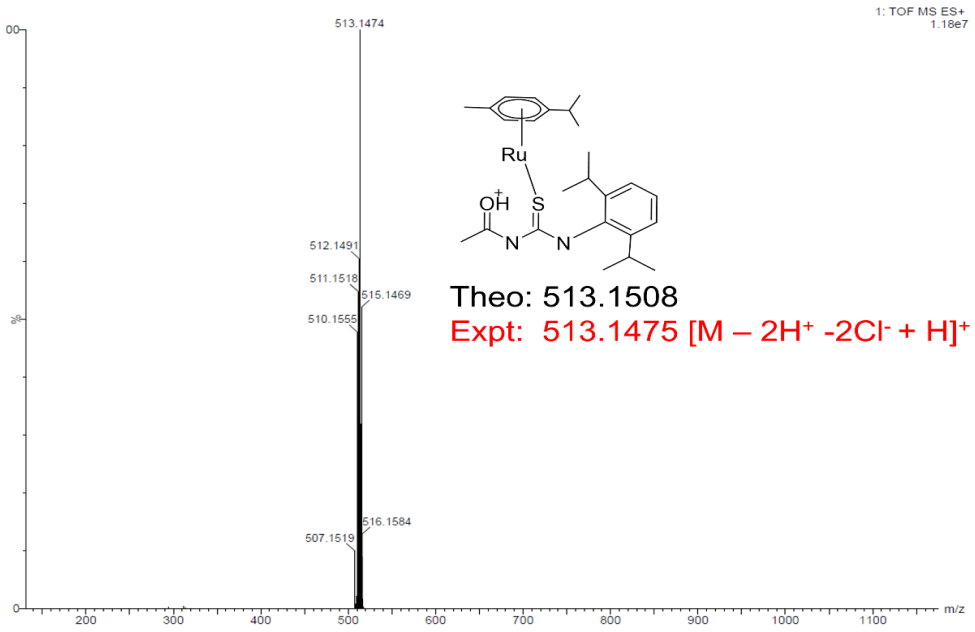


Figure 8: ESI-MS of complex (**1**)

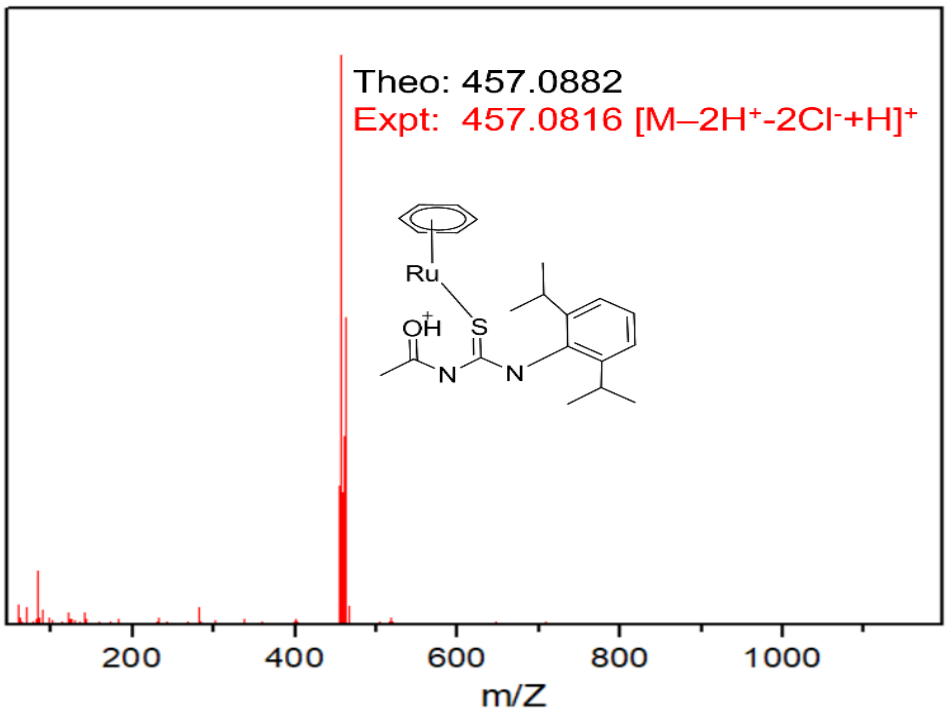


Figure 9: ESI-MS of complex (**2**)

Comparison of UV-Vis spectra of ligand (L) and ruthenium complexes

The electronic spectrum of (L) showed a band around 271-277 nm and a shoulder around 318-320 nm which were characteristics of π-π* and n-π* transition. The absorption spectra of the complexes were recorded in acetonitrile which further confirmed the formation of the complexes. One band appeared in the region 275-276 nm which is due to the ligand-based transition and an extra broad band around 442-445 nm was observed which is due to the *d* → *d* transition (Figure 10) [31].

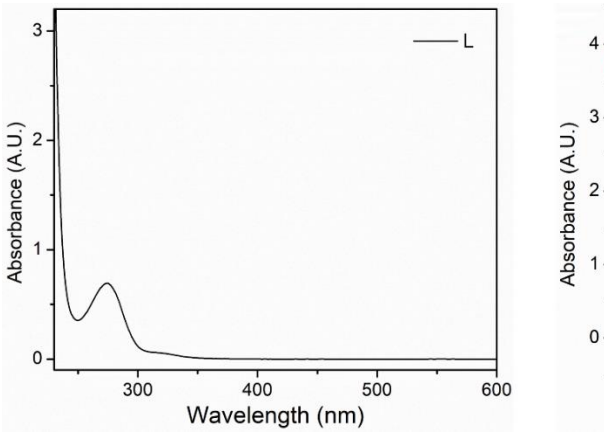


Figure 10: Comparison of UV-Vis spectra of Ligand (L) and ruthenium complexes.

Antibacterial Activity against S. aureus:

Screening novel classes of compounds for the development of new antibacterial medications is currently a primary goal to tackle the growing threat of drug-resistant problems. This is because there is serious worry that dangerous bacteria are becoming resistant to the antibacterial medications that are prescribed by doctors. The synthesized two complexes [Ru(η^6-*p*-cymene)(L)$\kappa^1_{(S)}$Cl$_2$] (**1**) and [Ru(η^6-benzene)(L)$\kappa^1_{(S)}$Cl$_2$] (**2**) showed for In vitro antibacterial activities for a preliminary evaluation. Their antibacterial activity was tested against *S. aureus* as Gram (+) using spot assay. All the complexes showed moderate antibacterial activities against *S. aureus* as shown in table 2. The value is comparable with the reference drug, Ciprofloxacin, see Table 2. These values offer an understanding of additional antibacterial activity optimization that may help create a series of derivatives and, perhaps, in the creation of new antibacterial drug inventions in the future.

Table 2: Antibacterial activity of complex (**1-2**), MIC (µg/mL)

S.NO.	Compound	*S. aureus*
1	**1**	55
2	2	58
5	**Ciprofloxacin**	17.25

Conclusion:

In this work, we report the synthesis of a bulky thiourea ligand which was used to synthesize *p*-cymene Ru and benzene Ru complexes. All these compounds were characterized by IR, ESI-MS, UV-Vis, and NMR studies. These spectroscopic results confirm the formation of the complexes and the complexes were isolated as neutral complexes. Evidence collected from spectroscopic analysis confirms that the mode of coordination of the ligand to the ruthenium is through the thione sulfur which maintains a three legged piano-stool geometry. The complexes (**1-2**) were screened In vitro antibacterial activities against S. aureus and showed moderate antibacterial activity with MIC values, 55 µg/mL, 58 µg/mL, respectively.

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