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Synthesis, Characterization And Antimicrobial Study of Pd(II) and Pt(II) complexes of 4-methyl-5-Imidazolecarboxaldehyde Thiosemicarbazone

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Abstract

Schiff bases are regarded as "privileged ligands" due to their capability to form complexes with a wide range of transition metal ions yielding stable and intensely colored metal complexes. In this study, equimolar amounts of 4-methyl-5-imidazolecarboxaldehyde and thiosemicarbazide were combined and the Schiff base 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone was prepared as a new bidentate complexing agent. The synthesized ligand was reacted with palladium (II) and platinum (II) ions yielding air-stable complexes. For characterization purpose, mass spectra and x-ray analysis of the ligand and infrared spectra, electronic spectra, thermal analysis, proton nuclear magnetic resonance and 13-carbon nuclear magnetic resonance spectra studies were carried out on the obtained ligand and its complexes. The characterization data showed that the ligand acts as a bidentate coordinate to the metal ions through azomethine nitrogen and sulfur atom. An *in vitro* antimicrobial investigation was also carried out for the free ligand and its metal complexes against four bacteria; *Bacillus cereus*, *Staphylococcus aureus* (Gram-positive), *Escherichia coli* and *Salmonella typhimurium* (Gram-negative) and one Fungi; *Candida albicans*. The results showed that the antimicrobial activity of the prepared complexes showed higher activity than the free ligand.

Keywords: Thiosemicarbazone, Schiff Base, metallic complexes, characterization,antibacterial activity.

1. INTRODUCTION

Schiff base compounds and their metal complexes have been extensively investigated due to their wide range of applications including catalysts [1, 2], medicine [3, 4] crystal engineering [5], anti-corrosion agent [6, 7]. Schiff bases are studied widely due to their synthetic flexibility, selectivity and sensitivity towards the central metal ions; structural similarities with natural biological compounds and also due to presence of azomethine group (-N=CH-) which imports in elucidating the mechanism of transformation and racemization reaction biologically [8]. Schiff bases having chelation with oxygen, nitrogen etc. donors and their complexes have been used as drugs and reported to possess a wide variety of biological activities against bacteria, fungi, and certain type of tumors and also, they have many biochemical, clinical and pharmacological properties [9-12]. Imine or azomethine groups are present in various natural compounds, naturally derived and non natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities [13, 14].

The present work is related to synthesis, characterization, antibacterial and antifungal activity of Pd(II) and Pt(II) complexes of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone.

2. EXPERIMENTAL

2.1. Materials and measurements

All chemicals and solvents of the highest analytical grade were used as received from Sigma-Aldrich and Alfa-Aesar. The melting points of the synthesized compounds were determined by a capillary melting point apparatus. Mass spectrum of the ligand was carried out on Esquire LC-00084 electronic spray ionization (ESI) Mass spectrometer. Infrared spectra of the ligand and its metal complexes were recorded on Vertex-183387000 FT-IR spectrometer by using KBr disk in the range 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR spectra of the ligand and its metal complexes were recorded on a Bruker AV-III 600 operating at 600 MHz for ^{1}H and 150 MHz for ^{13}C by using DMSO-*d*6 as a solvent. UV-Vis spectra in solid state were recorded on a Cary-EL05123055 4000 UV-Vis spectrophotometer

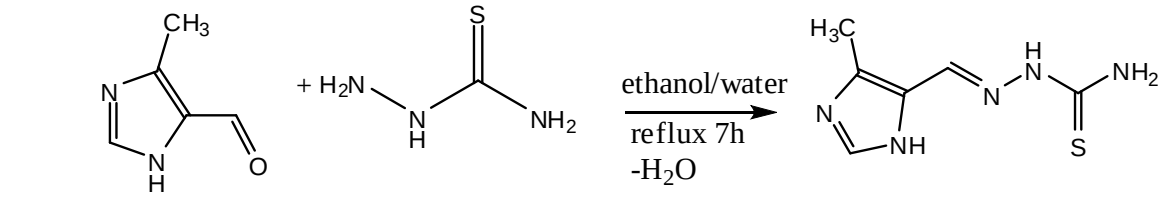
in the range 200-800 nm. Thermal analysis was carried out using DTA/TG HIGH RG2/S thermal analyzer. All measurements were carried out at technical University of Dresden, Germany.

2.2. Synthesis

2.2.1. Synthesis of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone ligand (4-Me-5-ITSC)

Equimolar amount of thiosemicarbazide (910mg, 0.001 mol) and 4-methyl-5-imidazolecarboxaldehyde (110 mg, 0.001 mol) were dissolved in 20 mL of ethanol:water (60:40, v:v) and refluxed for 7 h in an oil bath at 78 °C. The solution was allowed to cool at room temperature and left for slow solvent evaporation. After several days pale yellow crystals were obtained. The crystals were separated, washed with cold ethanol and dried under vacuum (Scheme 1)

Color: Pale yellow. Yield: 67%. M.p.: 203°C. FT-IR (KBr, ν, cm-1): 3429, 3271 (NH_2)**;** 3134 (NH)**;** 1598 (C=N)**;** 850 (C=S)**;** 1101 (N-N). ^{1}H NMR (600 MHz, DMSO-*d*6, δ, ppm): 2.2 (s, 3H, CH_3), 7.2-7.7 (s, 2H, NH_2), 12.3 (s, 1H, NH), 11..3 (s, 2H, HN2), 8.1 (s, 1H, =N-NH), 7.9 (s, 2H, HC_{ring}). ^{13}C NMR; δ=9.05 (CH_3); 131.35-136.34 (2Cq ring); 130.41(C-H ring), 134.82 (HC=N); 177.38 (C=S). Ms (ESI.m/z): M^- 184.2; Analysis for $C_6H_9N_5S$ (Mw 183.24). UV-Vis spectrum (λmax, nm): 318.



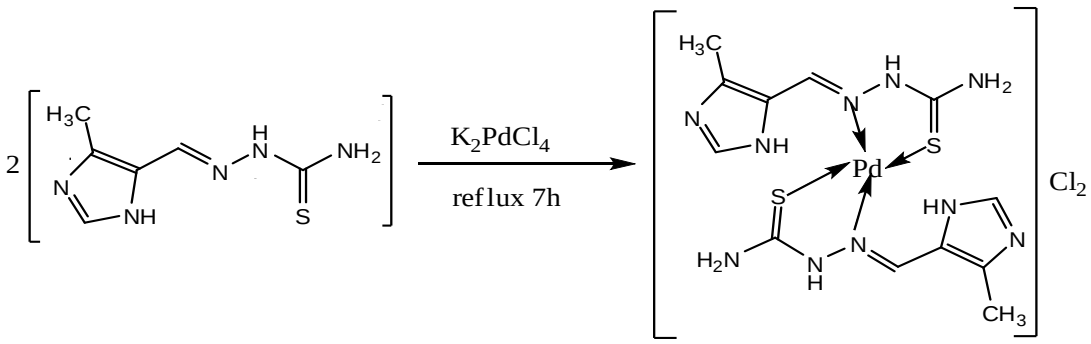
4-methyl-5-imidazolecarboxaldehyde Thiosemicarbazide 4-methyl-5-imidazolecarboxaldehyde Thiosemicarbazone

Scheme 1: Preparation of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone (4-Me-5-ITSC)

2.2.2. Synthesis of $[Pd(4\text{-}Me\text{-}5\text{-}ITSC)_2]Cl_2$

K_2PdCl_4 (16.32mg, $5.0x10^{-5}$mol) was dissolved in hot ethanol, and then mixed with a hot ethanolic solution containing 18.3 mg ($1.0x10^{-4}$ mol) of 4-Me-5-ITSC. The mixture was refluxed for 7 h at 78°C in an oil bath and then allowed to cool at room temperature and left for slow solvent evaporation for several days. The colored precipitate was filtered off, washed with cold ethanol and dried in air and a vacuum oven (Scheme 2).

Color: Orange. Yield: 81%. M.p: 253 °C. FT-IR (KBr, *v*, cm^{-1}); 3402, 3290 (NH_2); 3119 (NH); 1619; (C=N); 803 (C=S) ; 1093 (N-N). NMR spectrum (600 MHz for ^{1}H and 151 MHz for ^{13}C, DMSO-d_6, ppm): ^{1}H NMR; δ=2.4 (s, 6H, CH_3); 7.9 (s, 2H, CH ring), 7.2-7.8 (s, 4H, NH_2), 9.2(s, 2H, HC=N); 11.7 (s, 2H, NH), 13.3 (s, 2H, NH); ^{13}C NMR; δ=9.76 (CH_3); 127.83-134.65 (2Cq ring); 124.56 (C-H ring), 138.88(HC=N); 181.57 (C=S). UV-Vis spectrum (λ_{max} nm): 225, 288, 390.



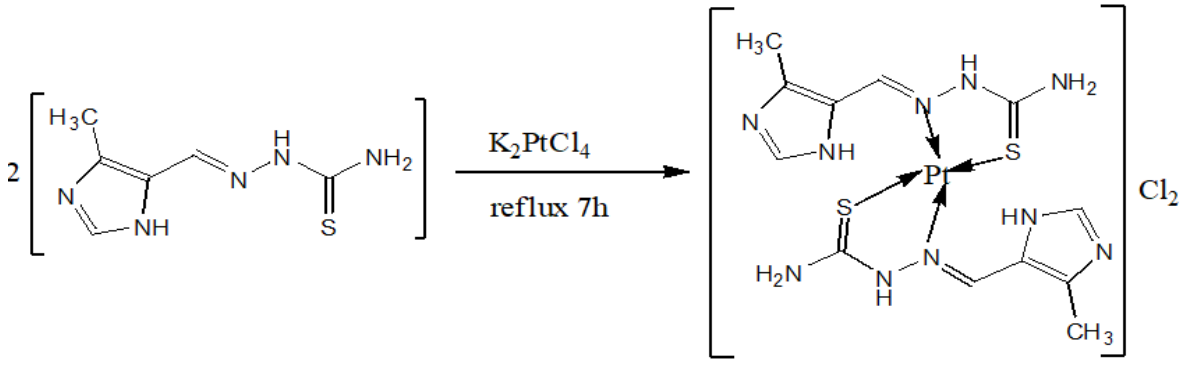
Scheme 2: Preparation of Pd(II) complex of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone

2.2.3. Synthesis of $[Pt(4\text{-}Me\text{-}5\text{-}ITSC)_2]Cl_2$

K_2PtCl_4 (20.75mg, $5.0x10^{-5}$mol) was dissolved in hot ethanol, and then mixed with a hot ethanolic solution containing 18.3 mg ($1.0x10^{-4}$ mol) of 4-Me-5-ITSC. The mixture was refluxed for 7 h at 78 °C in an oil bath and then allowed to cool at room temperature and left for slow solvent evaporation for several days. The colored precipitate was filtered off, washed with cold ethanol and dried in air and a vacuum oven (Scheme 3).

Color: yellow. Yield: 72%. M.p: 230 °C. FT-IR (KBr, *v*, Cm^{-1}); 3400, 3273 (NH_2); 3161 (NH); 1612 *v*(C=N); 803 (C=S); 1109 (N-N). NMR spectrum (600 MHz for ^{1}H and 151 MHz for ^{13}C, DMSO-d_6, ppm): ^{1}H NMR; δ 2.4 (3H, s, CH_3); 8.1 (1H, CH ring), 7.2-7.7(2H, s, NH_2), 9.3(1H, s, HC=N); 12.6 (1H, s, NH),

13.6(1H, s, NH); ^{13}C NMR; δ=9.79 (CH_3); 127.83-134.65 (2Cq ring); 124.57(C-H ring), 137.17 (HC=N); 178.38(C=S). UV-Vis spectrum (λ_{max} nm): 226, 336, 444.



Scheme 3: Preparation of Pt(II) complex of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone

2.3. Antimicrobial activity

2.3.1. Antifungal screening

Preliminary antifungal screenings of the prepared compounds at different concentrations were performed. Potato dextrose agar medium was prepared by using potato dextrose agar and distilled water. Appropriate amount of the compounds in DMSO was added to potato dextrose agar medium in order to get a concentration of 100 and 200 µg/mL of compound in the medium.

The medium was poured into a set of two Petri plates under aseptic conditions in a laminar flow hood. When the medium in the plates was solidified, a mycelial disc of 0.5 cm in diameter was cut from the periphery of the seven days old culture and it was aseptically inoculated upside down in the center of the Petri plates. These treated Petri plates were incubated at 26±1 °C until fungal growth in the control Petri plates was almost complete. The mycelial growth of fungi (mm) in each Petri plate was measured [15].

2.3.2. Antibacterial screening

The paper disc diffusion method was used to screen the antibacterial activity of the prepared compounds and performed by using Mueller Hinton agar (MHA) [15]. The ligand and its complexes were carried out according to the National Committee for Clinical Laboratory Standards Guidelines. Bacterial suspension was diluted with sterile physiological solution to 108 cfu/mL (Turbidity = McFarland standard 0.5). One hundred micro-liters of bacterial suspension were swabbed uniformly on the surface of Mueller Hinton agar and the inoculum was allowed to dry for 5 minutes. Sterilized filter paper discs (Whatman No. 1, 6 mm in diameter) were placed on the surface of the MHA and soaked with 20 µL of a solution of each sample. The inoculated plates were incubated at 37 °C for 24 h in the inverted position. The diameters (mm) of the inhibition zones were measured [15].

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

The synthesis of ligand containing an imidazole ring is outlined in Scheme 1 and the corresponding palladium (II) and platinum (II) complexes were shown in Scheme 2 and 3. In the first step the ligand was synthesized by condensing equimolar quantities of thiosemicarbazide and 4-methyl-5-imidazolecarboxaldehyde in ethanol: water mixture. In the second step, the prepared ligand was refluxed with metal:salt in 1:2 M ratio, to obtain the desired complexes. The obtained compounds were characterized by UV-Vis, FTIR, ^{1}H NMR, ^{13}C NMR, and thermogravimetric analyses and Mass spectrometry and x-ray analysis for the ligand was also investigated. Some physical characteristics of the ligand and its corresponding metal complexes are given in experimental section.

In the IR spectra, the absorption peaks at 3429 and 3271 cm^{-1} are assigned to ν(NH_2). The absorption peak at 3134 cm^{-1} is assigned to ν(N-H). In both complexes, the presence of a band in the region (3119 and 3161 cm-1) corresponds to NH vibration, which indicates that the ligand is coordinated in the neutral form. The strong band observed at 1598 cm^{-1} in the free ligand has been assigned to *ν*(C=N) stretching vibrations [16]. On complexation, this bands were observed to be shifted to higher frequencies (1619-1612 cm-1). These results indicate that the imine nitrogen is coordinated to the metal ion. The ligand showed a medium band at 850 cm^{-1} ascribed to *ν*(C=S) vibrations. These absorption bands shift to lower and higher frequencies on the coordination of the thiocarbonyl sulfur to palladium (II) or platinum (II) ions. These results agree with other thiosemicarbazone Complexes[17]. In addition, the vibrational frequencies of the NH_2 groups remain unchanged for the ligand and metal complexes. This evidence indicates the noncoordination of the NH_2 group on the metal ion [17].

The electronic spectra of 4-Me-5-ITSC, showed that a strong absorption band at 318 nm. This band assigned to $\pi \rightarrow \pi^*$ transition of the azomethine group [18]. The intra-ligand transitions for Pd (II) complex were observed at 225, 288, 290 nm and for Pt (II) complex was observed in 226, 336, 444 nm and these bands are mainly due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [17].

The electrospray ionization mass spectra (ESI-Mass) of the synthesized thiosemicarbazone; 2-((4-methyl-1-imidazol-5-yl)methylene)hydrazine-1-carbothioamide shows molecular ion (M^-) peak at *m/z* 181.7a.m.u corresponding to the species $[C_6H_9N_5S]^-$ confirming the empirical formula of the synthesized thiosemicarbazone.

The ^1H and ^{13}C NMR spectra and chemical shift values of the ligand and corresponding metal complexes were record in DMSO-*d6* solvent. The ^1H NMR of 4-ITSC ligand and its metal complexes show signal at δ 11.3, 11.7, and 12.6 ppm have been assigned to δ(NHCS)protons and the signals at δ 7.2, 7.7 and 7.8 ppm have been assigned to δ(CSNH2) protons. The signals at δ 8.1, 9.2, and 9.3 ppm assignable to azomethine protons (CH=N). The downfield chemical shift in the spectra of Pd (II) and Pt (II) complexes indicated the coordination through the azomethine nitrogen to the metal atom resulting in the formation of a coordinate N→M linkage and all imidazole ring protons were observed in the expected regions [19].

The ^{13}CNMR spectra revealed the presence of an expected number of signals corresponding to different types of carbon atoms present in the compounds. The spectra of the Schiff base ligand exhibit a strong band at δ 177.38 ppm due to (C=S) group. In the complex formation, the position of this band undergoes an up-field shift to δ 181.57 and 178.38 ppm. This indicates that sulphur is involved in coordination (S→M linkage) [17].

The ligand crystallized with two molecule per asymmetric unit into Triclinic crystal system with a space group of *P*1. The structure reveals that the ligand exists in the thione form. S1 and N3 atoms are At trans postion (E- configuration) [19] to each other with respect to the N2—C1 bond (Figure 1). This is confirmed by the torsion angle of −174.82 (10) of the S1—C1—N2—N3 moiety, which is close to that for a series of thiosemicarbazone derivatives torsion angles −179.5, 179.2, −178.7, −177.01, 5.86, 178.25, and −177.95 [20], thus, the N1 atom lies in trans postion to N3. The thione form in the solid state is strongly confirmed by the observed bond lengths: C1—S1 [1.6941 (16)Å] and C1—N2 [1.3450 (16) Å]. The C1—S1 distance of 1.6941 (16)Å is closer to the C=S bond length [1.62 Å] than to the C—S bond length [1.81 Å], and the C1—N2 distance of 1.3450 (16)Å is in the range of 1.349(6)—1.386(4) Å for other thiosemicarbazones having the C—N single bond reported earlier [21].

Table 1: Crystal data and structure refinement for ligasnd; [4-Me-5-ITSC]

Identification	**4-Me-5-ITSC**
Empirical formula	$C_6H_9N_5S$
Formula weight	183.24
Temperature/K	200(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.6796(4)
b/Å	9.7120(4)
c/Å	12.0578(5)
α/°	111.258(2)
β/°	102.668(2)
γ/°	100.979(2)
Volume/Å^3	882.53(7)
Z	4
ρ_{calc}g/cm^3	1.379
μ/mm^{-1}	0.319
F(000)	384.0
Crystal size/mm^3	0.139 × 0.108 × 0.097
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.82 to 61.416
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	28276
Independent reflections	5439 [R_{int} = 0.0352, R_{sigma} = 0.0328]
Data/restraints/parameters	5439/0/232
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0833
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.0948
Largest diff. peak/hole / e Å^{-3}	0.36/-0.27

Table 2: Selected bond lengths (Å), bond angles and torsion angle (°) of the ligand; [4-Me-5-ITSC]

Compound	Bond lengthÅ	Torsion angles
4-Me-5-ITSC	Atom atom length	Atom atom atom atom angle (°)
	S1 C1 1.6941 (16)	N3 N2 C1 S1 −174.82 (10)
	N1 C1 1.3212 (18)	
	N2 C1 1.3450 (16)	

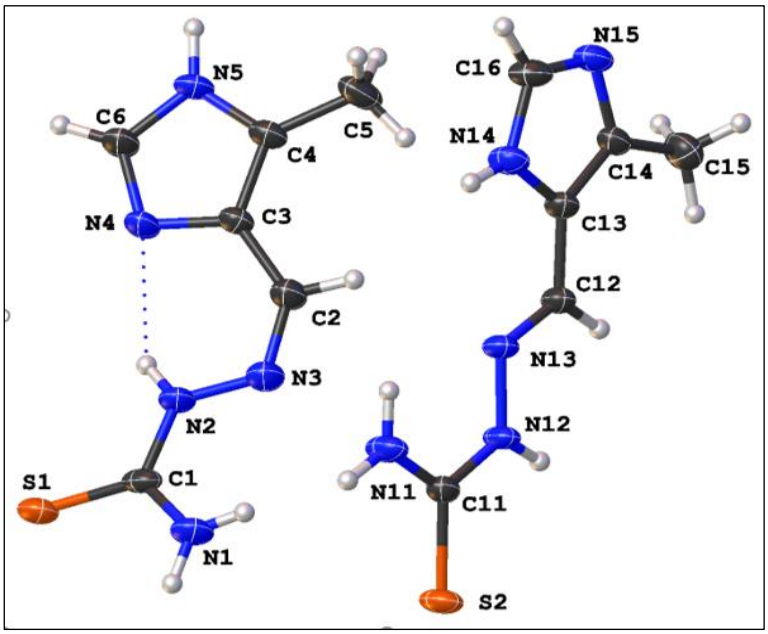


Figure 1: X-ray structure of 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone (4-Me-5-ITSC)

3.2. Thermal analysis (DTA and TG) of Pd(II) and Pt(II) complexes

Generally, not much was known about the thermal properties of transition metal complexes of imidazolecarboxaldehydethiosemicarbazones. The thermal behavior of the Pd(II) and Pt(II) complexes of the synthesized imidazole-carboxaldehyde thiosemicarbazones were studied under argon atmosphere using thermal analyzer (DTA-TG). The thermal decomposition of the complexes was recorded from ambient temperature to 1000°C. The results showed that the complexes, generally decomposed in several thermal events (decomposition steps). The complexes loss moisture around 100 °C, and then started to decompose at a temperature above this limit. The total weight loss around 1000 °C is nearly 70-80% and this equals the loss of two moles of ligand in agreement with the proposed metal:ligand ratio of 1:2 of the complex. The remaining weights correspond to the metallic residue.

Table 3: Thermoanalytical results (DTA-TG) of 4-Me-5-ITSC and its Pd(II) and Pt(II) complexes

Complexes	TG (°C) Range	DTA (°C) Range	Mass loss %*	Total mass loss %*	Metallic residue %*
$[Pd(4\text{-Me-5-ITSC})_2]Cl_2$	30-900	102(-) 621(-)	03.64, 17.31, 06.75 05.16,10.44,07.7628.06	79.12 (80.43)	Pd 20.93(19.56)
$[Pt(4\text{-Me-5-ITSC})_2]Cl_2$	30-870	563(-) 837(-)	04.58, 10.45, 11.93, 11.70, 08.64, 06.30 06.60, 03.84, 06.15	70.19 (69.15)	Pt 29.81(30.84)

* DTA:(-)), exothermic Mass loss: Found(Calculated).

3.3. Antimicrobial activity

The synthesized compounds were screened, *in vitro* for their antibacterial activity against four pathogenic bacteria; *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhimurium* and one fungi; *Candida albicans* at a concentration of 100 and 200 µg/mL with DMSO as the solvent. The results showed that the tested compounds possess moderate antimicrobial activity against most of the tested organisms.

Table 4: Antimicrobial activity of synthesized thiosemicarbazone a its complexes.

Compounds	Con. µg /mL	Diameter of inhibition zone (mm)				
		B. cereus	***S. aureus***	***E. coli***	***S. typhi***	***C. Albicans***
4-Me-5-ITSC	100	10	11	10	07	00
	200	11	12	11	10	08
$[Pd(4\text{-Me-5-ITSC})_2]Cl_2$	100	11	13	18	10	10
	200	13	14	13	13	11
$[Pt(4\text{-Me-5-ITSC})_2]Cl_2$	100	11	13	13	12	08
	200	12	15	20	11	10

Supplementary data

Appendix-1: Crystallographic Information Files (CIF)

Crystallographic data of Ligand (4-Me-5-ITSC)

Geometry

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2) for (4-Me-5-ITSC).

H-atom positions were not refined or were subject to constraints (Warning: refine-ls-hydrogen-treatment reports mixed) The following H sites were not refined or were subject to constraints: H14N, H12N, H11B, H11A, H5N, H2N, H1B, H1A, H16, H15F, H15E, H15D, H15C, H15B, H15A, H12, H6, H5C, H5B, H5A, H2

	X	Y	Z	Uiso*/Ueq	Occ. (<1)
C1	−0.29579 (18)	0.88085 (16)	0.45931 (14)	0.0284 (3)	
C2	0.04313 (19)	0.74746 (17)	0.53033 (14)	0.0327 (3)	
H2	0.1342 (16)	0.7674 (4)	0.6063 (13)	0.039*	
C3	0.04873 (17)	0.63706 (16)	0.41427 (13)	0.0262 (3)	
C4	0.16603 (17)	0.55981 (16)	0.40100 (14)	0.0282 (3)	
C5	0.3096 (2)	0.5594 (2)	0.49383 (16)	0.0443 (4)	
H5A	0.3104 (9)	0.4569 (11)	0.4756 (8)	0.066*	
H5B	0.3016 (8)	0.6059 (14)	0.5748 (9)	0.066*	
H5C	0.4080 (11)	0.6152 (14)	0.4899 (8)	0.066*	
C6	−0.0048 (2)	0.50319 (18)	0.21702 (15)	0.0346 (3)	
H6	−0.0541 (9)	0.4581 (9)	0.1285 (17)	0.042*	
C11	0.09746 (17)	1.12054 (16)	0.87446 (12)	0.0256 (3)	
C12	0.33102 (17)	0.86678 (16)	0.87880 (13)	0.0270 (3)	
H12	0.2831 (9)	0.8224 (8)	0.9275 (9)	0.032*	
C13	0.46086 (17)	0.81790 (15)	0.83535 (12)	0.0257 (3)	
C14	0.53327 (17)	0.70718 (16)	0.84637 (13)	0.0273 (3)	
C15	0.4959 (2)	0.6019 (2)	0.90706 (16)	0.0396 (4)	
H15A	0.558 (3)	0.529 (2)	0.890 (2)	0.059*	0.33 (2)
H15B	0.3800 (15)	0.548 (3)	0.874 (2)	0.059*	0.33 (2)
H15C	0.526 (3)	0.6612 (8)	0.9958 (11)	0.059*	0.33 (2)
H15D	0.418 (3)	0.629 (2)	0.950 (2)	0.059*	0.67 (2)
H15E	0.5956 (13)	0.611 (2)	0.966 (2)	0.059*	0.67 (2)
H15F	0.450 (3)	0.4973 (13)	0.8444 (8)	0.059*	0.67 (2)
C16	0.65625 (19)	0.81130 (17)	0.74741 (15)	0.0336 (3)	
H16	0.7310 (14)	0.8357 (5)	0.7037 (8)	0.040*	
N1	−0.25541 (16)	1.00392 (14)	0.56661 (12)	0.0348 (3)	
H1A	−0.1673 (12)	1.0241 (3)	0.6259 (8)	0.042*	
H1B	−0.3173 (8)	1.0636 (8)	0.5770 (2)	0.042*	
N2	−0.19340 (15)	0.79218 (14)	0.44922 (12)	0.0308 (3)	
H2N	−0.2096 (4)	0.7193 (16)	0.3826 (14)	0.037*	
N3	−0.06069 (16)	0.82456 (15)	0.55175 (12)	0.0342 (3)	
N4	−0.05964 (15)	0.59873 (14)	0.29615 (11)	0.0313 (3)	
N5	0.12971 (15)	0.47655 (14)	0.27599 (12)	0.0308 (3)	

	X	Y	Z	Uiso*/Ueq	Occ. (<1)
H5N	0.1854 (11)	0.4145 (12)	0.2389 (7)	0.037*	
N11	0.16370 (16)	1.17973 (15)	0.80704 (12)	0.0354 (3)	
H11A	0.2416 (11)	1.1479 (5)	0.7799 (4)	0.043*	
H11B	0.1297 (5)	1.2508 (10)	0.7896 (3)	0.043*	
N12	0.15496 (15)	1.01174 (14)	0.89823 (11)	0.0294 (3)	
H12N	0.1145 (8)	0.9687 (9)	0.9417 (9)	0.035*	
N13	0.27882 (14)	0.96966 (14)	0.85268 (11)	0.0279 (3)	
N14	0.54111 (15)	0.88248 (14)	0.77134 (12)	0.0305 (3)	
H14N	0.5221 (4)	0.9519 (15)	0.7514 (5)	0.037*	
N15	0.65547 (15)	0.70473 (14)	0.79022 (12)	0.0310 (3)	
S1	−0.46630 (5)	0.82882 (5)	0.33564 (4)	0.03500 (11)	
S2	−0.05557 (5)	1.17515 (5)	0.92748 (4)	0.03493 (11)	

Atomic displacement parameters (Å2) for (4-Me-5-ITSC)

	U11	U22	U33	U12	U13	U23
C1	0.0346 (7)	0.0307 (7)	0.0373 (8)	0.0210 (6)	0.0247 (6)	0.0199 (6)
C2	0.0342 (8)	0.0357 (8)	0.0306 (7)	0.0199 (6)	0.0107 (6)	0.0116 (6)
C3	0.0268 (7)	0.0269 (7)	0.0304 (7)	0.0159 (5)	0.0115 (6)	0.0127 (6)
C4	0.0267 (7)	0.0273 (7)	0.0354 (7)	0.0152 (6)	0.0123 (6)	0.0134 (6)
C5	0.0355 (9)	0.0499 (10)	0.0471 (10)	0.0282 (8)	0.0082 (7)	0.0151 (8)
C6	0.0410 (8)	0.0366 (8)	0.0313 (8)	0.0269 (7)	0.0127 (6)	0.0115 (6)
C11	0.0279 (7)	0.0272 (7)	0.0241 (6)	0.0155 (6)	0.0101 (5)	0.0089 (5)
C12	0.0308 (7)	0.0310 (7)	0.0275 (7)	0.0185 (6)	0.0148 (6)	0.0134 (6)
C13	0.0291 (7)	0.0263 (7)	0.0262 (7)	0.0155 (6)	0.0122 (5)	0.0103 (5)
C14	0.0285 (7)	0.0293 (7)	0.0266 (7)	0.0169 (6)	0.0090 (5)	0.0102 (6)
C15	0.0457 (9)	0.0434 (9)	0.0445 (9)	0.0254 (8)	0.0179 (7)	0.0265 (8)
C16	0.0330 (8)	0.0332 (8)	0.0430 (9)	0.0178 (6)	0.0218 (7)	0.0155 (7)
N1	0.0391 (7)	0.0326 (7)	0.0396 (7)	0.0240 (6)	0.0191 (6)	0.0123 (6)
N2	0.0366 (7)	0.0337 (6)	0.0292 (6)	0.0246 (5)	0.0154 (5)	0.0111 (5)
N3	0.0389 (7)	0.0370 (7)	0.0311 (6)	0.0233 (6)	0.0144 (5)	0.0113 (5)
N4	0.0356 (7)	0.0337 (6)	0.0301 (6)	0.0250 (5)	0.0117 (5)	0.0114 (5)
N5	0.0324 (6)	0.0312 (6)	0.0361 (7)	0.0221 (5)	0.0166 (5)	0.0126 (5)
N11	0.0450 (7)	0.0408 (7)	0.0462 (8)	0.0314 (6)	0.0301 (6)	0.0278 (6)
N12	0.0351 (7)	0.0368 (7)	0.0342 (6)	0.0259 (5)	0.0226 (5)	0.0201 (5)
N13	0.0311 (6)	0.0328 (6)	0.0296 (6)	0.0212 (5)	0.0172 (5)	0.0136 (5)
N14	0.0359 (7)	0.0279 (6)	0.0400 (7)	0.0196 (5)	0.0205 (6)	0.0176 (5)
N15	0.0303 (6)	0.0318 (6)	0.0349 (6)	0.0187 (5)	0.0140 (5)	0.0114 (5)
S1	0.0369 (2)	0.0412 (2)	0.0386 (2)	0.02720 (17)	0.01969 (16)	0.01715 (17)
S2	0.0375 (2)	0.0404 (2)	0.0461 (2)	0.02805 (17)	0.02646 (17)	0.02325 (18)

Geometric parameters (Å, º) for (L_1)

C1—N1	1.3212 (18)	C13—N14	1.3764 (18)
C1—N2	1.3450 (16)	C14—N15	1.3772 (18)
C1—S1	1.6941 (16)	C14—C15	1.485 (2)
C2—N3	1.2878 (17)	C15—H15A	0.958 (11)
C2—C3	1.4394 (19)	C15—H15B	0.958 (11)
C2—H2	0.999 (17)	C15—H15C	0.958 (11)
C3—C4	1.3785 (17)	C15—H15D	0.958 (11)
C3—N4	1.3951 (18)	C15—H15E	0.958 (11)
C4—N5	1.3549 (19)	C15—H15F	0.958 (11)
C4—C5	1.483 (2)	C16—N15	1.3130 (19)
C5—H5A	0.941 (10)	C16—N14	1.3434 (17)
C5—H5B	0.941 (10)	C16—H16	0.968 (18)
C5—H5C	0.941 (10)	N1—H1A	0.858 (12)
C6—N4	1.3127 (17)	N1—H1B	0.858 (12)
C6—N5	1.3491 (18)	N2—N3	1.3819 (17)

C6—H6	0.950 (17)	N2—H2N	0.817 (17)
C11—N11	1.3191 (18)	N5—H5N	0.898 (17)
C11—N12	1.3436 (17)	N11—H11A	0.874 (12)
C11—S2	1.6880 (13)	N11—H11B	0.874 (12)
C12—N13	1.2809 (17)	N12—N13	1.3741 (14)
C12—C13	1.4325 (18)	N12—H12N	0.870 (17)
C12—H12	0.962 (17)	N14—H14N	0.826 (17)
C13—C14	1.3761 (18)		
N1—C1—N2	116.98 (13)	H15A—C15—H15D	141.1
N1—C1—S1	124.37 (10)	H15B—C15—H15D	56.3
N2—C1—S1	118.65 (11)	H15C—C15—H15D	56.3
N3—C2—C3	130.26 (14)	C14—C15—H15E	109.5
N3—C2—H2	114.9	H15A—C15—H15E	56.3
C3—C2—H2	114.9	H15B—C15—H15E	141.1
C4—C3—N4	109.33 (12)	H15C—C15—H15E	56.3
C4—C3—C2	125.92 (13)	H15D—C15—H15E	109.5
N4—C3—C2	124.65 (12)	C14—C15—H15F	109.5
N5—C4—C3	105.76 (12)	H15A—C15—H15F	56.3
N5—C4—C5	122.17 (12)	H15B—C15—H15F	56.3
C3—C4—C5	132.06 (14)	H15C—C15—H15F	141.1
C4—C5—H5A	109.5	H15D—C15—H15F	109.5
C4—C5—H5B	109.5	H15E—C15—H15F	109.5
H5A—C5—H5B	109.5	N15—C16—N14	112.09 (13)
C4—C5—H5C	109.5	N15—C16—H16	124.0
H5A—C5—H5C	109.5	N14—C16—H16	124.0
H5B—C5—H5C	109.5	C1—N1—H1A	120.0
N4—C6—N5	112.12 (14)	C1—N1—H1B	120.0
N4—C6—H6	123.9	H1A—N1—H1B	120.0
N5—C6—H6	123.9	C1—N2—N3	119.95 (12)
N11—C11—N12	117.23 (12)	C1—N2—H2N	120.0
N11—C11—S2	122.17 (10)	N3—N2—H2N	120.0
N12—C11—S2	120.59 (11)	C2—N3—N2	115.98 (12)
N13—C12—C13	119.87 (13)	C6—N4—C3	104.81 (11)
N13—C12—H12	120.1	C6—N5—C4	107.98 (11)
C13—C12—H12	120.1	C6—N5—H5N	126.0
C14—C13—N14	105.83 (12)	C4—N5—H5N	126.0
C14—C13—C12	131.06 (13)	C11—N11—H11A	120.0
N14—C13—C12	123.11 (12)	C11—N11—H11B	120.0
C13—C14—N15	109.15 (13)	H11A—N11—H11B	120.0
C13—C14—C15	129.19 (13)	C11—N12—N13	118.84 (12)
N15—C14—C15	121.66 (12)	C11—N12—H12N	120.6
C14—C15—H15A	109.5	N13—N12—H12N	120.6
C14—C15—H15B	109.5	C12—N13—N12	116.68 (12)
H15A—C15—H15B	109.5	C16—N14—C13	107.08 (12)
C14—C15—H15C	109.5	C16—N14—H14N	126.5
H15A—C15—H15C	109.5	C13—N14—H14N	126.5
H15B—C15—H15C	109.5	C16—N15—C14	105.85 (11)
C14—C15—H15D	109.5		
N3—C2—C3—C4	−179.90 (16)	N5—C6—N4—C3	0.58 (18)
N3—C2—C3—N4	4.1 (3)	C4—C3—N4—C6	−0.65 (17)
N4—C3—C4—N5	0.48 (17)	C2—C3—N4—C6	175.89 (15)
C2—C3—C4—N5	−176.01 (14)	N4—C6—N5—C4	−0.30 (18)
N4—C3—C4—C5	179.08 (16)	C3—C4—N5—C6	−0.12 (17)
C2—C3—C4—C5	2.6 (3)	C5—C4—N5—C6	−178.89 (15)
N13—C12—C13—C14	−177.21 (15)	N11—C11—N12—N13	0.6 (2)
N13—C12—C13—N14	3.7 (2)	S2—C11—N12—N13	179.54 (10)
N14—C13—C14—N15	0.08 (16)	C13—C12—N13—N12	−179.52 (12)

C12—C13—C14—N15	−179.11 (14)	C11—N12—N13—C12	179.25 (13)
N14—C13—C14—C15	179.92 (15)	N15—C16—N14—C13	0.53 (18)
C12—C13—C14—C15	0.7 (3)	C14—C13—N14—C16	−0.36 (16)
N1—C1—N2—N3	5.1 (2)	C12—C13—N14—C16	178.92 (13)
S1—C1—N2—N3	−174.82 (10)	N14—C16—N15—C14	−0.47 (17)
C3—C2—N3—N2	3.7 (3)	C13—C14—N15—C16	0.23 (16)
C1—N2—N3—C2	−171.28 (14)	C15—C14—N15—C16	−179.62 (14)

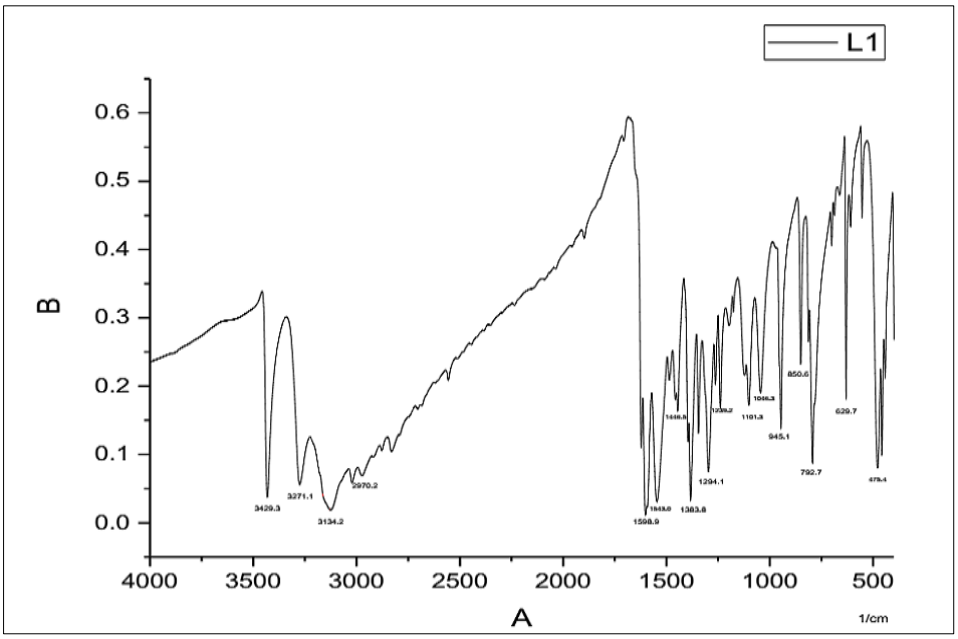


Figure 1: IR spectrum of the ligand (4-Me-5-ITSC)

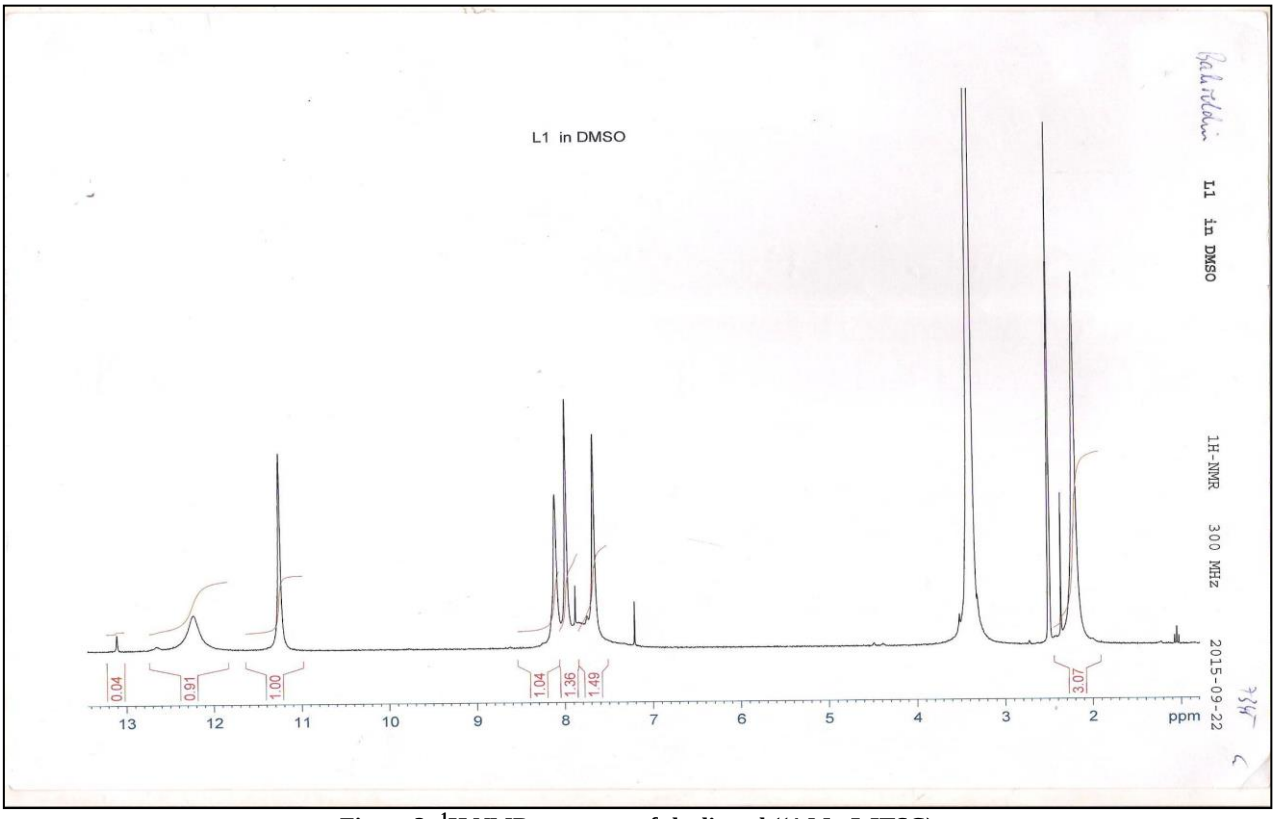


Figure 2: ^{1}H NMR spectrum of the ligand ((4-Me-5-ITSC)

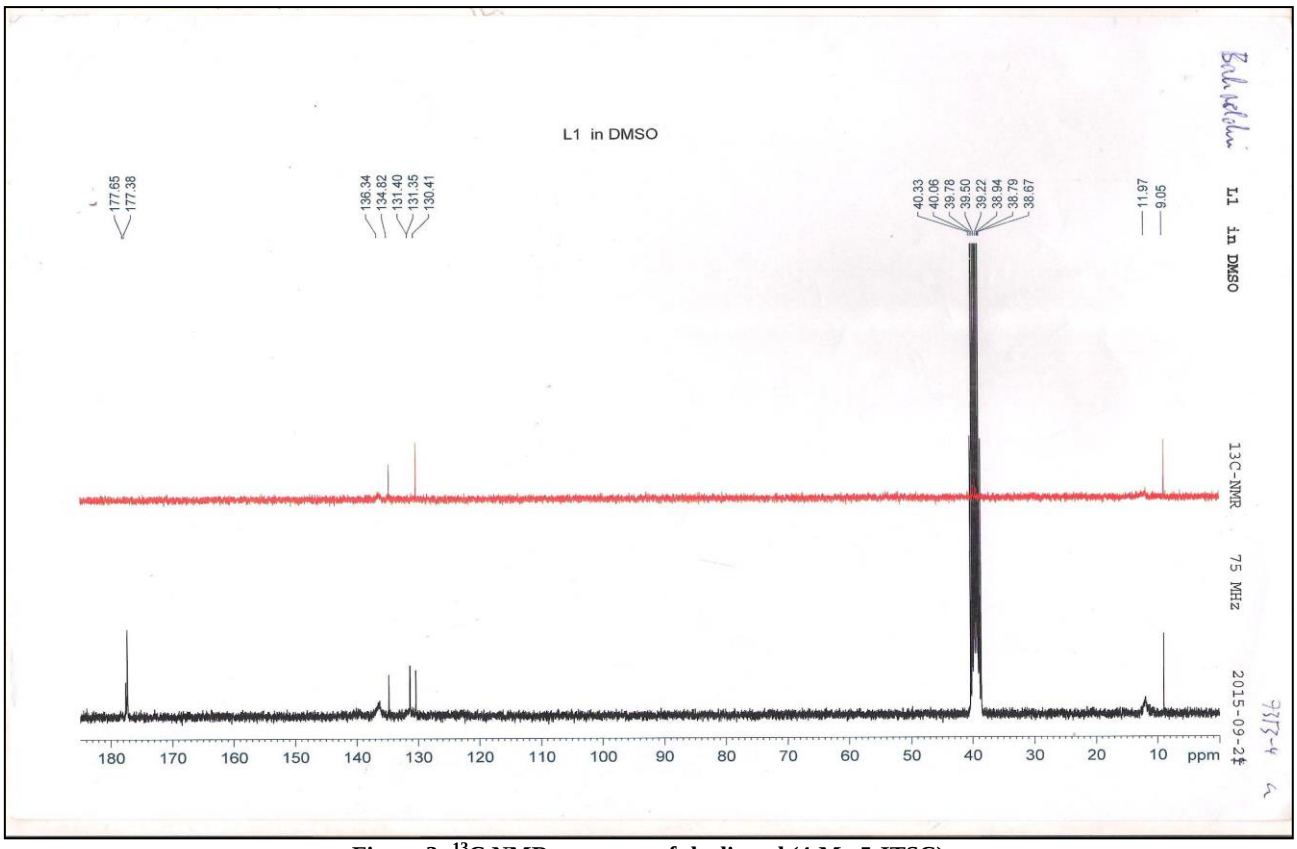


Figure 3: ^{13}C NMR spectrum of the ligand (4-Me-5-ITSC)

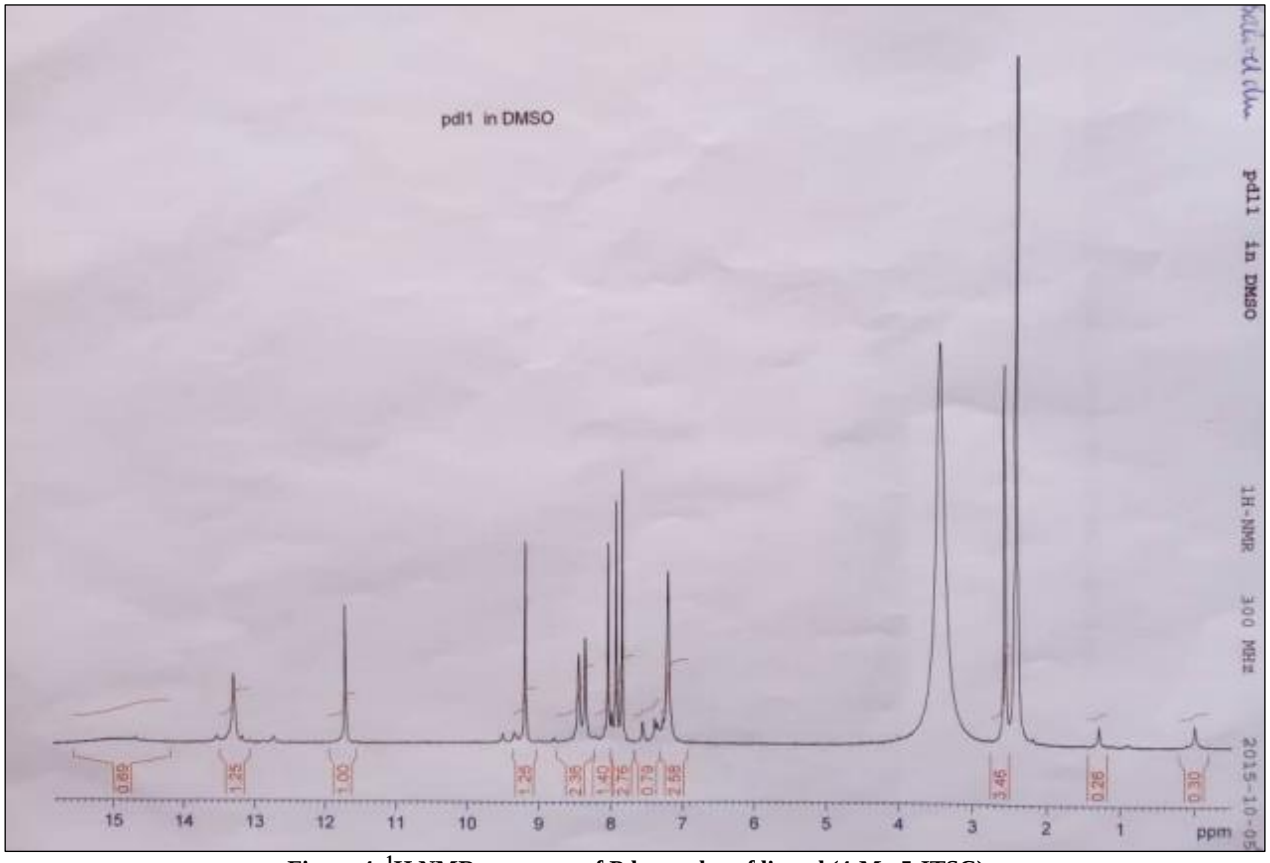


Figure 4: ^{1}H NMR spectrum of Pd complex of ligand (4-Me-5-ITSC)

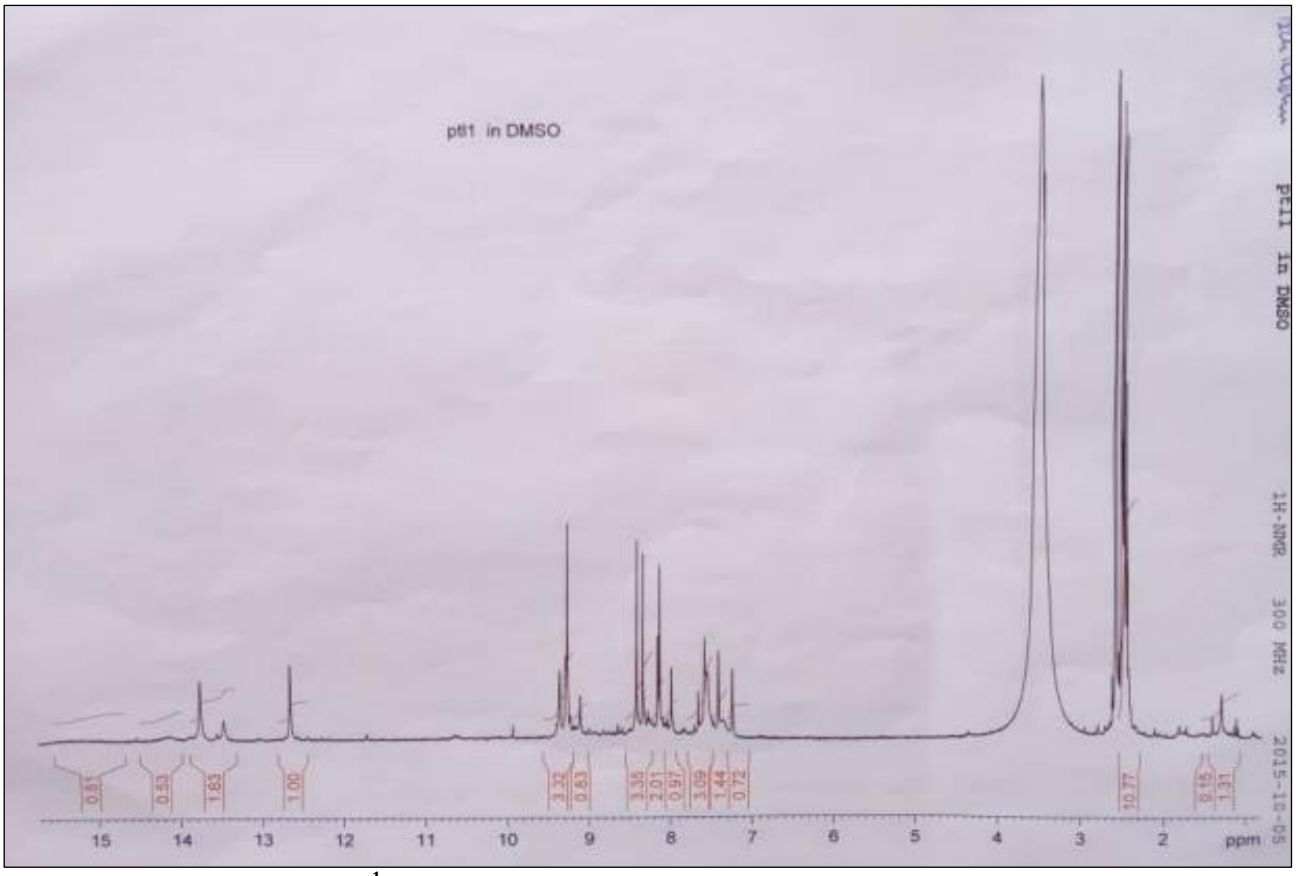


Figure 5: ^{1}H NMR spectrum of Pt complex of ligand (4-Me-5-ITSC)

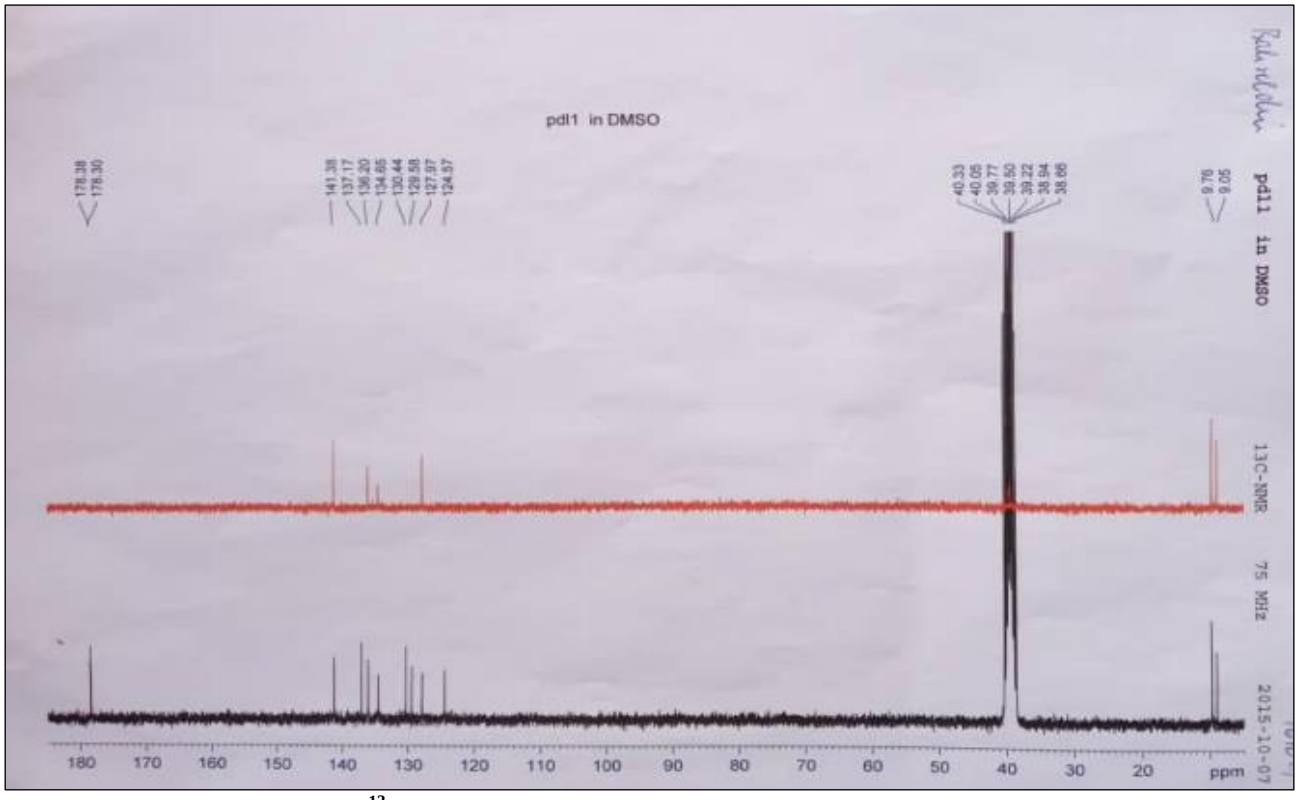


Figure 6: ^{13}C NMR spectrum of Pd complex of ligand (4-Me-5-ITSC)

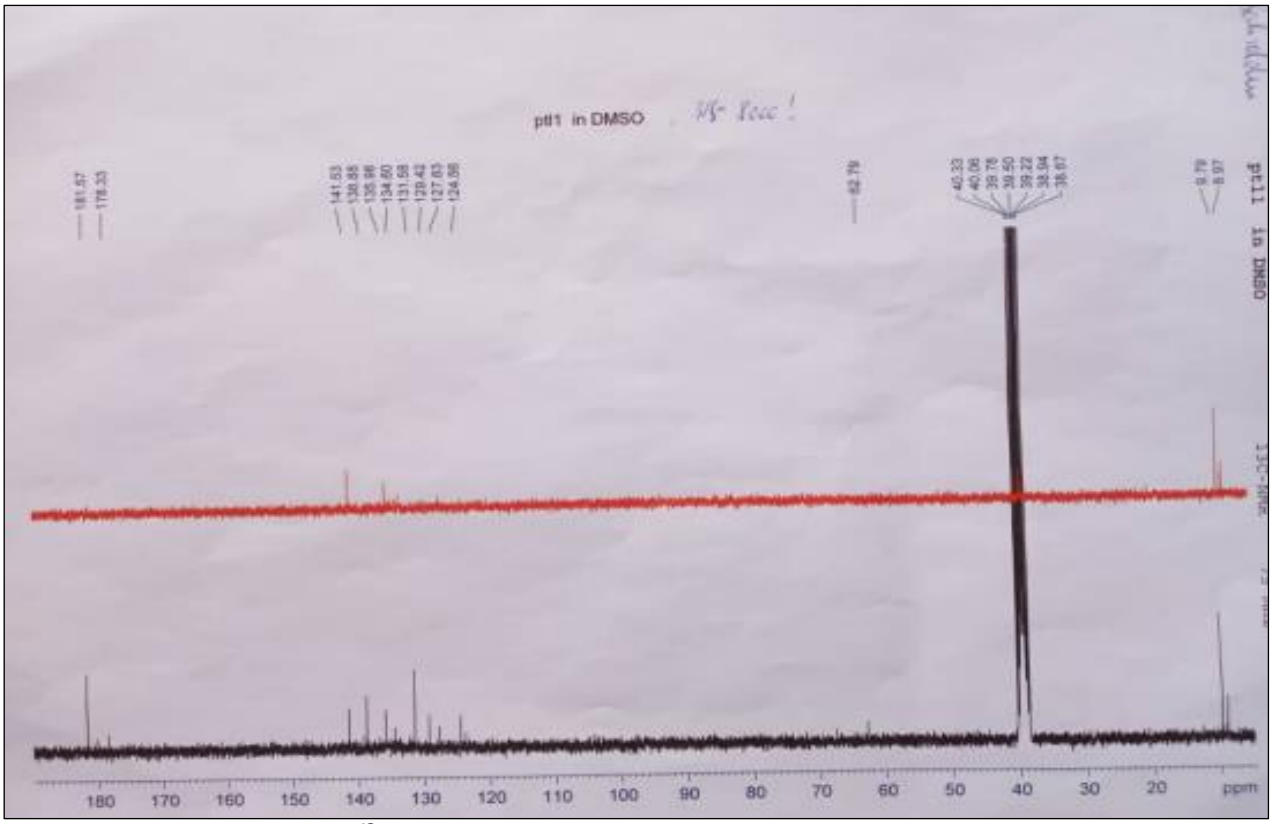


Figure 7: ^{13}C NMR spectrum of Pt complex of ligand (4-Me-5-ITSC)

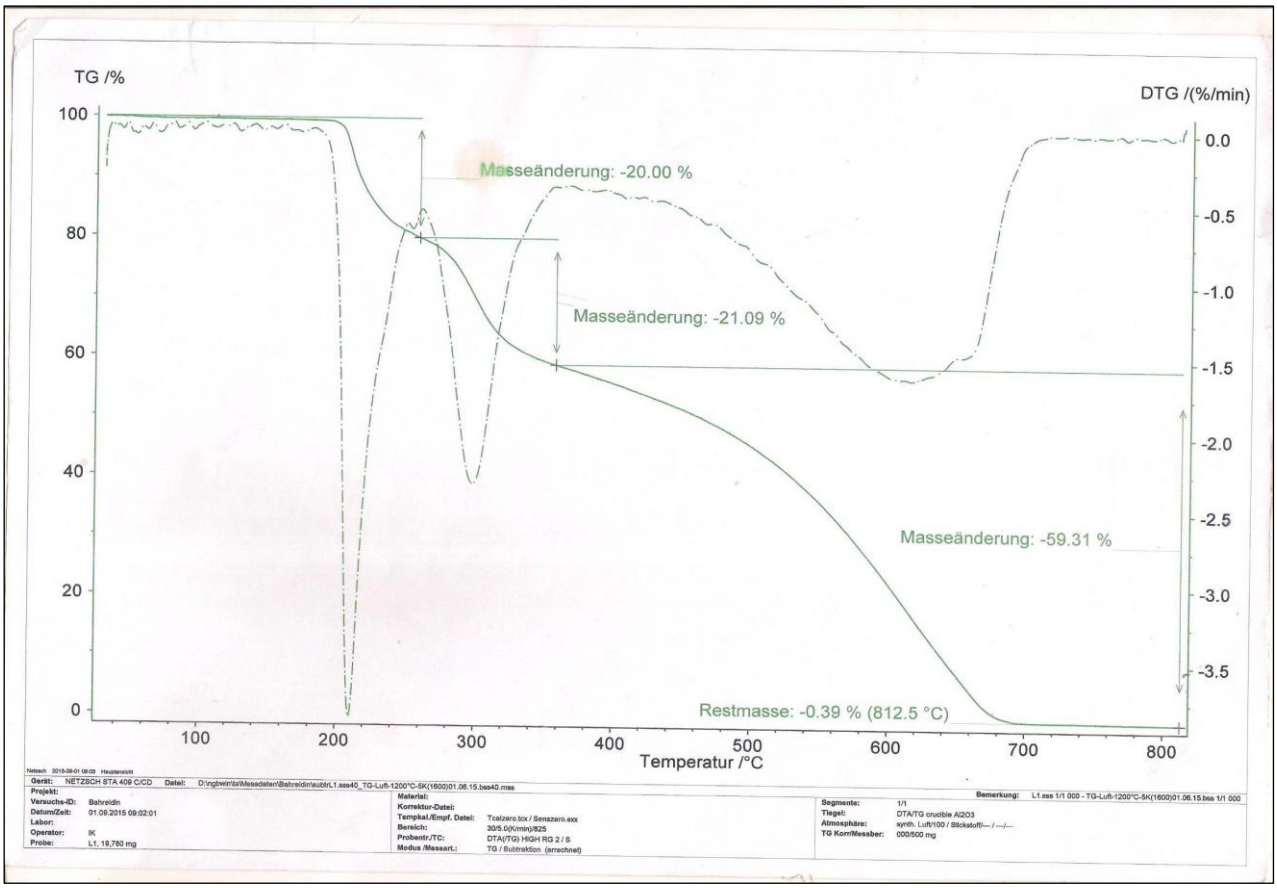


Figure 8: Thermogravimetric analysis curve of the ligand (4-Me-5-ITSC)

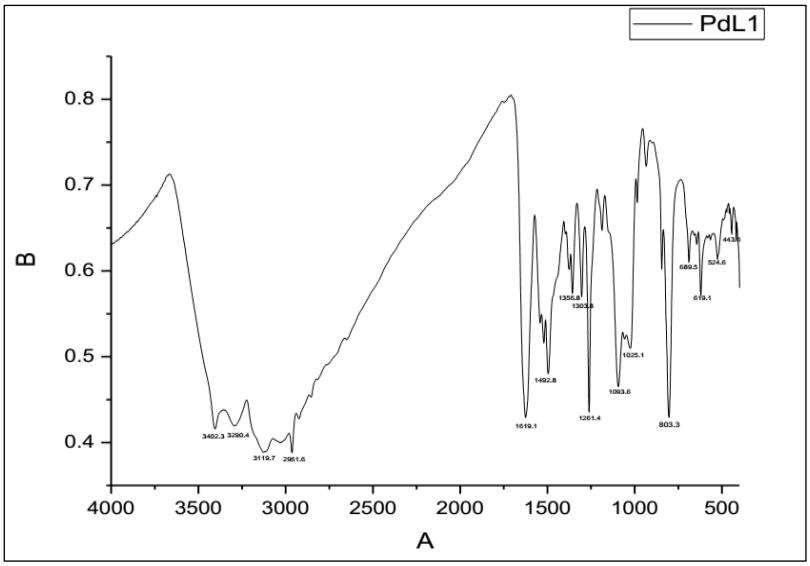


Figure 9: IR spectrum of the complex [Pd((4-Me-5-ITSC)$_2$]Cl$_2$

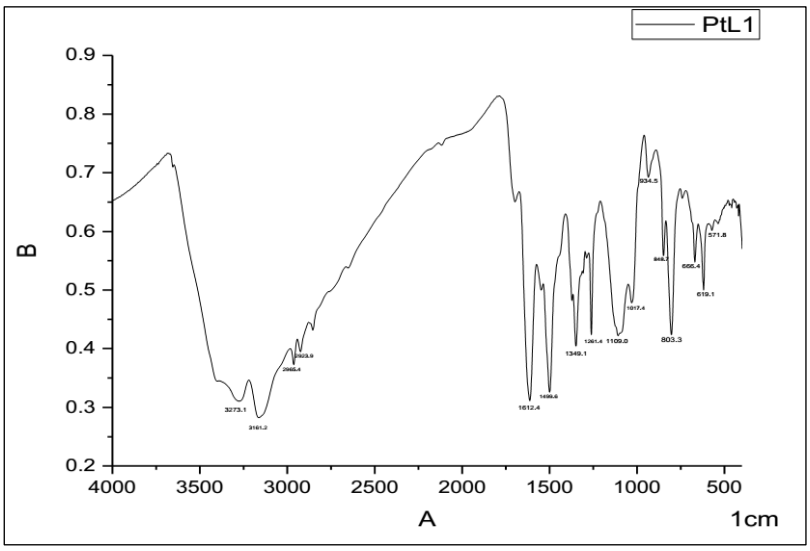


Figure 10: IR spectrum of the complex [Pt((4-Me-5-ITSC)$_2$]Cl$_2$

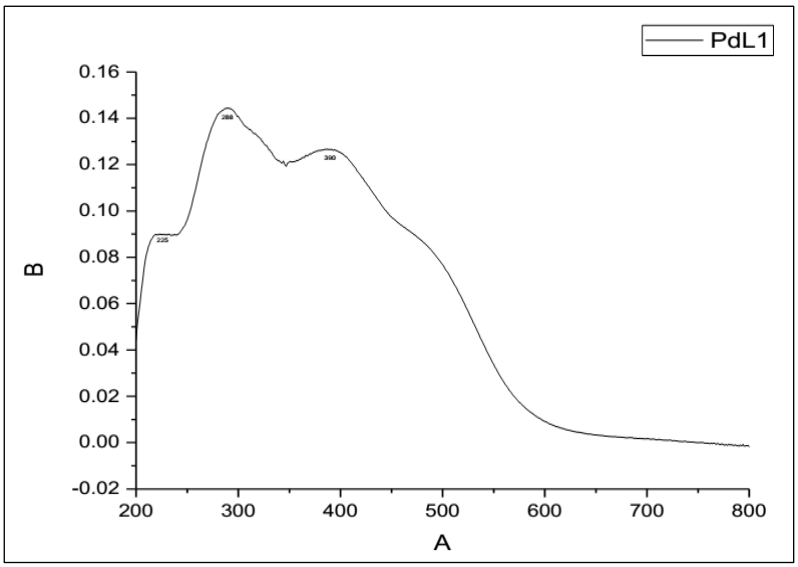


Figure 11: UV-Vis spectrum of the complex [Pd((4-Me-5-ITSC)$_2$]Cl$_2$

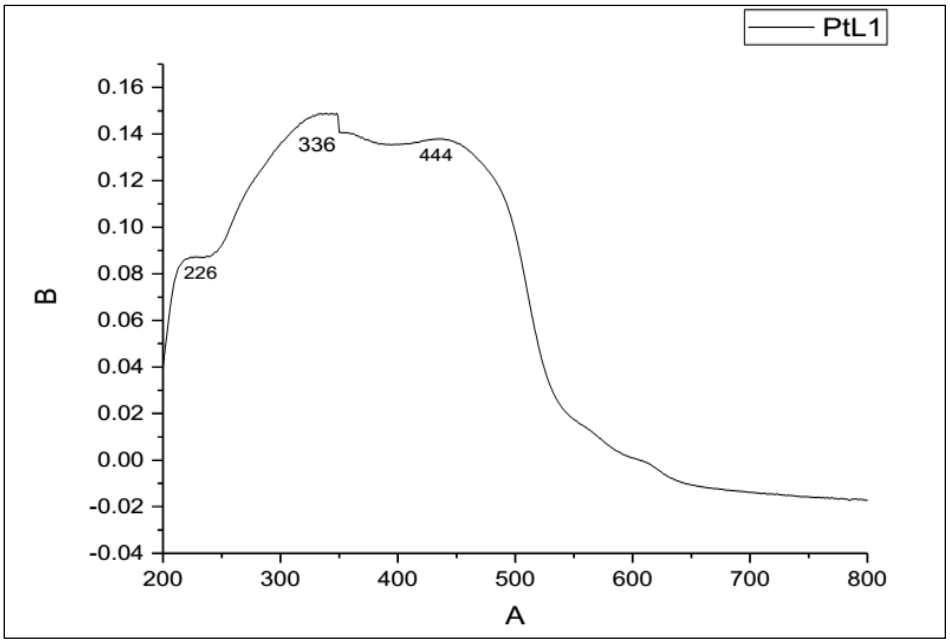


Figure 12: UV-Vis spectrum of the complex $[Pt((4\text{-Me-5-ITSC})_2]Cl_2$

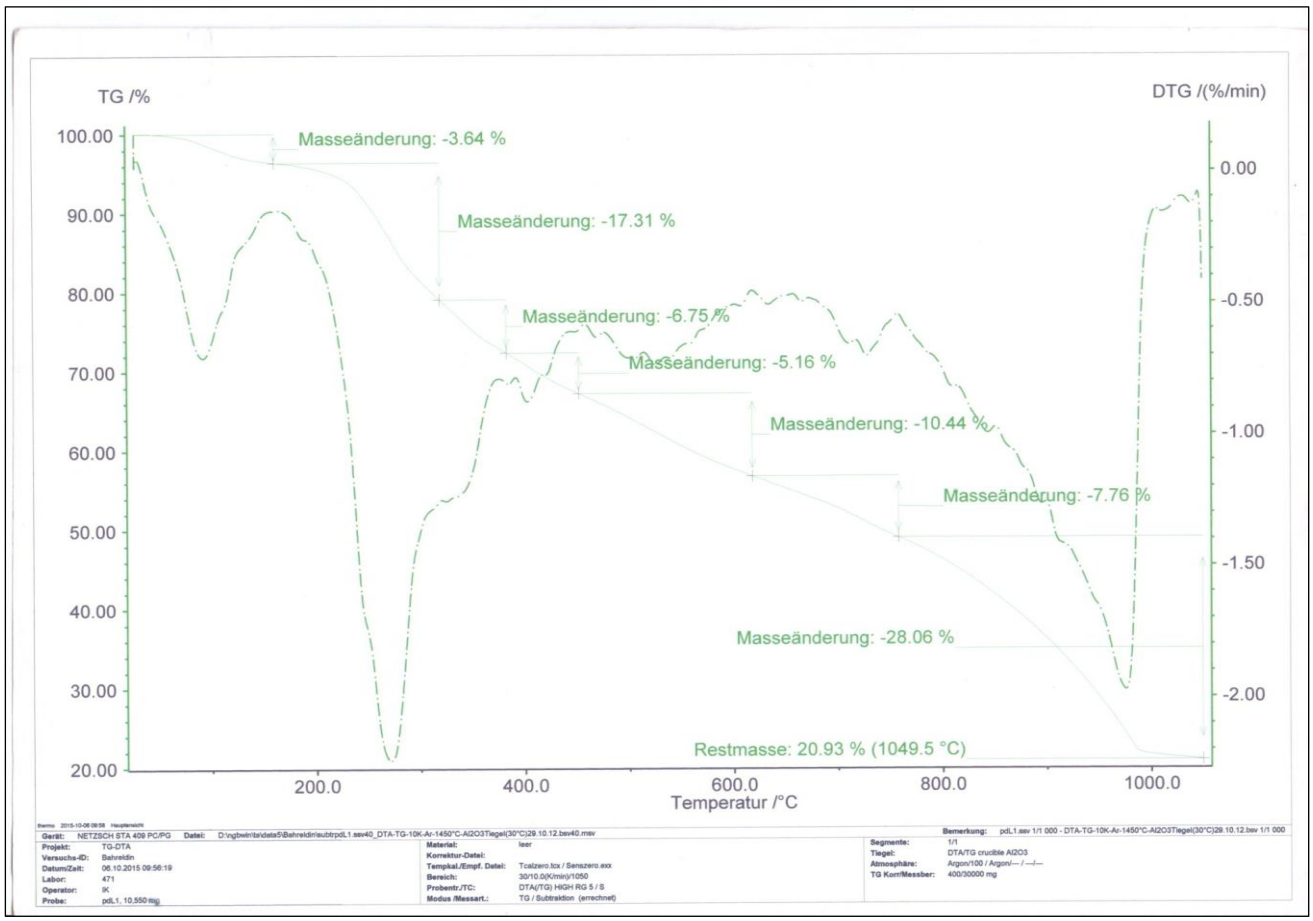


Figure 13: Thermogravimetric analysis curve of the complex $[Pd((4\text{-Me-5-ITSC})_2]Cl_2$

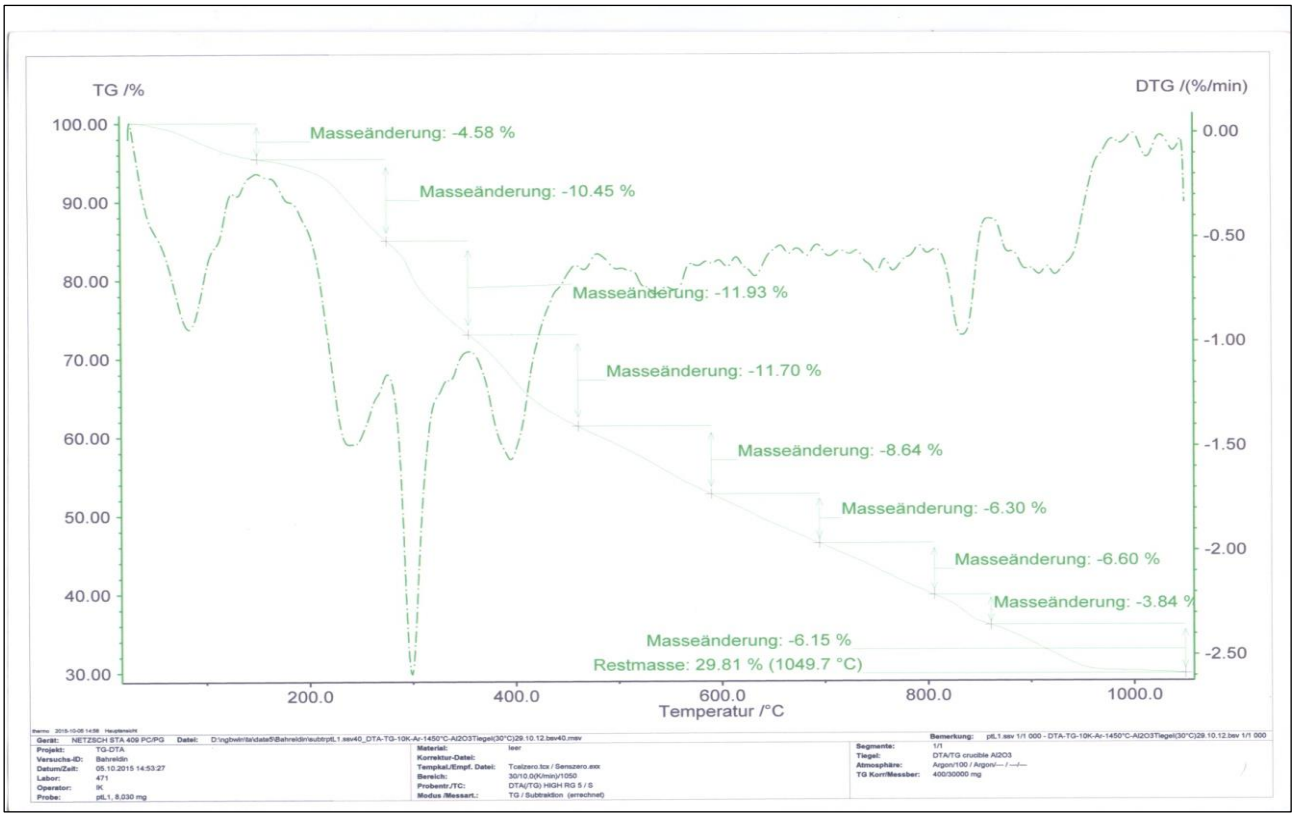


Figure 14: Thermogravimetric analysis curve of the $[Pt((4\text{-Me-5-ITSC})_2]Cl_2$

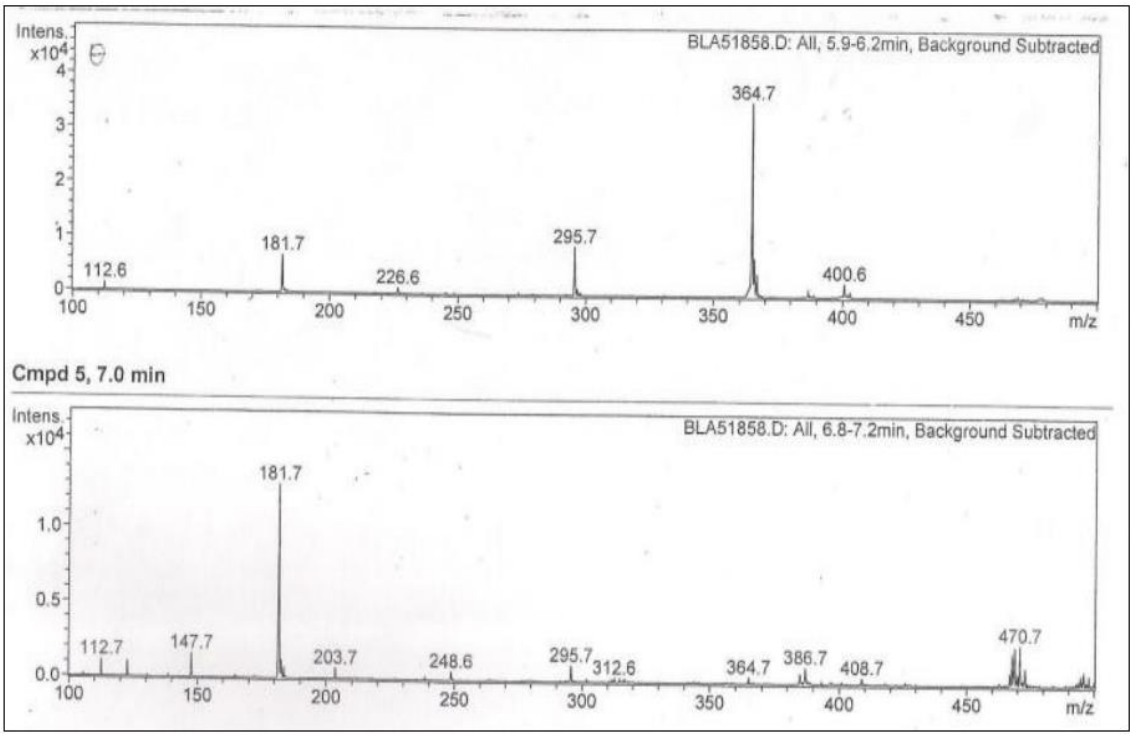


Figure 15: Mass spectral analysis of 4-Me-5-ITSC

4. CONCLUSION

In this study, condensation reaction was adopted for preparing new thiosemicarbazone ligand; 4-methyl-5-imidazolecarboxaldehyde thiosemicarbazone the ligand was fully characterized by X-ray crystallographic analysis, the ligand and its metal complexes were studied by spectroscopic analysis and thermal analysis and their antibacterial and antifungal activities were evaluated.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest. Author contributions: All authors are contributed in this work. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

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