

Synthesis and Spectroscopic Studies of Mixed Ligand Complexes of Pt(II) and Pd(II) with Ethyl- α -Isonitrosoacetoacetate and Dienes

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Abstract: The mixed ligand complexes of the kind $[M(L1)(L2)]$ where $M = Pt(II), Pd(II)$. $L1$ = primary ligand ethyl- α -isonitrosoacetoacetate derived from reaction between ethyl acetoacetate, acetic acid and sodium nitrite and $L2$ =secondary ligand *para*-phenyldiamine (PPD) are synthesized. All the prepared complexes were identified and confirmed by elemental analysis, molar conductance measurements, and infrared electronic absorption. Their complexes has been made based on elemental analysis, molar conductivity, UV-Vis, FT-IR and ¹HNMR spectroscopy and magnetic moment measurements as well as thermal analysis (TGA and DTA). The elemental analysis information recommends that the stoichiometry of the complexes to be 1:2:1. The molar conductance measurements of the complexes indicate their non-electrolytic nature. The infrared spectral information showed the coordination sites of the free ligand with the central metal particle. The electronic absorption spectral information disclosed the existence of an octahedral geometry for Pt(II) and Pd(II) complexes.

Keywords: mixed ligand; ethyl- α - isonitrosoacetoacetate; Pt(II); Pd(II)

1. INTRODUCTION

Metal ions play important role in a very huge variety of biological processes. The ions with biologically active ligands square measure are of appreciable interest. Some of these compounds act via chelation [1]. The coordination chemistry of transition metal complexes with mixed ligands are of current interest because they can give new materials with helpful properties like magnetic exchange [2-3] electrical physical phenomenon [4], photoluminescence [5], nonlinear optical property [6], and antimicrobial activity [7]. The biological importance of mixed ligand complexes is that they are more effective than the free ligands [8]. Mixed ligand complexes containing nitrogen and oxygen donors are important owing to their antifungal bactericide and antitumor activities [9].

In the present paper we synthesize and characterize the Pt(II), Pd(II) mixed ligand complexes with primary substance Ethyl- α - isonitrosoacetoacetate and secondary ligand para phenyl diamine.

2. MATERIAL AND METHODS

Physical Measurement

Solvents and chemicals used for the synthesis were of analytical grade.

The FT-IR spectra recorded in the range 4000-400 cm^{-1} on a FT-IR spectrophotometer as KBR discs. The NMR spectra were measured using Varian Gemini 200-200 MHz spectrophotometer and the spectra were recorded from 0-15 ppm using TMS as an internal standard in dimethylsulfoxide (*d*₆-DMSO) as the solvent. Thermal analysis (TG and DTG) were obtained in a nitrogen atmosphere using a type TGA 50 of Shimadzu deviatograph thermal analyzer. The molar conductivities were carried out using a Jenway 4310 conductivity meter. Electronic spectra were recorded in the range 200-800nm, on jasco V-530 UV-Vis, spectrophotometer. A Perkin Elmer 240C elemental analyzer was used to collect micro analytical data (C, H, N).

Synthesis of Ethyl- α - isonitrosoacetoacetate

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(HEINA): The reagent Ethyl- α -isonitrosoacetoacetate (HEINA) is also known as ethyloximimoacetoacetate, it is synthesized by following procedure [10-11]. Ethyl acetoacetate 1.4 moles and 3.5 mole of glacial acetic acid were taken in three naked round bottom flask fitted with thermometer, reflux condenser and mechanical stirrer and cooled in ice bath at 0 °C and a solution of 95 % sodium nitrite was added over a period of one hour and temperature being kept between 5 °C to 10 °C. This mixture mixed with double distilled water, stirring for two hours and extracted with ether. After drying ether solution with sodium sulphate the solvent was distilled off on a steam bath the crude product was dissolved in toluene and cooled to -13 °C to -15 °C. The separated white crystals were filtered, washed and analyzed.

Synthesis of Pt(EINA)₂PPD: The metal complex was prepared in aqueous solution of chloroplatinic acid (0.265 g, 0.1 mol), adding HEINA (0.318 g, 0.2 mol in water: alcohol 1;1 v/v previously prepared) and after the *p*-phenyldiamine (0.108 g 0.1 mol in water : alcohol 1;1 v/v), by correcting the pH to 5.5 to 6. Then the solution was kept in a boiling water bath for 30 minutes. The cooled green colored complex was thoroughly washed with water. Crystallization of the crude green product from chloroform yielded crystalline Pt(EINA)₂PPD. Yield, 60%. FT-IR (KBr, cm⁻¹): 1610 [ν (C=N)], 3474 [ν (OH)], 1660 [ν (C=O)]. (Found: C, 34.77; H, 4.83; N, 9.01; M, 31.40 calc. for C₁₈H₂₄O₆N₄ C, 34.83; H, 4.80; N, 9.15; M, 31.45).

Synthesis of Pd(EINA)₂PPD: The metal complex was prepared in alcoholic Palladium Chloride solution (0.177 g, 0.1 mol), adding HEINA (0.318 g, 0.2 mol in water: alcohol 1:1 v/v previously prepared) and after the para-phenyldiamine (0.108 g 0.1 mol in water: alcohol 1;1 v/v), by correcting the pH to 5.5 to 6. Then

the solution was kept in a boiling water bath for 30 minutes. The red colored complex was crystallized from chloroform yield 78% FT-IR (KBr, cm⁻¹) 1606 [ν (C=N)], 3474 [ν (OH)], 1690 [ν (C=O)]. (Found: C, 40.56; H, 5.63; N, 10.51; M, 19-98 calc. for C₁₈H₂₄O₆N₄. C, 40.72; H, 5.87; N, 10.40; M, 20.06).

The general structure of metal ligand complex is as follows.

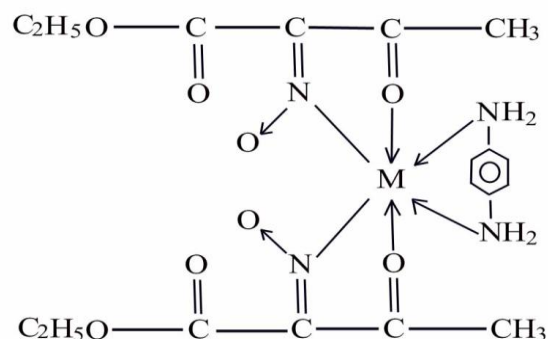


Figure 1. Structure of complex.

3. RESULTS AND DISCUSSION

The elemental analysis shown in table-1 indicates that all the metal complexes have 1:2:1 stoichiometry and are dark in color, soluble in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10⁻⁴ is in the range of 9.5 to 10.2 ohm⁻¹ mol cm². These values are too low to account for any dissociation of the complexes can be regarded as non- electrolyte. Square planer complexes of palladium and platinum (II) are diamagnetic while octahedral complexes are paramagnetic in nature [12-13]. The Pt(II) complexes were found to paramagnetic indicating octahedral coordination of ligands around Pt(II) ion. The Pd(II) complexes exhibit magnetic moment in the range of 2.91 BM suggestive of octahedral nature for these complexes.

Table 1. Elemental analysis and magnetic moment of the complexes.

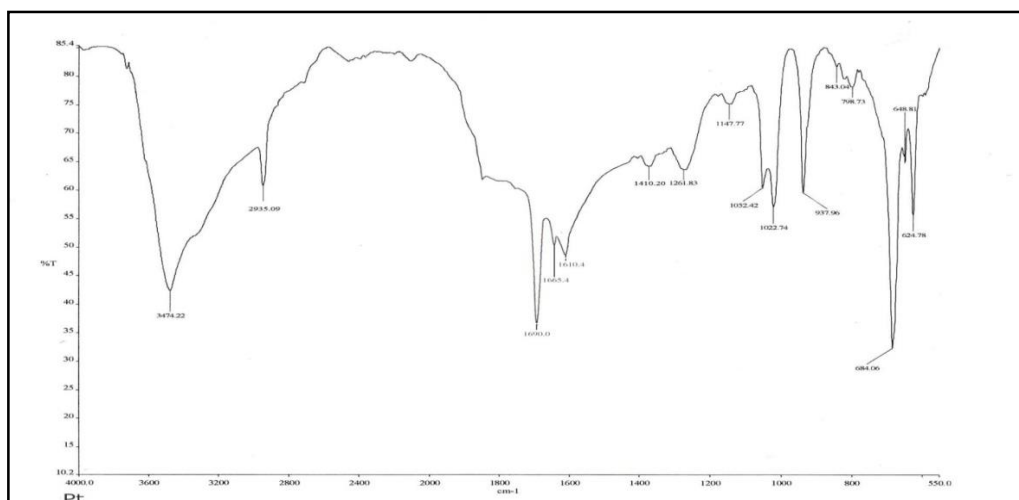
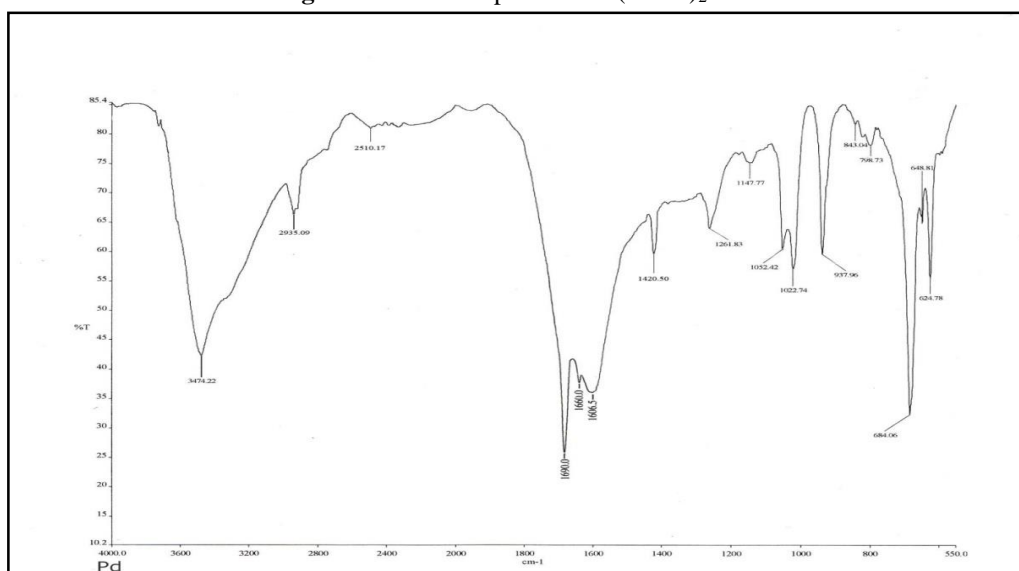
Compounds	Color	% C	% H	% N	% Metal	μ	Molar Conductance	Concentration
HEINA		45.30 45.28	5.66 5.70	8.80 8.78	----	----	----	----
Pt(EINA) ₂ PPD	Green	34.77 (34.80)	4.83 (4.80)	9.01 (9.15)	31.40 (31.45)	0.95	9.5	2.0x10 ⁻⁴
Pd(EINA) ₂ PPD	Red	40.56 (40.72)	5.63 (5.87)	10.51 (10.40)	19.98 (20.06)	2.91	10.2	2.0x10 ⁻⁴

Table 2. IR Assignments of Metal Complexes.

Assignments	HEINA	Pt(EINA) ₂ PPD	Pd(EINA) ₂ PPD
OH	3441	3474	3474
Ester C=O	1760	1690	1690
Ketone C=O	1745	1665	1660
C=N	1620	1610	1606
CH ₃	1418	1410	1420
COOC ₂ H ₅	1261	1261	1261

IR spectra of the complex were compared with those of the HEINA in order to find out the point of attachment of the HEINA. The IR spectra of the free HEINA showed a strong absorption at around 3441 cm⁻¹ due to the N-OH stretching. This absorption is shifted to lower frequency in the complex indicating the coordination of N-OH to metal ion. The presence of a

band in the region 1690 cm⁻¹ is another indication of the involvement of ester group in coordination. The –C=O band that appeared at around 1745 cm⁻¹ in the HEINA. This absorption is shifted to the lower frequency region 1665 cm⁻¹ which may be attributed to the coordination through the oxygen atom in metal complex.

**Figure 2.** Infrared Spectra of Pt(EINA)₂PPD.**Figure 3.** Infrared Spectra of Pd(EINA)₂PPD.

^1H NMR spectra of both the $\text{Pt}(\text{EINA})_2\text{PPD}$ and $\text{Pd}(\text{EINA})_2\text{PPD}$ complexes have been recorded in EtOD solution. In the ^1H NMR spectra of ligand HEINA a sharp singlet at 8.65 ppm is observed which may be assigned to N-OH. Absence of this signal in the spectra of the metal complex confirms the coordination through N-OH group. The signal due to the CH_3 proton

in the spectra of the HEINA undergoes a downfield shift in the spectra of the complexes at $\sigma = 2.50$ - 2.55ppm confirming the coordination through N-OH. The signal due to CH_2-CH_3 - protons is a singlet at $\sigma = 4.224$ - 1.375 ppm. While the aryl protons of the compound gave a signal at $\sigma = 6.6$ ppm.

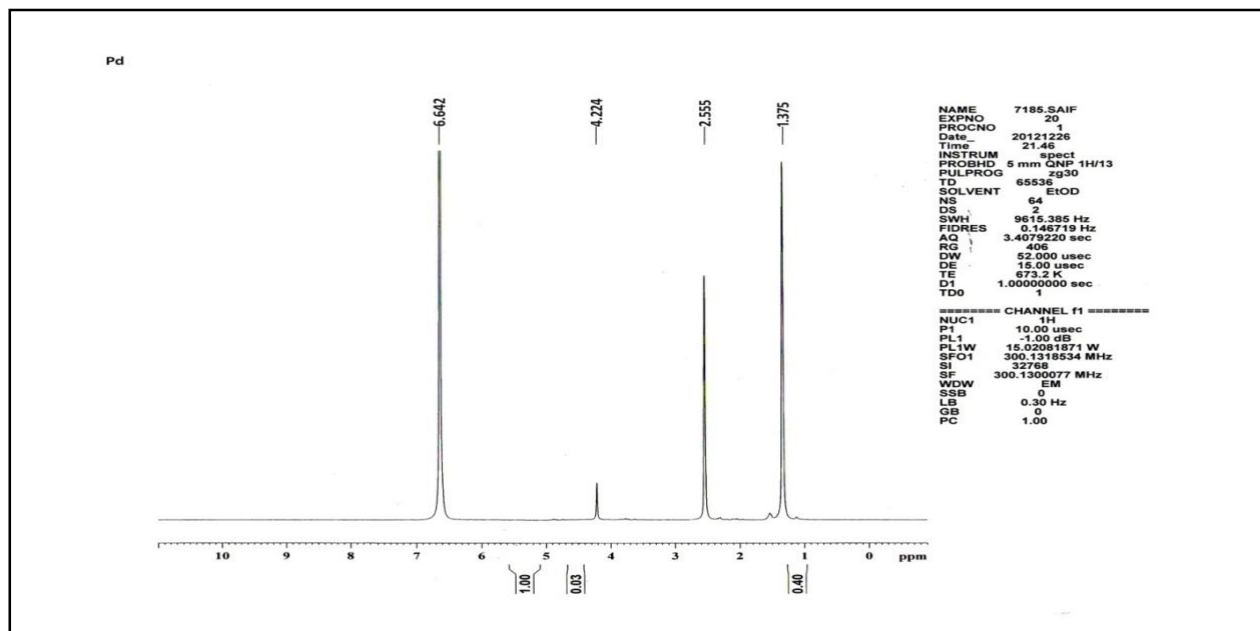


Figure 4. NMR Spectra of $\text{Pd}(\text{EINA})_2\text{PPD}$.

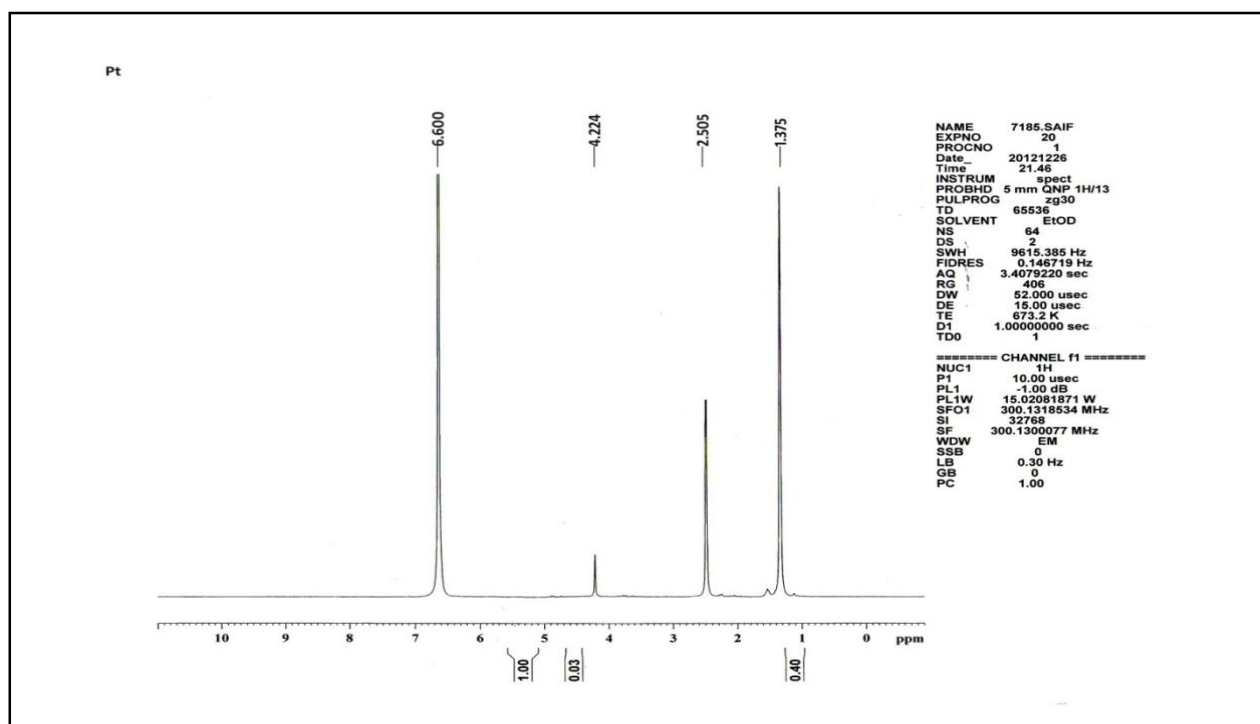


Figure 5. NMR Spectra of $\text{Pt}(\text{EINA})_2\text{PPD}$.

The appearance of $\pi-\pi^*$ Band in metal complex at different positions compared to those of

$\pi-\pi^*$ bands of ligand indicates that the energy states of π electron system of ion ligand suffer substantial

alteration on complex formation. $\text{Pt}(\text{EINA})_2\text{PPD}$ which reveals the d-d transition band at 348 nm in DMSO. $\text{Pd}(\text{EINA})_2\text{PPD}$ complex shows $\pi - \pi^*$

transition at 198 nm. The assignments of the band are observed as suggested by Mason and Gray [14].

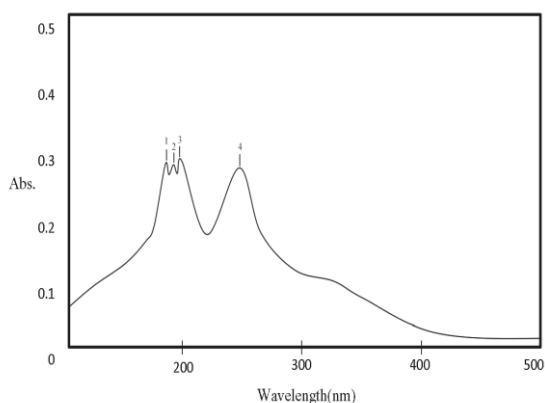


Figure 6. Absorption Spectra of $\text{Pd}(\text{EINA})_2\text{PPD}$.

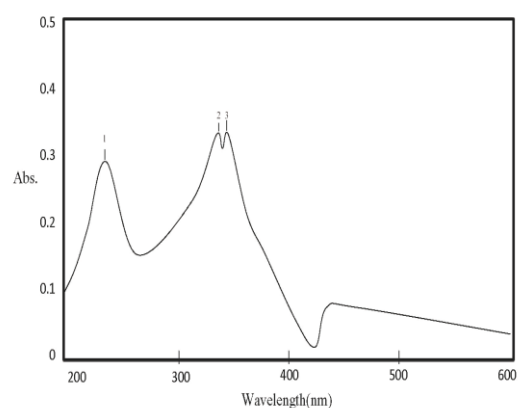


Figure 7. Absorption Spectra of $\text{Pt}(\text{EINA})_2\text{PPD}$.

$\text{Pd}(\text{EINA})_2\text{PPD}$ Complex

The TGA curve of compound $\text{Pd}(\text{EINA})_2\text{PPD}$ shows a significant reduction in weight (25%) due to decomposition of compound at lower temperatures. The resulting decomposed compounds are not stable to heat and losing their weight gradually up to 700 °C.

The results of DTA curve show an endothermic peak at 441.24 °C which indicates the formation of stable compound from decomposition of $\text{Pd}(\text{EINA})_2\text{PPD}$. The resulting compound undergoes decomposition above 700 °C both in DTA & TGA by forming oxides of palladium at 480.27 °C. Thermal activation energy was 31.91 J / Mole and order of reaction was 1.

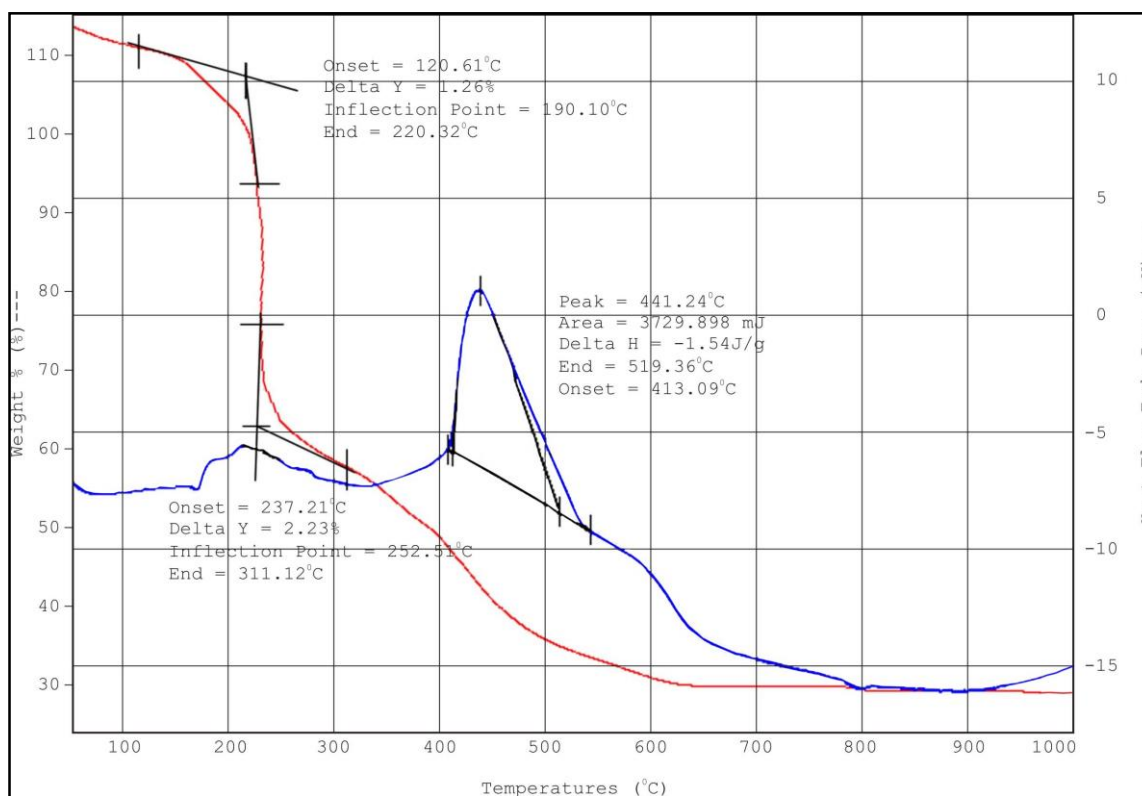


Figure 8. Thermogram of $\text{Pd}(\text{EINA})_2\text{PPD}$.

Pt (EINA)₂PPD Complex

The TGA spectrum of compound Pt(EINA)₂PPD does not show the sharp reduction in the weight with respect to temperature, continuous gradual reduction of weight is observed up to 500 °C. The corresponding DTA curve of the same compound

indicates an onset of exothermic peak at 406.64 °C which decompose completely at 480.27 °C by forming oxides of platinum. Thermal activation energy was found to be 49.11 J and order of reaction was found to be 1.

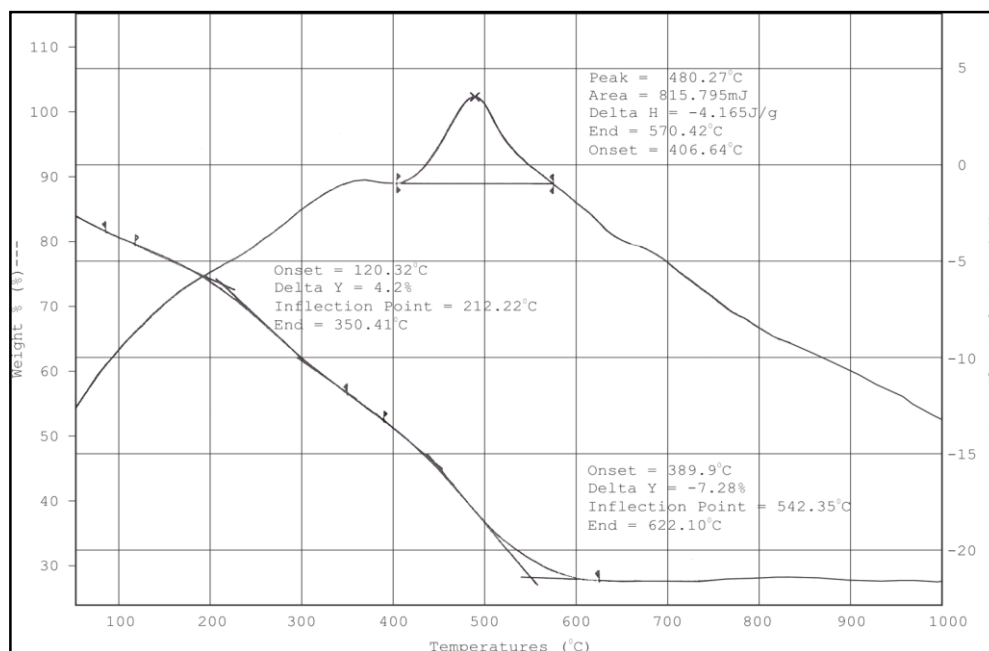


Figure 9. Thermogram of Pt (EINA)₂PPD.

Table 3. Elemental Analysis and Magnetic Moment of the Complexes.

Complex	λ_{\max}	Excitation	ϵ
Pt(EINA) ₂ PPD	232	$\pi - \pi^*$	232000
	338	$\pi - \pi^*$	338000
	348	d-d	348000
Pd(EINA) ₂ PPD	196	$\pi - \pi^*$	196000
	198	$\pi - \pi^*$	198000
	200	d-d	200000

4. CONCLUSION

The Elemental analysis, Magnetic susceptibility, Electronic and ¹HNMR, FTIR observations suggest that the octahedral geometry for Pt(II) and Pd(II) complexes and exhibit coordination number six. The general structure of the complex is shown in Figure 1.

6. REFERENCES AND NOTES

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