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Spectroscopic Elucidation, Conductivity and Activation Thermodynamic Parameters Studies on Pt(IV), Au(III) and Pd(II) 1,5-Dimethyl-2-phenyl-4-[(thiophen-2-ylmethylene)-amino]-1,2-dihydro-pyrazol-3-one Schiff Base Complexes

Foziah A. Al-Saif

Department of Chemistry, Faculty of Science, Princess Nora Bint Abdul Rahman University, Riyadh, Kingdom Saudi Arabia
E-mail: drmsrefat@yahoo.com

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Noble metal complexes of Schiff bases derived from 2-thiophenecarboxaldehyde and 4-aminoantipyrine (4APT) are discussed and characterized based on elemental analyses, IR, Raman, ^{1}H-NMR, molar conductance, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy and thermal analysis (TGA). The complexes are found to have the formulas $[Pt(4APT)Cl]Cl_3$, $[Pd(4APT)(Cl)_2]$ and $[Au(4APT)(Cl)_2]Cl$. The molar conductance data reveal that all the metal chelates of the 4APT ligand are non-to-electrolytes with difference degree of ionizable chloride ions. IR spectra show that 4APT is coordinated to the metal ions in a tridentate manner, with SNO donor sites of azomethine–N and thiophene-S in case of platinum(IV) complex, whereas the palladium(II) and gold(III) complexes are coordinated to the 4APT in a bidentate manner with SN donor sites of azomethine–N and thiophene-S. From the Raman spectra, it is found that the fluorescence natures of these complexes are displayed upon the broadening and scattering spectra. The thermal features of these chelates shows that the Pt(IV) hydrated complex lose water molecules of hydration in the first step and is immediately followed by decomposition of the anions and ligand moieties in the subsequent steps. The activation thermodynamic parameters of E*, ΔH*, ΔS*, and ΔG*, are calculated from the DrTG curves using the Coats-Redfern isothermal method. The synthesized ligand was also checked using mass spectroscopy and the fragmentation patterns are assigned.

Keywords: 4-Amino antipyrine, 2-thiophenecarboxaldehyde, conductivity, noble metal, IR, ^{1}H-NMR, thermal analysis.

1. INTRODUCTION

Schiff base compounds derived from aromatic amines and aromatic aldehydes have a wide range of applications in many fields like biological, inorganic and analytical chemistry [1-5]. They are known to exhibit potent antibacterial, anticonvulsant and anti-inflammatory activities [6]. Schiff bases of isatin derivatives have been used to demonstrate a variety of biological activities, such as anti-inflammatory anti HIV [7] and anti-depressant activities. In addition some Schiff bases show pharmacologically useful activities like anticancer [8], anti-hypertensive and hypnotic [9, 10] activities. Schiff bases are important class of compounds due to their flexibility, structural similarities with natural biological substances and also due to the presence of imine moiety (-N=CH-) which is potential in elucidating the mechanism of transformation reaction in biological system. These novel compounds could also act as valuable ligands whose biological activity has been shown to increase on complexation. Because of the fundamental and technological reasons, considerable interest has been shown in the synthesis and study of organic solids and metal complexes which behave like semiconducting materials [11]. The electrical properties of the organic ligands and their metal complexes have been intensively studied by many of the research groups all over the world [12-19]. Metal complexes of the Schiff bases derived from reaction of 2-methylbenzopyrrole-3-carboxaldehyde with some aniline derivatives showing slight semiconducting behavior have been reported [20]. Their conductivity and activation energy were found to depend on molecular structure as well as the ionic radii of the metal ions. Singh measured the electrical conductivity of the complex salts and the heterobimetallic coordination polymers bis(1-ethoxycarbonyl-1-caynoethelene-2,2-dithiolato)cuprate(II) ion [21] and [MM′(cdc)$_2$], [M= Zn(II), Cd(II), Hg(II); M′= Ni(II) or Cu(II); cdc^{2-} =cyanodithioimidocarbonate] [22]. All the complexes exhibited semiconducting behavior. Semiconducting properties of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) complexes of Schiff base derived from resdiacetophenone and S-benzyldithiocarbazate were studied by Makode. It was found that complexes are semiconducting in nature [23].

The aim of this work is to interpretative the structural and conductivity properties of the noble metal (Pt(IV), Pd(II) and Au(III)) Schiff base ligand derived from 2-thiophenecarboxaldehyde and 4-aminoantipyrine in chelating situation. There are many spectroscopic tools utilized to characterized the synthesis complexes elemental analysis, molar conductivity, (NMR, infrared and UV-Vis) spectra, thermal analyses (TG/DTG), X-ray power diffraction (XRD) as well as scanning electron microscopy (SEM).

2. EXPERIMENTAL

2.1. Chemicals

All chemicals (purity from 98-99%) were purchased and used without further purification. 4-aminoantipyrine, 2-thiophenecarboxaldehyde, platinum(IV) chloride, palladium(II) chloride and sodium gold(III) chloride hydrate were received from BDH Company (UK), and other chemicals and solvents used without purification.

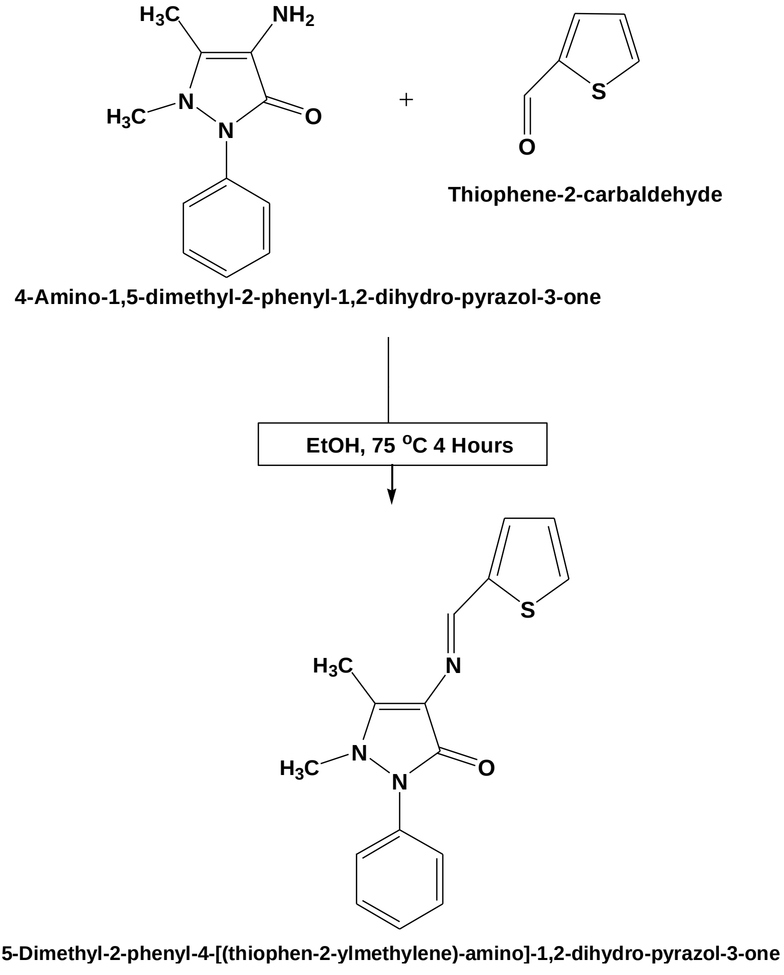
2.2. Synthesis of Schiff base ligand

The Schiff base (4APT, Scheme 1) was prepared according to the previous procedure [24-31]: An ethanolic solution of 2- thiophenecarboxaldehyde (1 mmol, 25 mL) was added to an ethanolic solution of 4-aminoantipyrine (1 mmol, 25 mL) and refluxed for 4 hour in a hotplate 75 ^{o}C. After cooling of the solution, the precipitate was separated, filtered, re-crystallization with ethanol, and dried over anhydrous calcium chloride under vacuum.

2.3. Synthesis of Au(III), Pt(IV) and Pd(II) complexes

To 1.0 mmol solution of $PtCl_4$ as ((H_2PtCl_6)) (0.410 g), $PdCl_2$ (0.177) or $NaAuCl_4.2H_2O$ (0.40 g) which dissolved in 20 mL ethanol 98%, the (0.298 g, 1.0 mmol) of 4APT Schiff base ligand dissolved in 40 mL ethanol 98% was added and stirred at 70 ^{o}C temperature for about 45 min, leading to isolation of solid products which was left overnight till precipitated, washed with methanol and diethyl ether then finally dried under vacuum over anhydrous calcium chloride.

2.4. Measurements



Scheme 1. Preparation design of 4APT Schiff base ligand

The elemental analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer CHN 2400 (USA). The molar conductivities of freshly prepared 1.0×10^{-3} mol/cm^3 dimethylsulfoxide (DMSO) solutions were measured for the dissolved 4APT complexes using Jenway 4010 conductivity meter. The electronic absorption spectra of 4APT complexes were recorded in DMSO solvent within 900-200 nm range using a UV2 Unicam UV/Vis Spectrophotometer fitted with a quartz cell of 1.0 cm path length. The infrared spectra with KBr discs were recorded on Bruker FT-IR Spectrophotometer (4000–400 cm^{-1}). The Raman laser spectra of the samples were measured on a Bruker FT-Raman spectrophotometer equipped with 50 mW laser. The ^{1}HNMR spectra were recorded on Varian Mercury VX-300 NMR spectrometer. ^{1}H spectra were run at 300 MHz spectra in deuterated dimethylsulphoxide (DMSO-d_6). Chemical shifts are quoted in δ and were related to that of the solvents. The thermal studies TG/DTG–50H were carried out on a Shimadzu thermogravimetric analyzer under nitrogen till 800 ^{o}C. Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment. The X-ray diffraction patterns for the selected 4APT complexes were recorded on X 'Pert PRO PANanalytical X-ray powder diffraction, target copper with secondary monochromate.

3. RESULTS AND DISCUSSION

3.1. Microanalytical and molar conductance assessments

Table 1. Analytical and physical data for 4APT Schiff base metal complexes

Complexes Empirical formula (M.Wt.)/yield (%)	Color	Λm ($\Omega^{-1}cm^{-1}mol^{-1}$)	Elemental analysis (%) Found (Calcd.)			
			C	H	N	M
[Pt(4APT)Cl].3Cl (619.23)/ 80%	Brown	208	28.95(29.09)	1.75(1.95)	6.54(6.79)	29.98(31.50)
[Pd(4APT)(Cl)$_2$] (489.74)/ 88%	Brown	54	41.54(41.69)	3.51(3.70)	8.32(8.58)	21.52(21.73)
[Au(4APT)(Cl)$_2$]Cl (615.73)/ 83%	Brown	93	32.97(33.16)	2.88(2.95)	6.79(6.82)	31.75(31.99)

The data of elemental analyses (C, H, and N), molecular formulas, and colors as well as molar conductance are displayed in Tables 1. The results obtained are in good agreement with those calculated for the suggested formulas and the clear melting points with high values above 200 ^{o} C give an impression about the synthesis of homogenous uni-molecule from both Schiff base and their complexes without any contaminated materials. The structure of 1,5-dimethyl-2-phenyl-4-[(thiophen-2-ylmethylene)-amino]-1,2-dihydro-pyrazol-3-one Schiff base under study is given in Figure 1.

The structure of this Schiff base is also confirmed by IR and Mass spectra. 1,5-Dimethyl-2-phenyl-4-[(thiophen-2-ylmethylene)-amino]-1,2-dihydro-pyrazol-3-one Schiff base ligand with the noble metal ions Pt(IV), Pd(II), and Au(III) complexes have not been previously published, hence, these complexes were prepared and fully characterized. Moreover, the conductivity on the solution form of the metal complexes of 4APT ligand and their thermal stability were discussed. The kinetic parameters calculated applying the Coats-Redfern method.

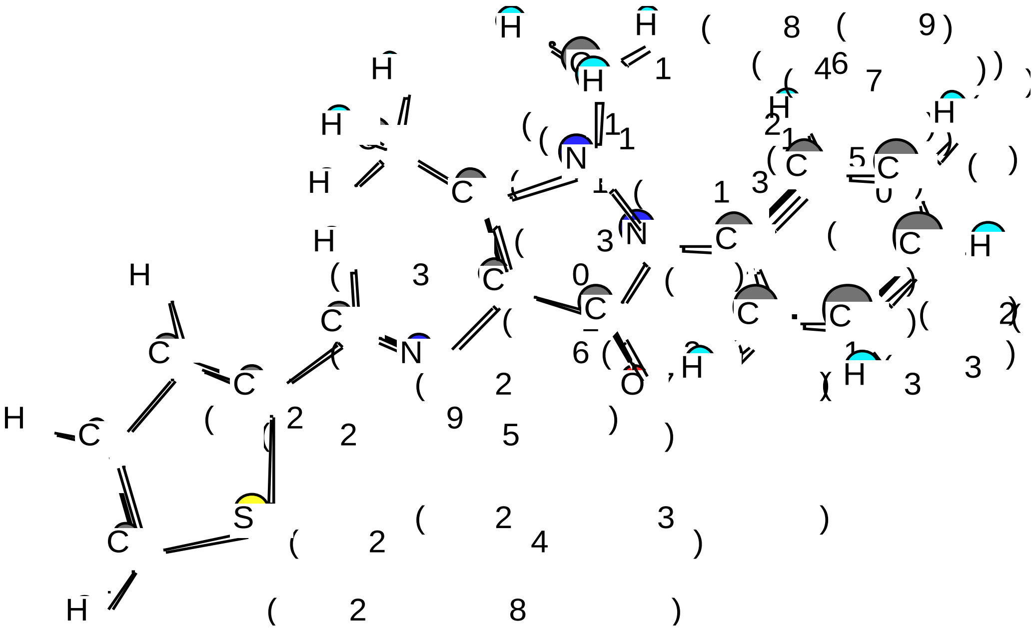


Figure 1. 3D structure of 1,5-dimethyl-2-phenyl-4-[(thiophen-2-ylmethylene)-amino]-1,2-dihydro-pyrazol-3-one Schiff base ligand

Therefore, the main task of this paper is to prepare the solid complexes of this ligand and to thoroughly characterize those using different physicochemical techniques, as well as studying their electrical properties. The isolated solid complexes of Pt(IV), Pd(II), and Au(III) ions with the Schiff bases 4APT ligand were studied upon elemental analyses (C, H, N and metal content), infrared spectral studies (IR), Raman spectra, nuclear magnetic resonance (^{1}H-NMR), UV-Vis. spectra, molar conductance, XRD, SEM, EDX, and thermal analysis (TGA) to identify their definite formulas with speculated structures. The formation of these complexes suggested according to the following equations;

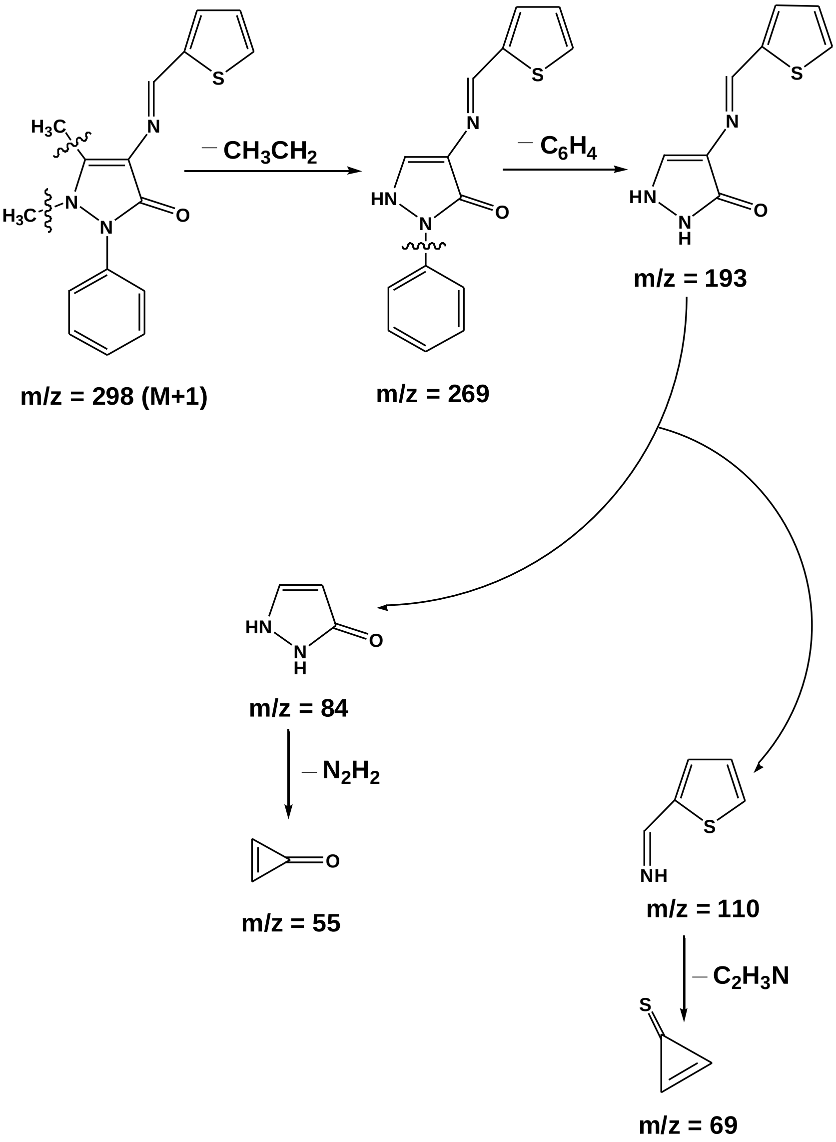
$H_2PtCl_6 + 4APT \rightarrow [Pt(4APT)Cl]Cl_3$

$PdCl_2 + 4APT \rightarrow [Pd(4APT)(Cl)_2]$

$NaAuCl_4.2H_2O + 4APT \rightarrow [Au(4APT)(Cl)_2]Cl$.

Using the relation $\Lambda m= K/C$, the molar conductance of the complexes (Λm) can be calculated, where C is the molar concentration of the metal complex solutions. The Pt(IV), Pd(II) and Au(III) complexes were dissolved in DMSO solvent with molar conductivities of 10^{-3} M at 30 ^{o}C were measured. A table 1 has contained the molar conductance values of the 4APTcomplexes. It is concluded from the data that Pt(IV) and Au(III) chelates of the 4APT ligand are found to have molar conductance values of 208 and 93 $\Omega^{-1}.cm^2.mol^{-1}$, respectively, indicating the ionic nature of these complexes with different number of ionizable chloride ions outside the coordination sphere. Consequently, the Pt(IV) complex is considered as 1:1 electrolytes with existed three chloride ions outside the coordination sphere but Au(III) complex has only one ionizable chloride ions outside and two coordinated chloride ions. On the other hand, the molar conductivity values of Pd(II) complex with the 4APT ligand under investigation is 54 $\Omega^{-1}.cm^2.mol^{-1}$. It is obvious from this data that this complex is covalently in nature and its non-electrolytes. This result was strongly supported with the chemical analysis where Cl^- ions were checked by addition of $AgNO_3$ solution.

3.2. Mass spectra



Scheme 2. Mass fragmentation proposal of 4APT Schiff base ligand

The electron impact mass spectra of 1,5-dimethyl-2-phenyl-4-[(thiophen-2-ylmethylene)-amino]-1,2-dihydro-pyrazol-3-one Schiff base ligand (4APT) was performed and discussed. The mass spectrum of 4APT shows a well-defined molecular ion peak at m/z = 298 (M+1), with a relative intensity = 27%. The fragments patterns obtained by cleavage in different positions in the 4APT molecule are shown in Scheme 2. The base peak fragment at m/z = 69 (Relative intensity = 100%) is attributed to the C_3H_2S ion as shown in the mass spectrum of 4APT. The pattern of mass spectrum gives an impression of the successive fragmentations of the Schiff base compound with the series of various peaks corresponding to the different patterns and their intensities. Their intensity gives an idea about stability of fragments. The recorded mass spectrum of the free ligand and molecular ion peaks have been used to confirm the proposed formula (Scheme 2). In 4APT Schiff base ligand, the degradation pattern shows peaks at 269(15% m/z), 191(22% m/z), 110(50% m/z), 84(77% m/z) and 55(89% m/z), respectively, assigned in (Scheme 2).

3.3. Infrared and Raman spectra

Table 2. IR spectral data of 4APT Schiff base metal complexes

Compounds	Assignments							
	ν(CH) Aliphatic	ν(CH) Aromatic	ν(C=O)	ν(C=N)	ν(C=C) δ(CH)	ν(C-S)	Ring def. in-plane	Ring def. out-of-plane
4APT	3115 3045	2966 2926	1639	1574	1485 1412 1305 1211 1131 1048 950	850	765 694 618	594 562 502 420
[Pt(4APT)Cl].3Cl	3055	2906 2839	1576	--	1491 1455 1394 1314 1218 1160 1074 1050 1021	761	695 666 620	581 521 496 470 434
[Pd(4APT)(Cl)$_2$]	3321 3049	2904	1621	1577	1502 1455 1413 1340 1219 1204 1173 1158 1134 1110 1059 996	762	687 651 617	565 493 434
[Au(4APT)(Cl)$_2$]Cl	3050	2933	1627	1591	1491 1454 1409 1348 1292 1261 1021 958 910	755	691 640	588 499 477

The infrared spectral data of 4APT Schiff base ligand and their complexes are refereed in Tables 2 and Fig. 2. The IR data of the complexes were compared with respective of the free ligand in order to identify the coordination modes upon the chelation process. There are some distinguish bands in the spectra of the free ligand, which were helpful in detection of donation sites. The shifting in wavenumber and their intensities of referenced bands led to predict the chelation behavior. By comparison between free 4APT and there noble metal complexes, it was that the υ(C=N) stretching vibration is found in the free ligand at 1574 cm^{-1}. This band was absence in the Pt(IV) complex, indicating the participation of the azomethine nitrogen in coordination [32, 33]. The participation of the C=O group in chelation is ascertained from the shift of the υ(CO) from 1639 cm^{-1} to lower wavenumbers at 1576, 1621and 1627 cm^{-1}, in the spectra of the Pt(IV), Pd(II) and Au(III) complexes, respectively.

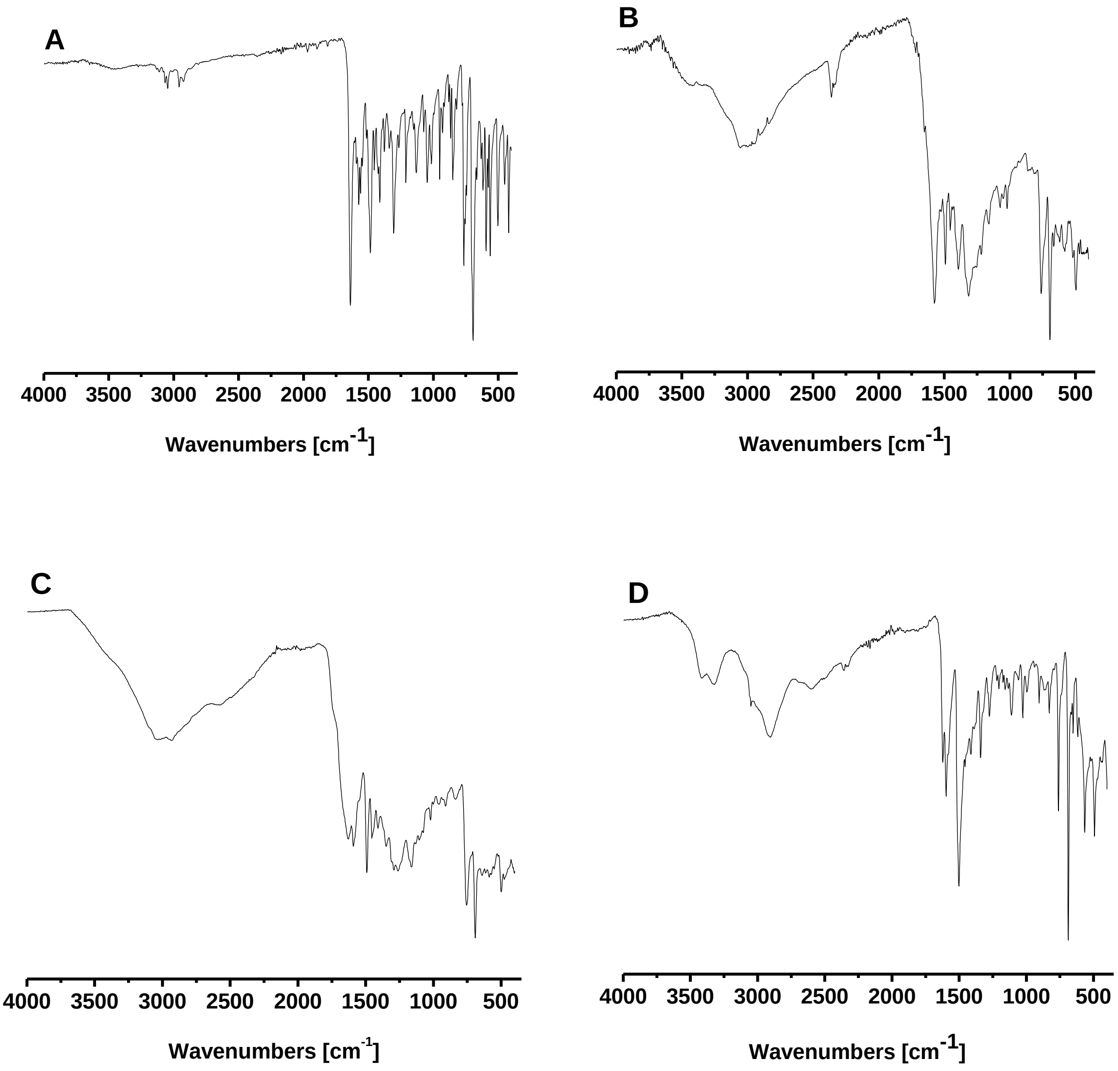


Figure 2. Infrared spectra of (A): 4APT free ligand, (B): Pt^{IV} complex, (C): Au^{III} complex and (D): Pd^{II} complex

Strong to medium strong bands, due to υ(C-S) stretching vibration of thiophene, appeared at 850 cm^{-1} in the free Schiff base ligand [33]. This band shifted to 761, 762 and 755 cm^{-1} in Pt(IV), Pd(II) and Au(III) metal complexes. These shifts refer to the coordination through a thiophene S atom. New bands are found in the spectra of the complexes in the regions ~ 500 cm^{-1} (C=O; oxygen), which are assigned to υ(M-O) stretching vibrations for 4APT metal complexes. The band at ~ 400 cm^{-1}

Pt(IV) metal complex has been assigned to *υ*(M-N) mode. Therefore, from the infrared spectral data, it is concluded that the 4APT ligand behaves as a neutral tridentate ligand coordinated to the Pt(IV) metal ions via azomethine N, carbonyl O and thiophene S; whereas 4APT behaves as a bidentate ligand coordinated to the metal ions via thiophene S and carbonyl O in case of both Pd(II) and Au(III) complexes. Raman spectra of Pt(IV), Pd(II), and Au(III) complexes (Fig. 3) has a scattering and sharp broadening with distorted in the stretching and bending vibration bands, this can be discussed under the knowledge that Raman analysis of fluorescent materials and compounds is a challenging task experimentally due to the overlap of fluorescence which, even when very weak, can overwhelm the inherently weak Raman scattering signal [34, 35].

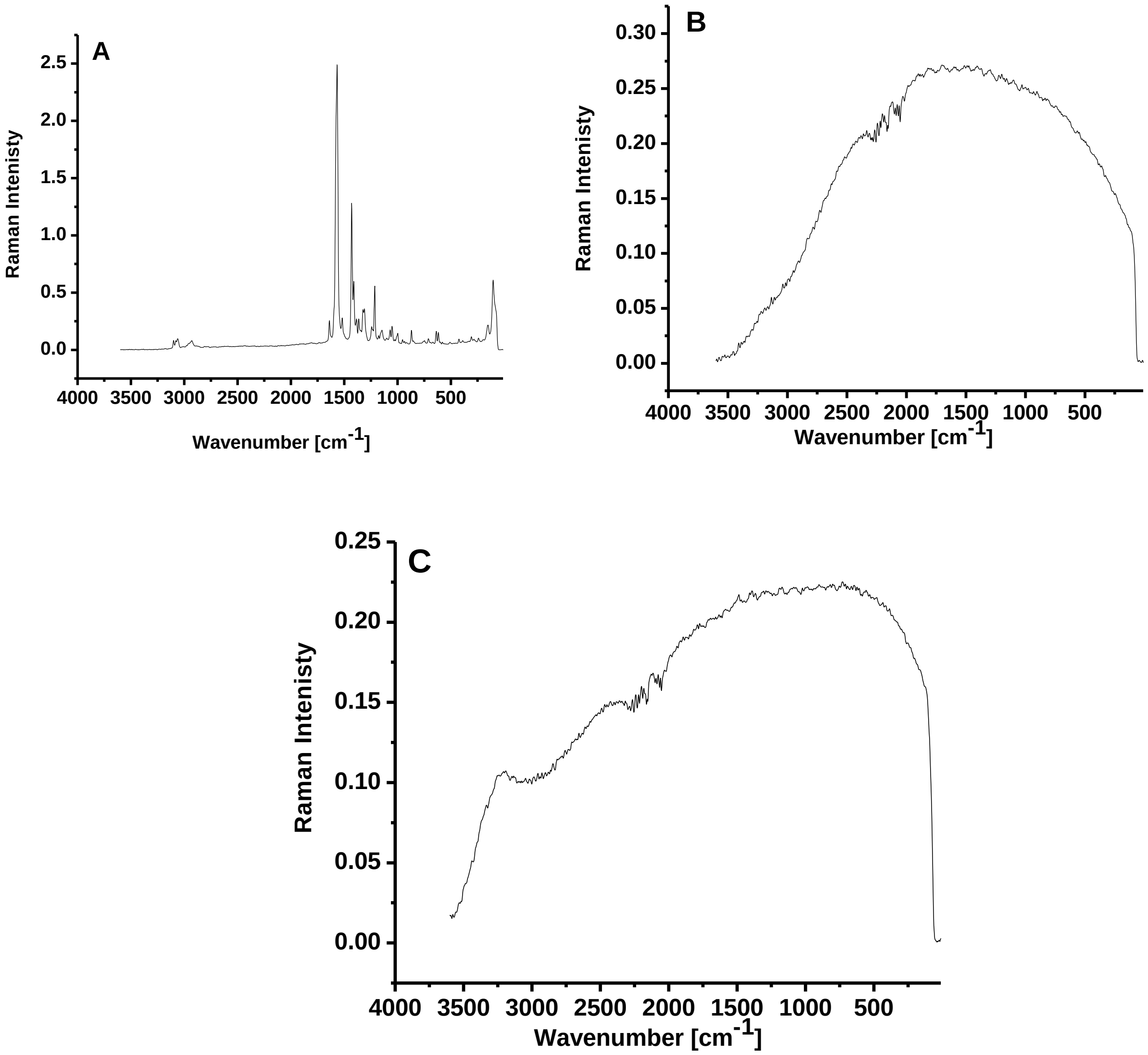


Figure 3. Raman spectrum of (A): 4APT free ligand, (B): Pd^{II} and (C): Pt^{IV} complexes

3.4. UV-vis. electronic spectra

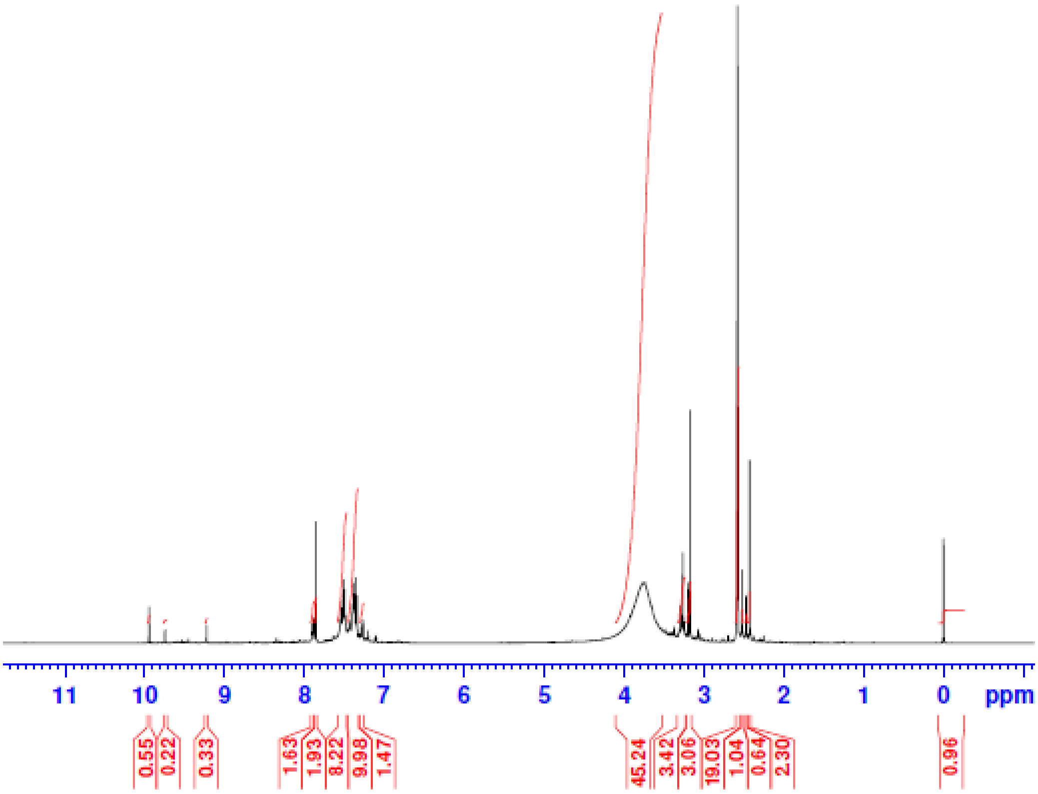
The electronic spectra of the DMSO solutions of the 4APT free ligands, recorded in the 200 – 800 nm exhibit bands in the range 200 – 300 nm and 300 – 500 assigned to the π →π* and n→π* transitions, respectively, of the azomethine group, thiophene and 4-aminoantipyrine moieties, and it is shifted to lower or longer wavelength on coordination through azomethine nitrogen in the complexes [35]. The n-π^* transition undergoes a blue shift indicating that the lone pair electrons of oxygen and nitrogen are coordinated to the metal ion. The $\pi-\pi^*$ transition of C=O group, thiophene and organic moieties of Pt(IV), Pd(II) and Au(III) complexes is found at 292, 289 and 284 nm, respectively. The $\pi-\pi^*$ transition undergoes red shift with an increase in wavelength. Similarly the absorption bands seen at 356, 359 and 357 nm are attributed to n-π^* transitions of thiophene and C=N groups. Spectra of all complexes exhibit blue shift for n$-\pi^*$ transition which is observed at 361 nm transition in free Schiff base ligand, suggesting the coordination of oxygen, nitrogen and sulfur atoms.

3.5. ^{1}H-MNR spectra

Table 3. ^{1}H-NMR spectral data of 4APT Schiff base metal complexes

Assignments	Compounds			
	4APT	Pt(IV)	Pd(II)	Au(III)
C-CH_3	2.122	2.428	2.608	2.244
N-CH_3	2.820	3.174	3.243	2.947
Thiophene ring Ph; amino antipyrine	7.116 7.225 7.327 7.422	7.00-8.00	7.00-8.00	7.00-8.00
HC=N	9.220	9.949	9.953	10.00

The ^{1}H-NMR spectra of free 4APT free Schiff base ligand and all Au(III), Pt(IV) and Pd(II) complexes (Table 3 and Fig. 4) were recorded to confirm the binding of the Schiff base to the metal ions. ^{1}H-NMR (300 MHz, DMSO-*d*6): δ, 2.122 (3H, C-CH_3, aminoantipyrine), 2.820 (3H, N-CH_3), (7.116 and 7.327) (3H, thiophene), (7.225, 7.422 and 7.464) (5H, Ph, aminoantipyrine) and 9.220 ppm (1H, CH=N) (Scheme 3). The spectra of all the complexes showed a singlet peak at δ 9.220 ppm, which has been assigned to the azomethine proton (-HC=N). The position of the azomethine signal in the Pt(IV) complex is shifted in comparison with that of the free ligand, suggesting deshielding of the azomethine proton due to its coordination to metal ions through the azomethine nitrogen. In the region 7.0 – 8.0 ppm were assigned chemical shifts for hydrogen of symmetrical aromatic ring of ligand.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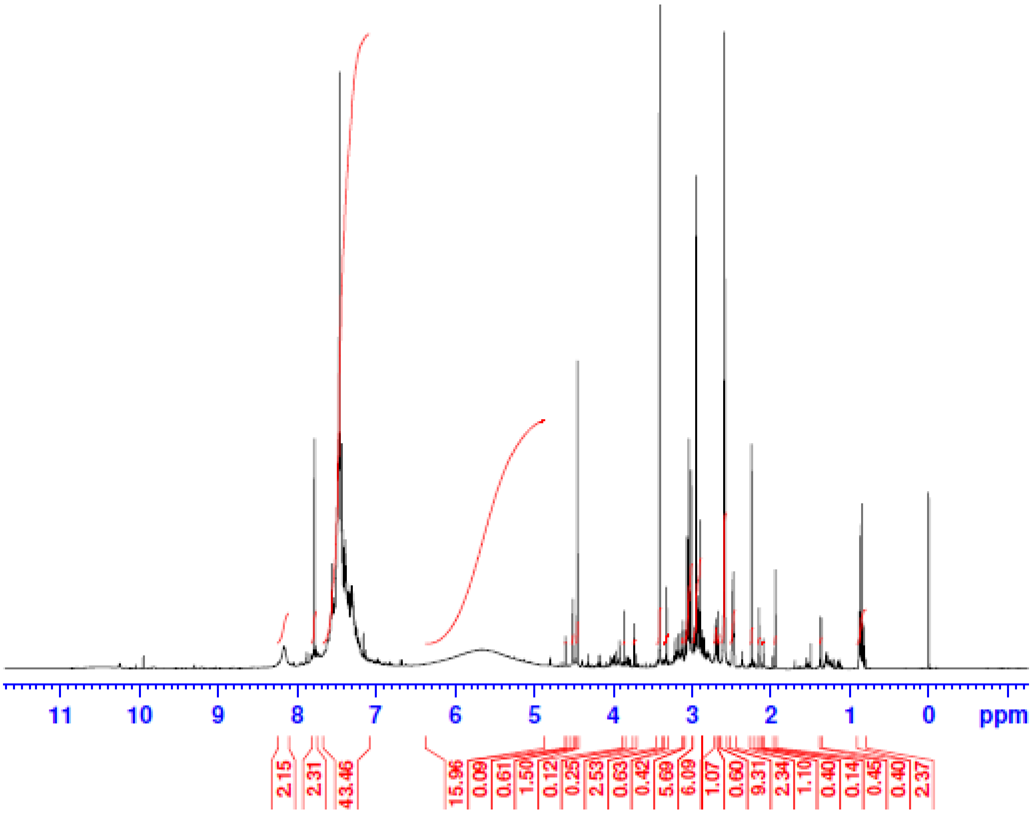
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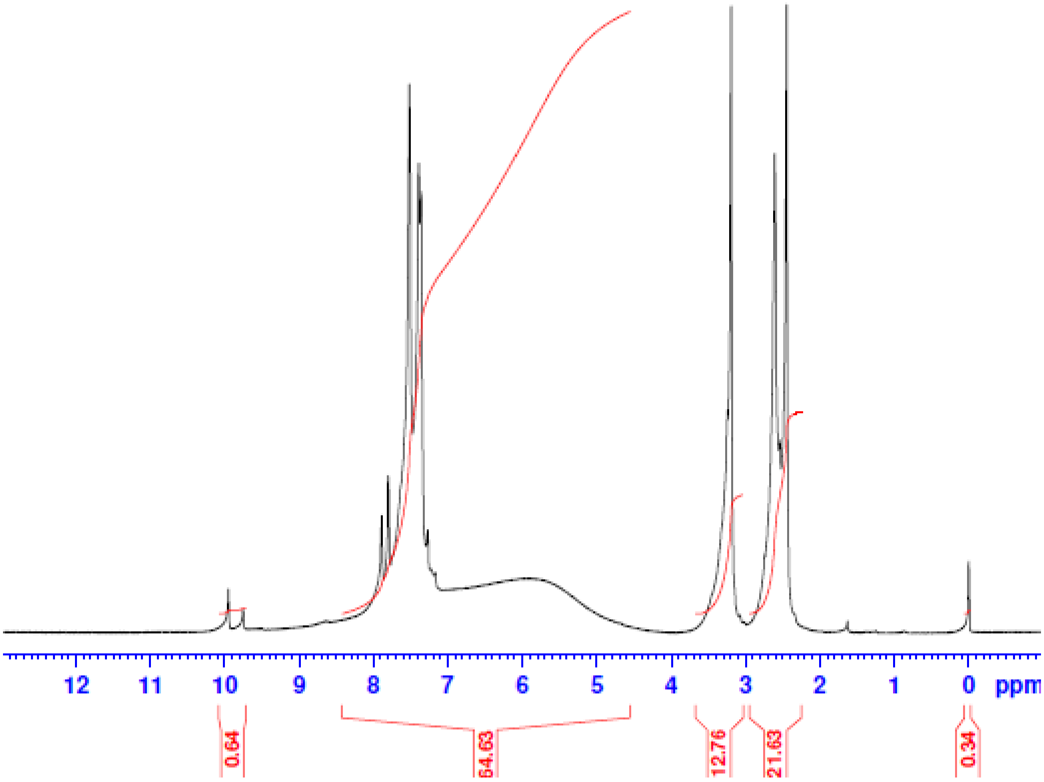

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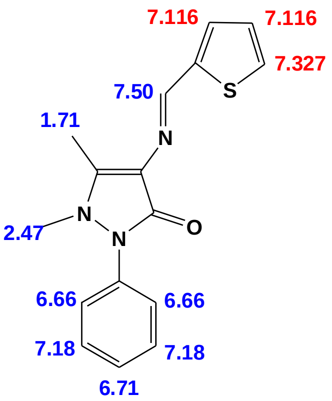
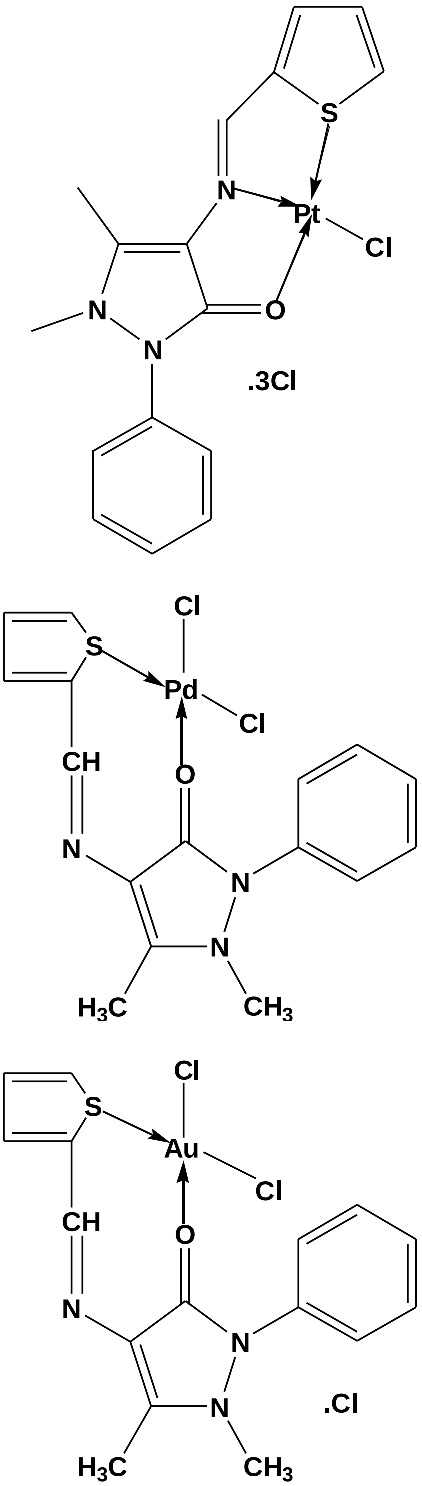
Figure 4. ^{1}H-NMR spectra of (A): Pt^{IV} complex, (B): Au^{III} complex and (C): Pd^{II} complex

Protons of methyl group attached to carbon or nitrogen atom (N-CH_3- or C-CH_3-) at δ 3.174 or 2.428 ppm, respectively, as singlet peak. The [Pt(4APT)Cl]Cl_3, [Pd(4APT)$(Cl)_2$] and [Au(4APT)$(Cl)_2$]Cl complexes have the following ^{1}H-NMR data: δ, 2.428 (3H, C-CH_3), 3.174 (3H, N-CH_3), (7.00-8.00) (3H, thiophene and 5H, Ph, aminoantipyrine) and 9.949 ppm (1H, CH=N); δ, 2.608 (3H, C-CH_3), 3.243 (3H, N-CH_3), (6.00-8.00) (3H, thiophene and 5H, Ph, aminoantipyrine) and 9.953 ppm (1H, CH=N); and δ, 2.244 (3H, C-CH_3), 2.947 (3H, N-CH_3), (7.00-8.00) (3H, thiophene and 5H, Ph, aminoantipyrine) and 10.00 ppm (1H, CH=N), respectively. On the basis of the above studies; the suggested structures of the 4APT complexes can be represented in Scheme 4.



Scheme 3. ^{1}H-NMR data of 4APT free Schiff base ligand



Scheme 4. Suggested structures of 4APT complexes

3.6. SEM, EDX and XRD spectra

The x-ray powder diffraction patterns for the new 4APT Schiff base complexes, $[Pt(4APT)Cl]Cl_3$, $[Pd(4APT)(Cl)_2]$ and $[Au(4APT)(Cl)_2]Cl$ are depicted in Fig. 5. Inspecting these patterns, we notice that the systems $[Pt(4APT)Cl]Cl_3$, $[Pd(4APT)(Cl)_2]$ and $[Au(4APT)(Cl)_2]Cl$ are well semi-crystalline, amorphous and crystalline, respectively.

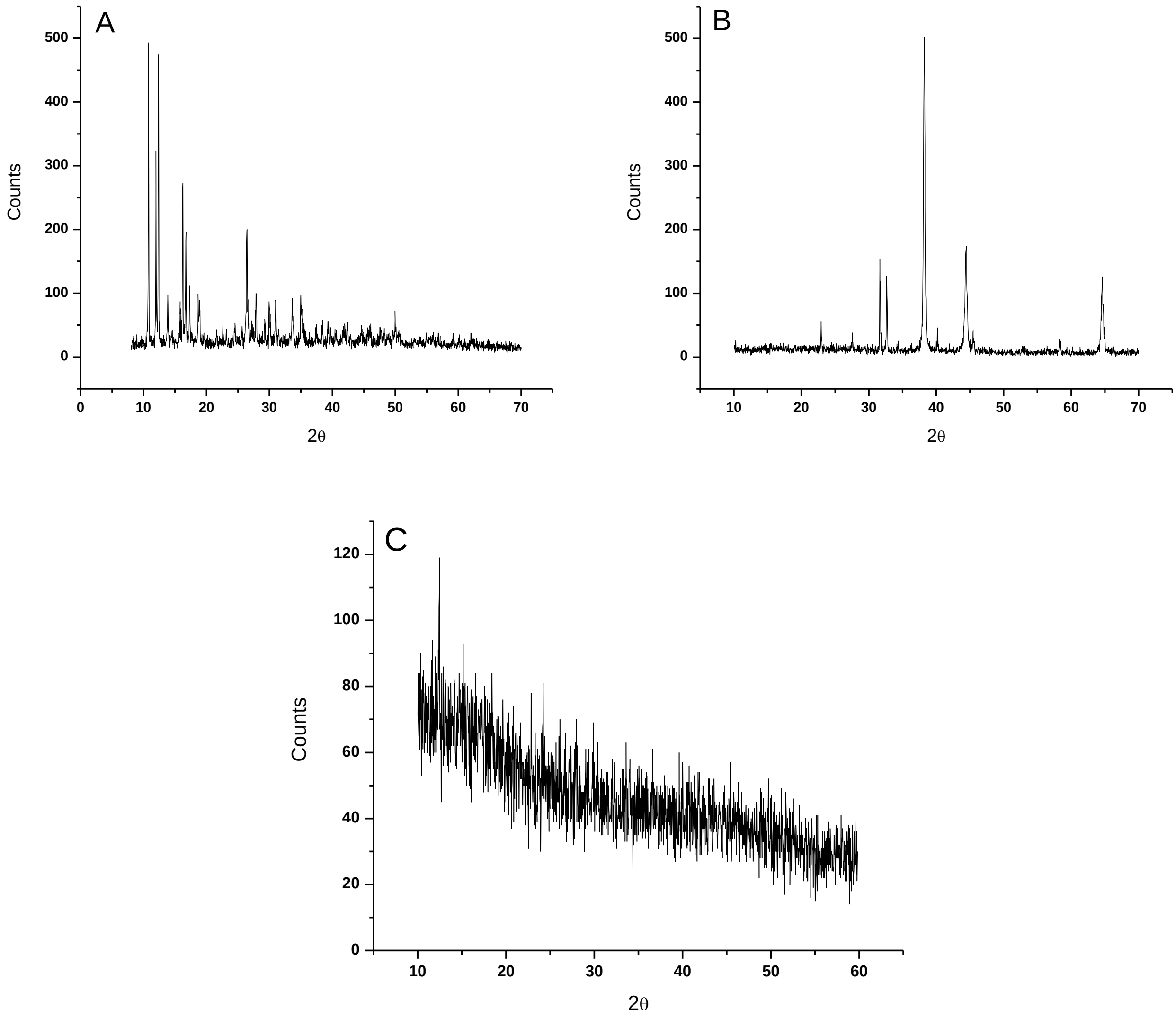
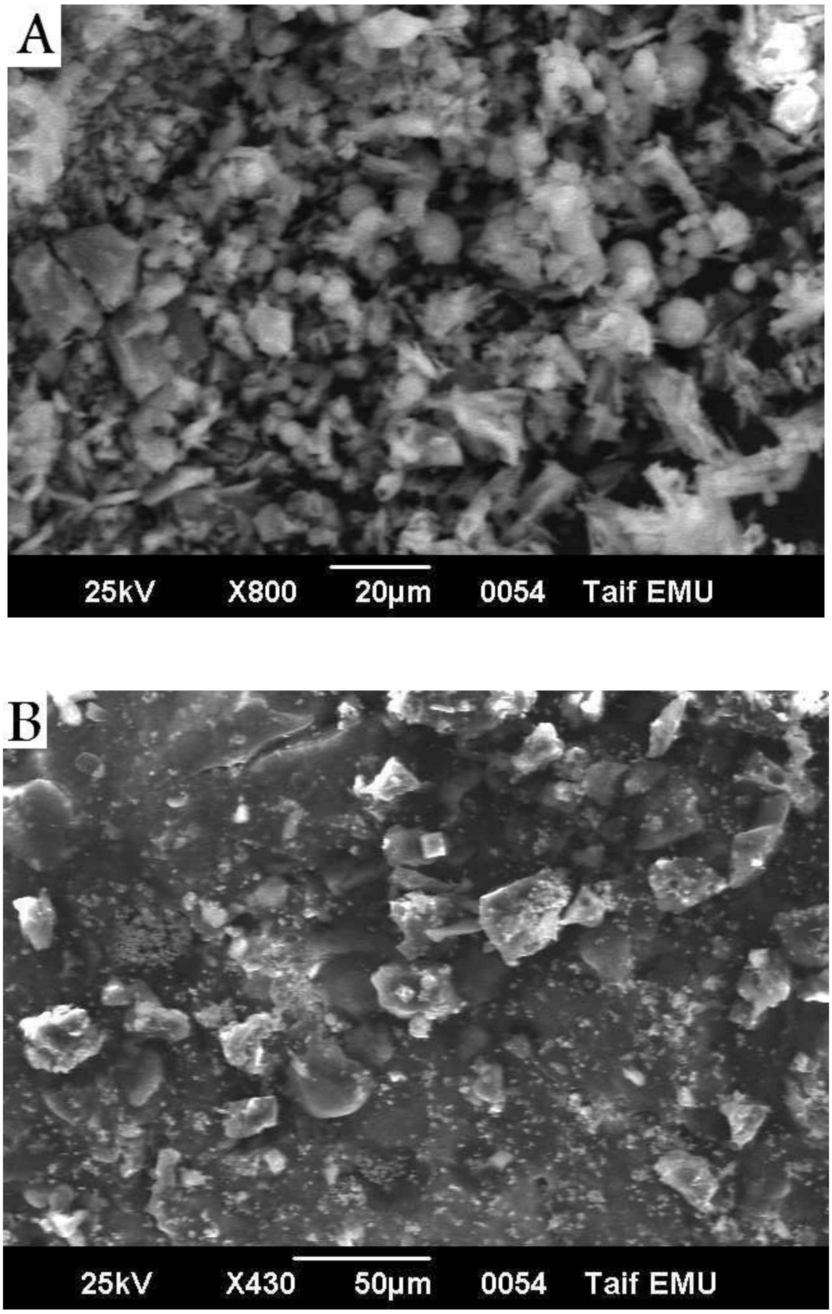


Figure 5. XRD spectra of (A): Pt^{IV} complex, (B): Au^{III} complex and (C): Pd^{II} complex

The definite diffraction data like angle ($2\theta^o$), interplanar spacing (d value, Angstrom), and relative intensity (%) have been calculated. The values of 2θ, d value (the volume average of the crystal dimension normal to diffracting plane), full width at half maximum (FWHM) of prominent intensity peak, relative intensity (%) and particle size of gold(III) and platinum(IV) complexes were estimated. The maximum diffraction patterns of Au^{III} and Pd^{II} complexes exhibited at $2\theta^o$ (Intensity (counts)) = 38(100%) and 10(100%), respectively. The crystallite size could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Deby-Scherrer equation 1 [36].

$D= K\lambda/\beta Cos\theta$ ……….. (equ. 1)

Where D is the particle size of the crystal gain, K is a constant (0.94 for Cu grid), λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size of gold(III) complex located within nano scale range. Surface image using SEM (Fig. 6) demonstrate to the structures of surface of prepared Schiff base complexes. Analysis of these images shows the size of pores to be quite different with different metal ions. The chemical analysis results by EDX for the formed Schiff base complexes show a homogenous distribution of each metal ion. SEM examinations were checked the surfaces of these Schiff base complexes that show a small to medium particles which tendency to agglomerates formation with different shapes comparison with the start materials.



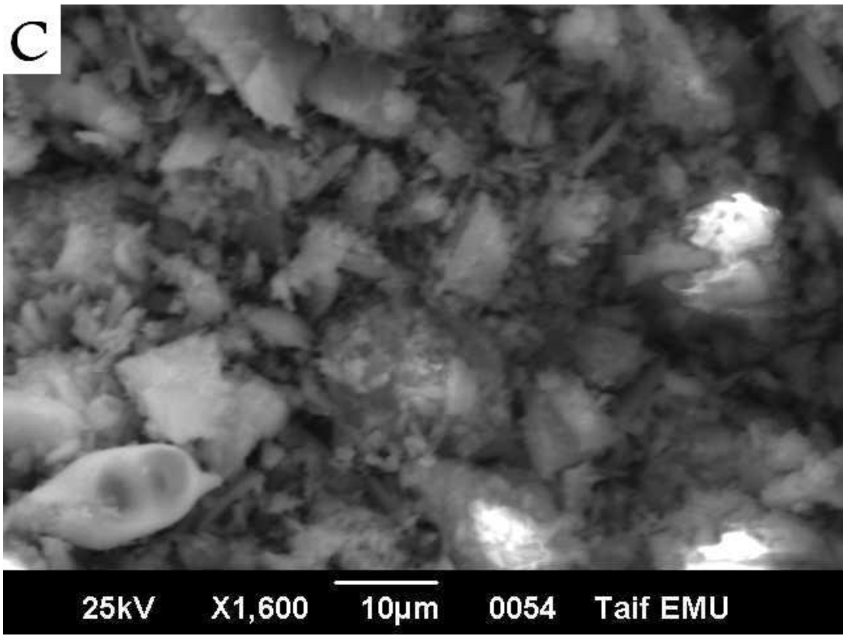
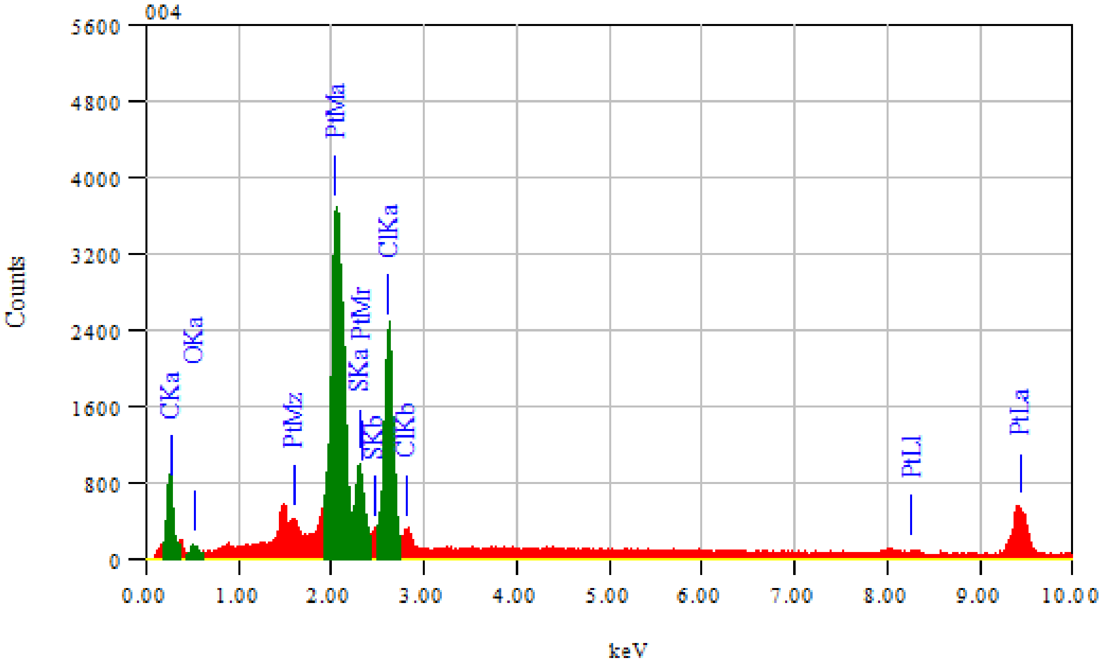


Figure 6. SEM pictures of (A): Pt^{IV} complex, (B): Au^{III} complex and (C): Pd^{II} complex

The chemical compositions of the Schiff base complexes were determined using energy-dispersive X-ray diffraction (EDX). In the EDX profile of these complexes (Fig. 7), the peaks of the essential two elements like carbon and oxygen, and respective gold(III), palladium(II) and platinum(IV) elements, which constitute the molecules of [Pt(4APT)Cl]Cl$_3$, [Pd(4APT)(Cl)$_2$] and [Au(4APT)(Cl)$_2$]Cl complexes, are clearly identified confirming the proposed structures.



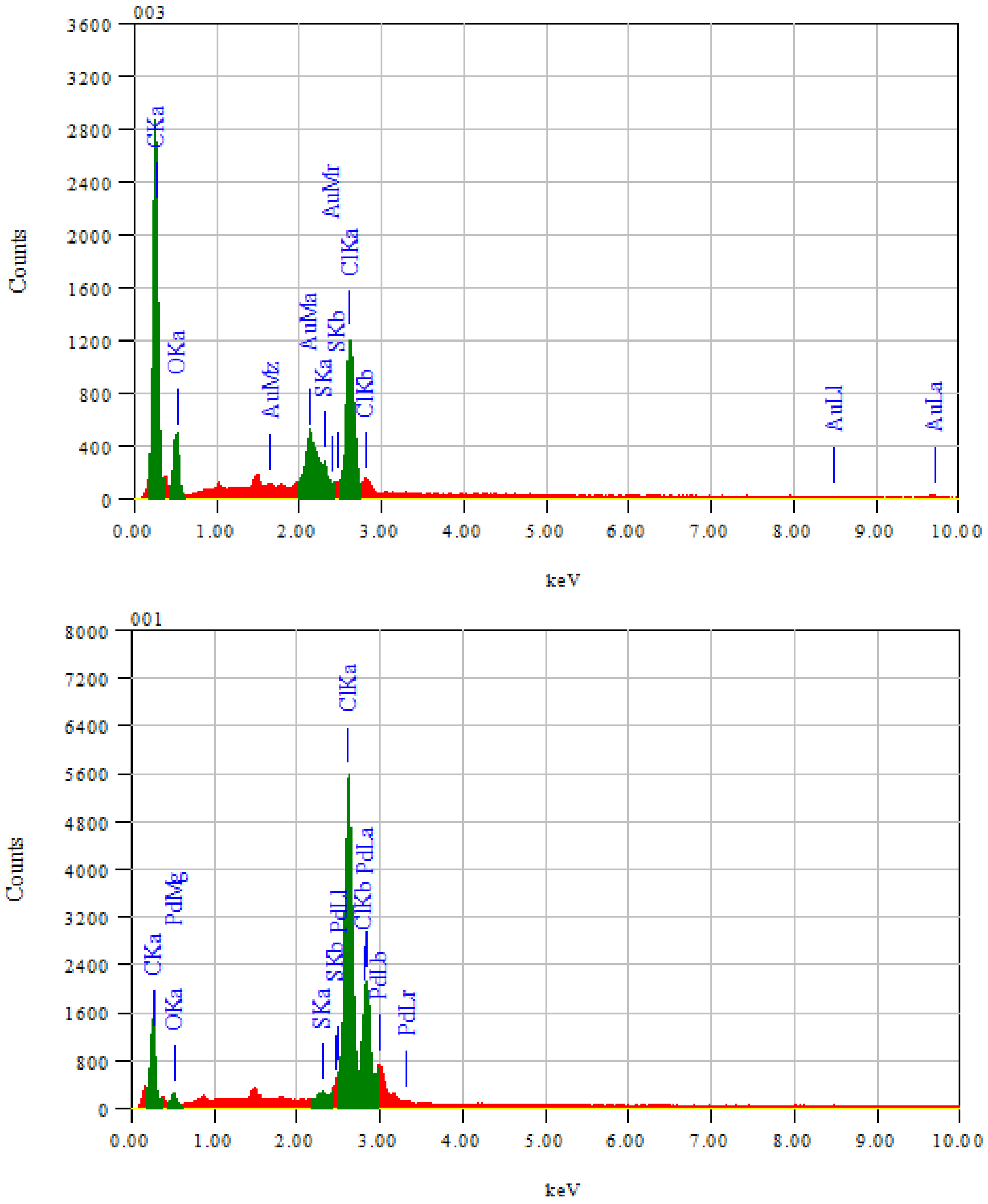


Figure 7. EDX analyses of (A): Pt^{IV} complex, (B): Au^{III} complex and (C): Pd^{II} complex

3.7. Thermo gravimetric analysis

Figure 8 and table 4 give the maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of the Pt(4APT)Cl]Cl$_3$, [Pd(4APT)(Cl)$_2$] and [Au(4APT)(Cl)$_2$]Cl complexes. The decomposition occurs in at least three major detectable steps, each step does not referred in generally to single process but rather is reflects of two or three overlapping process and attributed to the ligand alone or companied by chlorine atoms. The data obtained support the proposed structure and indicate that Pt(IV) complex undergo three steps degradation reaction, the first step occur at maximum peak lying in 142 ^{o}C, the weight loss associated with this step agrees quite well with the loss two terminal methyl groups in 4-amino antipyrine moiety and one chlorine atom, the second step occur at T_{max} 291 °C, and it referred to loss three of chlorine atoms, and the third decomposition step referred to a single process but its reflective of two or three overlapping processes and attributed to loss of the 4-amino antipyrine and thiophene moieties. The residual is in agreement with Pt metal.

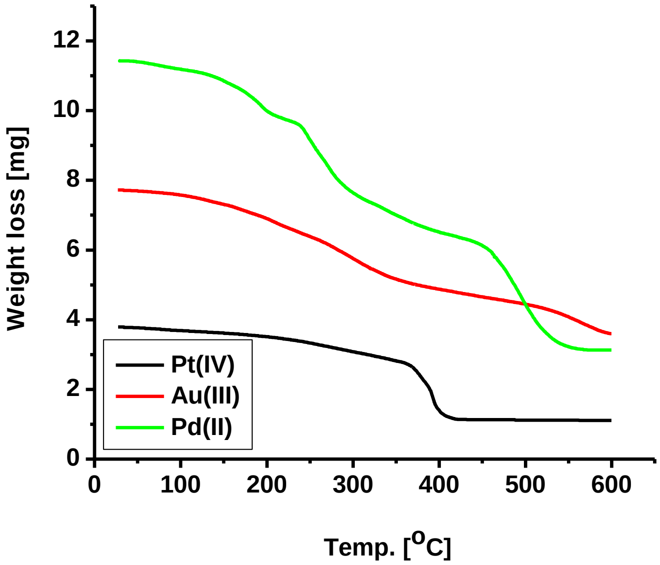


Figure 8. TG curves of Pt^{IV} , Au^{III} and Pd^{II} complexes

Table 4. Thermal data of the 4APT Schiff base metal complexes

Compounds	Steps	DTG Peak/ °C	TG mass loss/ %	Assignments
Pt^{IV}	1st	142	8.413	$2CH_3 + Cl$
	2nd	291	17.884	3Cl
	3rd	390	43.968	Thiophene + 4-amino antipyrine (decomposed)
	Residue			Pt metal + residual carbon
Au^{III}	1st	101	4.504	Cl
	2nd	190	11.843	Thiophene + 4-amino antipyrine rings + 2Cl
	3rd	298	20.515	
	4th	515	16.166	
	Residue			Au metal + residual carbon
Pd^{II}	1st	60	2.520	CH_3
	2nd	145	4.016	Thiophene + 4-amino antipyrine rings + 2Cl
	3rd	187	8.303	
	4th	262	25.311	
	5th	487	32.441	
	Residue			PdO + residual carbon

The thermal decomposition of Au(III) complex may be characterized as a four decomposition steps in temperature range 86-587 °C, the first stage 86-127 °C (T_{max} = 101 °C) is due to initial decomposition of this complex with mass lose 4.504% for one chlorine atom and concerning second, third and fourth decomposition steps at 174-277 ^{o}C (T_{max}= 190 ^{o}C) with mass loss of 11.843%, and 267-587 ^{o}C (T_{max}= 298 and 515 ^{o}C) with mass loss of 36.681% assigned to liberated two chlorine atoms and thiophene + amino antipyrine moieties. The residual is in agreement with gold metal attached with polluted carbon atoms. For the pd(II) complex the first mass loss is due to losses one methyl group and occurs between 50 ^{o}C and 78 ^{o}C, and has loss of 2.520%, then, the rest of thiophene, antipyrine, and two chlorine atoms decomposed in the second-to-fifth stage between 136 and 529 ^{o}C with mass loss 70.071% The residual is in agreement with PdO contaminated with few carbon atoms.

3.8. Calculation of activation thermodynamic parameters

The thermodynamic activation parameters of decomposition processes of $[Pt(4APT)Cl]Cl_3$, $[Pd(4APT)(Cl)_2]$ and $[Au(4APT)(Cl)_2]Cl$ complexes, namely activation energy (E*), enthalpy (ΔH*), entropy (ΔS*), and Gibbs free energy change of the decomposition (ΔG*), were evaluated graphically by employing the Coats-Redfern relation [37]. The entropy of activation (ΔS*), enthalpy of activation (ΔH*), and the free energy change of activation (ΔG*) were calculated using the following equations:

$$\Delta S^* = 2.303[\log(Ah/kT)]R \text{ ……….. (equ. 2)}$$

$$\Delta H^* = E^* - RT \text{ ……….. (equ. 3)}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \text{ ……….. (equ. 4)}$$

Table 5. Kinetic thermodynamic data of 4APT Schiff base metal complexes Coats–Redfern equation

Complex	stage	parameter					r
		*E**	*A*	Δ*S**	Δ*H**	Δ*G**	
		(J mol^{-1})	(s^{-1})	(Jmol^{-1}K^{-1})	(J mol^{-1})	(J mol$^{-1)}$	
Pt^{IV}	1st	7.66×10^{4}	2.67×10^{9}	-6.50×10^{1}	6.79×10^{4}	8.87×10^{4}	0.9963
Au^{III}	1st	5.47×10^{5}	4.97×10^{6}	-1.17×10^{2}	5.20×10^{4}	8.93×10^{4}	0.9960
Pd^{II}	1st	4.37×10^{5}	1.57×10^{4}	-1.07×10^{2}	4.11×10^{4}	8.88×10^{4}	0.9947

The data are summarized in Tables 5. The activation energies of decomposition were in the range 43.7-76.6 kJ mol^{-1}. The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation had negative values in all the complexes, which indicates that the decomposition reactions proceed with a lower rate than the normal ones.

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