Synthesis, characterization and antibacterial studies of new complexes of 2-(4-Chlorophenyl)-2-[(2,4-Dimethyl-phenyl)amino] acetonitrile with some metal ions

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Abstract

New metal ion complexes of some transition metal ions [Cr(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] of previously prepared ligand2-(4-chlorophenyl)-2-[(2,4-dimethylphenyl)amino]acetonitrile were synthesized. Ligand prepared by Strecker's procedure included the reaction of P-chlorobenzaldehyde with 2,4-Dimethyl aniline and the structures of the new metal complexes were characterized by Elemental Micro Analysis (C.H.N), Chloride Content, FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-Vis spectra, Thermal Gravimetric Analysis (TGA-DTG), Flame Atomic Absorption, Molar Conductivity as well as Magnetic Susceptibility measurement. According to the obtained data, the probable coordination geometries of these complexes were suggested as octahedral. All complexes were found to be non-electrolyte except C_1.

The antibacterial activity of the ligand and its metal ion complexes have been studied by screening against various microorganisms: Staphylococcus aureus, Bacillus subtilis (Gram-positive), Escherichia and Pseudomonas aeruginosa (Gram-negative). Agar (well-diffusion method) was used to determine the activity. The metal ion complexes gave the suggested formulas: $[ML_2Cl_2].nH_2O$ and $[CrL_2Cl_2]Cl.nH_2O$.

Keywords: 2-(4-chlorophenyl)-2-[(2,4-dimethylphenyl) amino] *acetonitrile*, Transition, metal ions, 2,4-Dimethyl aniline.

Introduction

The Strecker reaction was a milestone in organic synthesis and is still the classical method used to obtain α-aminonitriles[1] which in turn are very important precursors of natural and non-natural α-amino acids[2],1,2-amino alcohols, 1,2-diamines and intermediates for several transformations[3]. α-aminonitrile compounds and their derivatives has received special attention because of their application as potential ligands for a large number of metal ions[4].

Nitriles and α-aminonitrile derivatives had biological activities as herbicides[5], pharmacological agents[6] and biological synthesis of chemical compounds by its microbial metabolism in some organisms[7]. α-Aminonitriles among many other ligands are known to be bidentate ligands, which coordinate to the metal ions through the nitrogen of the nitrile group and that of amine group[8]. Complexes with dinitrogen N2 ligand are of interest not only theoretically but also from a practical point of view. They have found application as antitumor activity[9], antibacterial activity and antiviral activity in agriculture field[10].

Material and Methods

Materials: The chemicals used included 4-chlorobenzaldehyde (HiMedia), 2,4-Dimethyl aniline (Fluka), $CrCl_3.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.2H_2O$, $HgCl_2$ and NaCN (BDH). The organic solvents which were used included Ethanol 95% (Analar), Absolute ethanol, Glacial acetic acid, Dimethyl sulphoxide (BDH) and Petroleum ether (30-60ºC) (SCR-China).

Synthesis of Ligand: Sodium cyanide (0.098gm, 0.002mol) was dissolved in 4mL of distilled water and cooled below 5°C. To this solution, 4-chlorobenzaldehyde (0.281gm, 0.002mol) in 12mL of 95% ethanol was added. The mixture was stirred maintaining temperature below 5°C. Glacial acetic acid (0.12gm, 0.002mol) was added with constant stirring keeping temperature below 5°C, this was followed by the addition of primary amine (2,4-Dimethyl aniline) (0.002mol, 0.242gm) in 10mL of 95% ethanol and 5mL of glacial acetic acid (cooled below 5°C) with continuous stirring in well ventilated hood.

During addition, temperature was maintained at 15°C. The mixture was stirred for 2 hrs. and it was kept at room temperature for 24 hrs. The obtained compound was pale yellow and was washed with dilute hydrochloric acid (0.2M) to remove any excess of cyanide. The compound was re-crystallized with 95% ethanol[11]. The yield percentage of this procedure was 85.8%. The synthesis route of the ligand was illustrated in reaction equation 1.

Synthesis of complexes: A solution of 0.541gm, 0.002mol of the ligand (L) in 10mL of absolute ethanol was added drop wise to warm solution (0.001mol) of metal chlorides (0.267gm, 0.238gm, 0.170gm, 0.136gm, 0.219gm and 0.271gm for $CrCl_3.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.2H_2O$ and $HgCl_2$ respectively) which were dissolved in 20 mL absolute ethanol and the mixture was refluxed for 4 hrs. Some complexes were gummy precipitate and were treated with 30-60 ºC petroleum ether for several times. The resulting complexes were filtered and washed several times with absolute ethanol until the filtrates become clear. The solid complexes were then dried in desiccators over anhydrous calcium chloride.

Results and Discussion

Microanalysis: The importance of preparing α-aminonitrile ligand compounds arises from their versatility as starting materials for the synthesis of many compounds. The structures of the prepared α-aminonitrile ligand with its metal ion complexes were identified by C.H.N. (table 1), FT-IR (table 2), UV-visible (table 3), ^{1}H-NMR (table 4), ^{13}C-NMR (table 5), (TGA-DTG) (table 6) and X-Ray diffraction (table 7) with some other techniques. Important characteristic stretching frequencies of the ligand and its metal ion complexes are described in table 2 and their spectra are shown in figures 1 to 7. 2-(4-chlorophenyl)-2-{(2,4-dimethylphenyl) amino} acetonitrile (L) as a bidentate ligand normally coordinates with metal ions through nitrogen of the nitrile group and the nitrogen of the υ(N-H) group[12].

The bands related to υ(C≡N) stretching vibration of the free ligand (L) appeared at 2167 cm^{-1}. The band related to υ(N-H) stretching vibration appeared at 3475 cm^{-1}.[13] The bands related to υ(C≡N) stretching vibrations of the complexes were shifted to higher frequencies 2204, 2181, 2349, 2374, 2175, 2171 cm^{-1} respectively of the complexes C_1, C_2, C_3, C_4, C_5 and C_6 as a result of coordination with metal ions through the lone pair electrons of nitrogen atom[14]. The band at (1623) cm^{-1} which was assigned to the δ(N-H) bending vibration of δ(N-H) group of (L) was shifted in the spectra of complexes C_1- C_6 to 1625, 1627, 1627, 1625, 1625 and 1625 cm^{-1} respectively.

The peaks which appeared at 314, 349, 314, 356, 373 and 337 cm^{-1} respectively of complexes (C_1- C_6) were attributed to υ (M-Cl), while the peaks at (437, 406, 405, 410, 406 and 406) cm^{-1} respectively refer to υ(M-N)[15]. This is in support of the complex's formation.

Molar conductance measurement: The molar conductance values of the synthetic complexes obtained in DMSO as a solvent at room temperature were listed in table 3. The results which are given in this table showed that all complexes have non-electrolytic nature except (C_1)[16].

Electronic spectra (UV-visible) studies: The UV-visible spectra of the ligand (L) showed intense bands at 29940 and 37453 cm^{-1} which belonged to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ respectively. The two bands were attributed to conjugate of nitrile group and aromatic ring[17,18] as shown in table 3. The electronic spectra of the ligand complexes were recorded for their solution in DMSO at room temperature (10^{-4}M). The electronic spectrum of the (C_1) complex showed three bands (*d-d* transition) observed at 13440, 18552 and 27624 cm^{-1}; these bands may be assigned to the transitions $\upsilon_1[^4A_2g \rightarrow {}^4T_2g)]$, $\upsilon_2[^4A_2g \rightarrow {}^4T_1g(F)]$ and $\upsilon_3[^4A_2g \rightarrow {}^4T_1g(P)]$ respectively. The magnetic moment values (4.0) B.M. suggested octahedral complex[19]. The spectrum of the (C_2) complex showed three bands (*d-d* transition) observed at 12738, 14880 and 17452 cm^{-1}; these bands may be assigned to the transitions $\upsilon_1[(^3A_2g \rightarrow {}^3T_2g(F)]$, $\upsilon_2[^3(A_2g(F) \rightarrow {}^3T_1g(F)]$ and υ_3 $[^3A_2g\ (F) \rightarrow {}^3T_1g(P)]$ respectively[20]. The value of magnetic moment is 2.9 B.M.

The spectra of (C_3) complex showed one band (*d-d* transition) observed at 23529 cm^{-1}; this band may be assigned to the transition $[^2Eg \rightarrow {}^2T_2g]$. The magnetic moment value (1.80) B.M. was in accordance with those having distorted octahedral structure[21]. Since the UV-visible spectrum of (d^{10}) ion gave a lot of information about some shifting and changes in the shape of the bands were compared with those of the ligand[22]. The electronic spectra of these complexes exhibited charge transfer from (M→L) as tabulated in table 3. Zn(II), Cd(II) and Hg(II) complexes are diamagnetic. The spectra of the ligand and complexes are shown in figures 8 to 14. According to the empirical formulae, an octahedral geometry was proposed for these complexes.

^{1}H-NMR and ^{13}C-NMR spectra: The ligand was characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopic methods, in addition of some complexes using DMSO d^6 as a solvent. The ^{1}H-NMR spectrum of the ligand (L) showed six peaks; the first one appeared at 1.56 ppm which corresponded to the (-C$\underline{H}_3$) protons and the peak at 2.27 ppm back to the second group of -C$\underline{H}_3$. The third one appeared at ~2.5 ppm and was assigned to the solvent peak (DMSO). The fourth peak appeared at (3.40) ppm and corresponded to the (-N-$\underline{H}$) proton, the fifth peak appeared at 5.59 ppm which was attributed to the (-C$\underline{H}$-C≡N) proton and the last peak appeared at 6.99−8.51 ppm which corresponded to the aromatic protons[23].

The ^{1}H-NMR spectra of the complexes C_1, C_2, C_3, C_4, C_5 and C_6 were also similar to that of the ligand, the only difference was that the signal of (N-$\underline{H}$) of the ligand shifted in these complexes by 0.03, 0.10, 0.05, 0.03, 0.04 and 0.05 ppm respectively and the signal of (-C$\underline{H}$-C≡N) shifted in these complexes by 0.46, 0.37, 0.37, 0.39, 0.32 and 0.34 ppm respectively, this gave an indication for complexes formation. The ^{1}H-NMR data were listed in table 4 and shown in figures 15 to 21. The ^{13}C-NMR spectrum of the ligand (L) showed five peaks; the first and second peaks appeared at δ 18.33 and 21,53 ppm corresponding to the groups of (-$\underline{C}H_3$). The third peak at ~40 corresponded to the solvent (DMSO), the fourth peak appeared at 58.04 ppm which corresponded to the (-$\underline{C}$H-C≡N) carbon, the last peak appeared at 118.27 ppm and was assigned to the (-CH-$\underline{C}$≡N) carbon atom[24].

The ^{13}C-NMR spectra of the complexes (C_2, C_4, C_5 and C_6) were similar to that of the ligand, the only difference was that the signal of (-$\underline{C}$H-C≡N) carbon of the ligand was shifted in these complexes by 1.7, 0.8, 1.95 and 0.99 ppm respectively. The signal of (-CH-$\underline{C}$≡N) carbon was shifted in these complexes by 0.1, 0.26, 0.07 and 0.19 ppm respectively. The ^{13}C-NMR data were listed in table 5 and shown in figures 22 to 26.

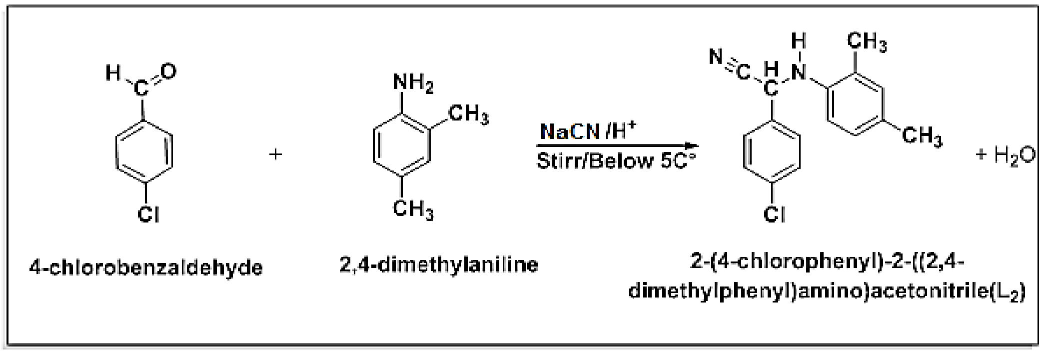
Thermal analysis of the metal ion complexes: TGA and DTG of the complexes were studied under nitrogen gas at heating range (25-800)°C and heating rate (10ºC/min). The thermal analysis was performed to prove the suggested structures and study the thermal stability of the complexes. The results were listed in table 6 and shown in figures 27 to 32.

X-Ray diffraction: X-ray powder diffraction pattern of the ligand (L) and the metal ion complexes were carried out in the range of $3° < 2\theta < 70°$ in order to give an insight about the lattice dynamics of these complexes. The X-ray powder diffraction obtained reflects a shadow on the fact that each solid represents a definite compound of a definite structure which is not contaminated with the starting materials. The metal ion complexes show sharp crystalline XRD patterns which differ considerably from that of the ligand. The appearance of crystallinity in the metal ion complexes is due to the inherent crystalline nature of the metallic compounds[25]. The XRD patterns of the complexes showed shift in peaks of Bragg angle of the ligand (L), this gave an indication that the metal ions interact with the crystalline structure of the ligand and new phases were formed (table 7).

***In vitro* antibacterial activity:** The antibacterial activities of the ligand (L) and all complexes were screened against test bacteria namely; *Staphylococcus aurous, Bacillus subtilis* (Gram+), *Escherichia* and *Pseudomonas aerugin* (Gram-). Agar, well-diffusion method was used to determine the activity[26,27]. Borer of 0.6 mm diameter was used; the concentration of all complexes was 10^{-3}M using DMSO (dimethyl sulphoxide) as a solvent and was used as a control gram negative while tetracycline was used as a control gram positive. The solvent (DMSO) showed no activity against the tested bacteria, while some of the prepared complexes showed good results.

Table 8 shows the inhibition zones of the solvent, ligand and the prepared complexes. The inhibition zones were measured in mm and compared to the inhibition zone of antibiotic (Tetracycline). The ligand showed inhibition towards *Pseudomonas aeruginosa* only, but it is no activity to other bacterial**.** In some cases, the metal ion complexes are more active than the ligand expectedly due to chelation, which reduced the polarity of the metal atom, mainly because of partial sharing of its positive charge with donor groups of the ligand and possible π-electron delocalization on the aromatic rings.

This increased the lipophilic character, favoring its permeation into the bacterial membrane, causing the death of the organisms[28]. When the antimicrobial activity of metal ion complexes was investigated, the following principal factors[29] should be considered: (i) the chelate effect of the ligand; (ii) the nature of the N-donor ligand; (iii) the total charge of the complex; (iv) the existence and the nature of the ion neutralizing the ionic complex and (v) the nuclearity of the metal center in the complex. In general, most of the complexes exhibit better inhibition than the free ligand (L) against *Bacillus subtilis*, *Staphylococcus aureus*, *Beisseria gonorrhoeae* and *Escherichia coli.*



Equation 1: Preparation of 2-(4-chlorophenyl)-2-[(2,4-dimethylphenyl) amino] acetonitrile (L)

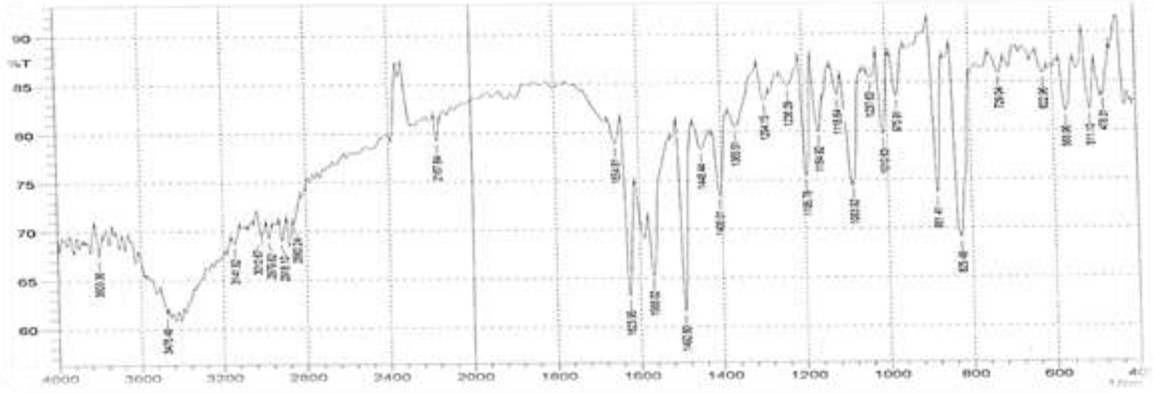


Fig. 1: FT-IR spectrum of the ligand (L)

Table 1
Elemental, micro analysis and some physical properties of the ligand and the prepared complexes

Comp.	**Formula M.w.t (gm/mol)**	**Yield %**	**Color**	**M.P (°C)**	**C % Cal (Found)**	**H % Cal (Found)**	**N % Cal (Found)**	**M % Cal (Found)**	**Chloride % Cal (Found)**
L	$C_{16}H_{15}ClN_2$ (270.76)	85.80	Pall-Yellow	130-134	70.91 (70.17)	5.54 (5.50)	10.34 (9.94)	-----	13.11 ------
C_1	$]CrL_2Cl_2[Cl.3H_2O$ (753.91)	88.00	Light-green	278-282	50.93 (50.00)	4.81 (4.83)	7.43 (6.90)	6.90 (6.65)	23.51 (23.29)
C_2	$]NiL_2Cl_2[1.5H_2O$ (698.14)	89.00	Greenish-yellow	210 Dec.	55.00 (54.80)	4.76 (4.32)	8.03 (7.76)	8.41 (7.58)	20.31 (20.18)
C_3	$]CuL_2Cl_2[H_2O$ (693.98)	81.33	Black	300-304	55.33 (54.97)	4.65 (4.43)	8.07 (7.90)	8.70 (8.43)	19.16 (19.00)
C_4	$]ZnL_2Cl_2[2.H_2O$ (713.83)	90.00	Light - Yellow	255-259	53.79 (53.40)	4.80 (4.42)	7.85 (7.78)	9.16 (9.00)	19.87 (19.54)
C_5	$]CdL_2Cl_2[2.H_2O$ (760.86)	81.00	Light - Yellow	280-284	50.47 (50.20)	4.50 (4.13)	7.36 (7.14)	14.77 (14.60)	18.64 (18.34)
C_6	$]HgL_2Cl_2[1.68\ H_2O$ (843.28)	67.00	Off-White	235 Dec.	45.54 (45.04)	3.99 (3.64)	6.64 (6.52)	23.79 (24.00)	16.82 (16.67)

Dec. = Decomposed

FT-IR spectral studies

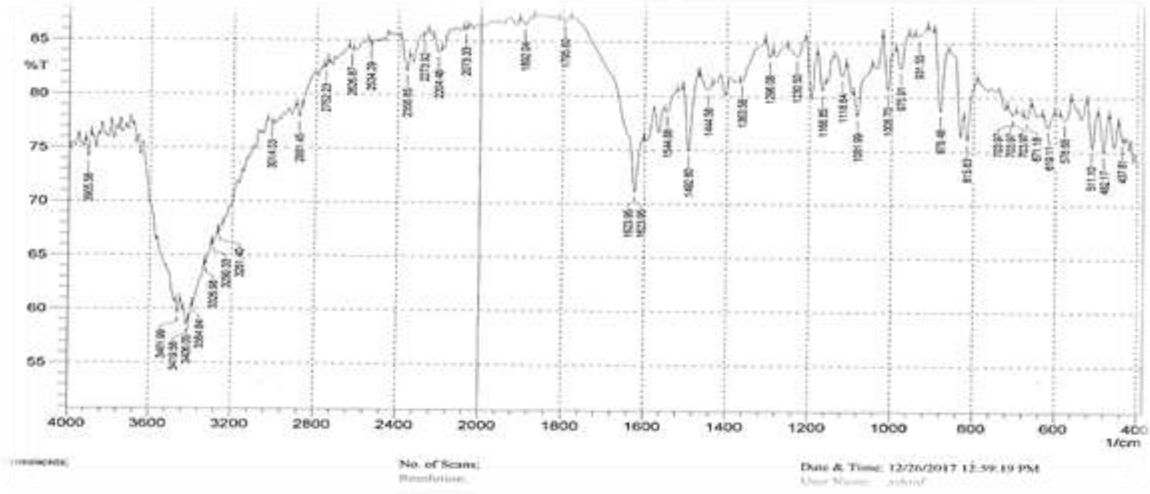


Fig. 2: FT-IR spectrum of C_1 complex

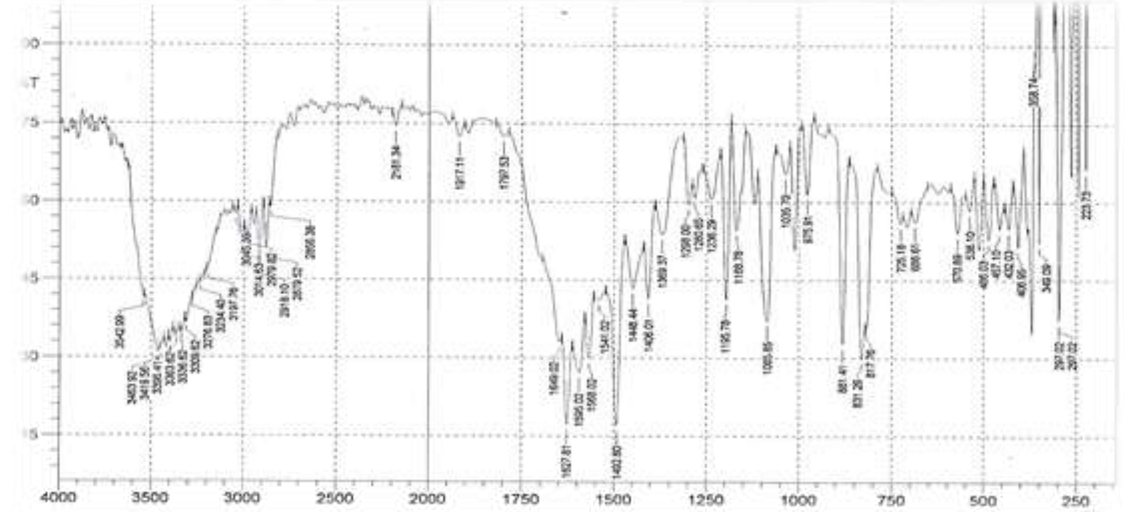


Fig. 3: FT-IR spectrum of C_2 complex

Table 2
FT-IR spectra of the ligand (L) and its metal ion complexes

Comp.	υ(N−H) cm^{-1}	υ(C≡N) cm^{-1}	δ(N−H) cm^{-1}	υ (C-N) cm^{-1}	υ(M-N) cm^{-1}	υ(M-Cl) cm^{-1}
L	3475 w.sh	2167 m.sh	1623 s.sh	1118 m.sh	------	------
C_1	3406 w.br	2204 m.br	1624 s.sh	1008 m.sh	349 m.sh	297 v.s.sh
C_2	------	2181 s.sh	1627 m.sh	1085 s.sh	406 m.sh	349 v.s.sh
C_3	3344 w.br	2349 w.br	1627 m.br	1089 m.br	405 w.sh	314 v.s.sh
C_4	3398 w.sh	2374 w.br	1625 s.sh	1083 s.sh	410 m.sh	356 v.s.sh
C_5	3319 w.br	2175 w.br	1625 s.sh	1085 s.sh	406 m.sh	373 v.s.sh
C_6	3294 m.sh	2171 w.br	1625 m.sh	1085 s.sh	406 m.sh	337 v.s.sh

Where: s= strong, m= medium, w= weak, v= very, br= broad, sh= sharp

Table 3
Electronic spectra, spectra parameter and magnetic susceptibility molar conductance and suggested stereo chemical of the ligand and its metal ion complexes

Comp.	Wavelength λ(nm)	Wave no. ῡ (cm^{-1})	Assignment	Molar Cond. S.cm^2 moL^{-1}	µ eff (B.M)	Geometry Suggested
L	334 267	29940 37453	n→π* π→π*	……..	……..	……..
C_1	744 539 362	13440 18552 27624	$^{4}A_{2}g\rightarrow{}^{4}T_{2}g$ $^{4}A_{2}g\rightarrow{}^{4}T_{1}g(F)$ $^{4}A_{2}g\rightarrow{}^{4}T_{1}g(P)$	34.0	4.0	Octahedral
C_2	785 672 573	12738 14880 17452	$^{3}A_{2}g(F)\rightarrow{}^{3}T_{2}g(F)$ $^{3}A_{2}g(F)\rightarrow{}^{3}T_{1}g(F)$ $^{3}A_{2}g(F)\rightarrow{}^{3}T_{1}g(P)$	7.3	2.9	Octahedral
C_3	425	23529	$^{2}Eg\rightarrow{}^{2}T_{2}g$	4.9	1.8	Distorted Octahedral
C_4	335 264	29850 37878	C.T (M→ L)	3.6	Diam.	Octahedral
C_5	487 318 233	20533 31446 42918	C.T (M→ L)	2.8	Diam.	Octahedral
C_6	325 269	30769 37174	C.T (M→ L)	11.0	Diam.	Octahedral

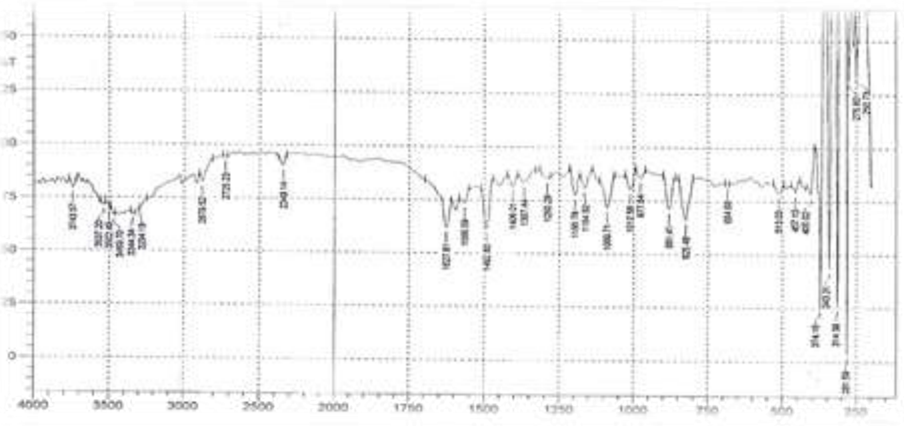


Fig. 4: FT-IR spectrum of C_3 complex

Table 4
^{1}H-NMR data of the ligand (L) and the metal ion complexes

Comp.	Formula	Groups	Chemical Shifts δ(ppm) ^{1}H-NMR
L	$C_{16}H_{15}ClN_2$ (270.76)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	1.56 2.27 3.40 5.59 6.99-8.51
C_1	$]CrL_2Cl_2[Cl.3H_2O$ (753.91)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	2.14 2.26 3.37 6.05 7.04-8.54
C_2	$]NiL_2Cl_2[1.5H_2O$ (698.14)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	2.02 2.32 3.3 5.96 6.98-8.46
C_3	$]CuL_2Cl_2[H_2O$ (693.98)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	2.18 2.33 3.35 5.96 7.22-9.94
C_4	$]ZnL_2Cl_2[\ .2H_2O$ (713.83)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	1.75 2.27 3.37 5.98 6.99-8.51
C_5	$]CdL_2Cl_2[\ .2H_2O$ (760.86)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	1.81 2.27 3.36 5.91 6.99-8.51
C_6	$]HgL_2Cl_2[\ 1.68H_2O$ (843.28)	$(-C\underline{H}_3)$ $(-C\underline{H}_3)$ $(-N\underline{H})$ $(-C\underline{H}-C\equiv N)$ $(Ar-\underline{H})$	2.13 2.27 3.35 5.93 6.99-8.51

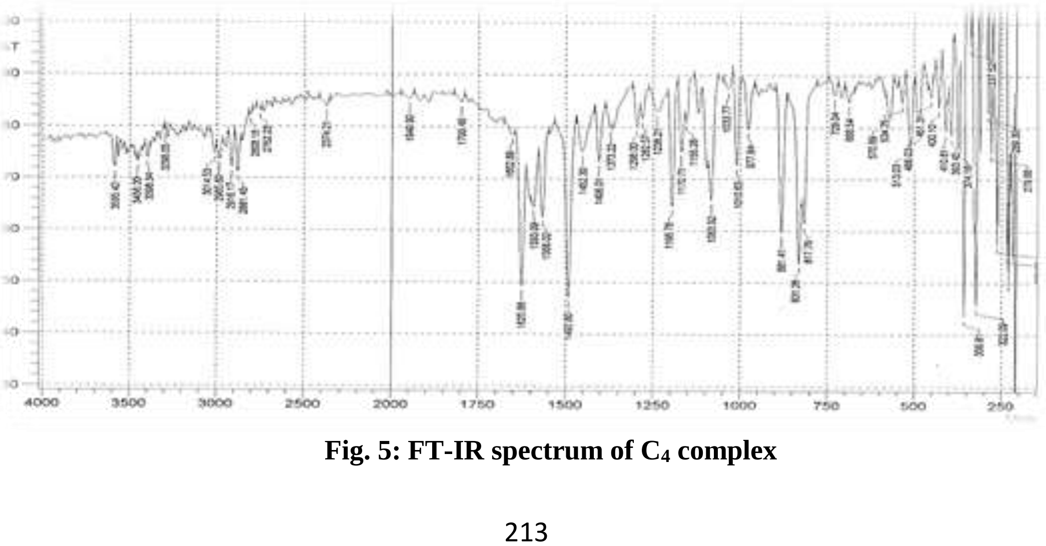


Fig. 5: FT-IR spectrum of C_4 complex

Table 5
^{13}C-NMR data of the ligand (L) and some metal ion complexes

Comp.	Formula	Groups	Chemical Shifts δ(ppm) ^{13}C-NMR
L	$C_{16}H_{15}ClN_2$ (270.76)	$(-\underline{C}H_3)$ $(-\underline{C}H_3)$ $(-\underline{C}H-C\equiv N)$ $(-CH-\underline{C}\equiv N)$	18.33 21.53 58.04 118.27
C_2	$]NiL_2Cl_2[1.5H_2O$ (698.14)	$(-\underline{C}H_3)$ $(-\underline{C}H_3)$ $(-\underline{C}H-C\equiv N)$ $(-CH-\underline{C}\equiv N)$	18.43 21.36 59.36 118.37
C_4	$]ZnL_2Cl_2[2H_2O$ (713.83)	$(-\underline{C}H_3)$ $(-\underline{C}H_3)$ $(-\underline{C}H-C\equiv N)$ $(-CH-\underline{C}\equiv N)$	18.36 21.43 57.24 118.01
C_5	$]CdL_2Cl_2[2H_2O$ (760.86)	$(-\underline{C}H_3)$ $(-\underline{C}H_3)$ $(-\underline{C}H-C\equiv N)$ $(-CH-\underline{C}\equiv N)$	18.37 21.43 59.99 118.34
C_6	$]HgL_2Cl_2[1.68H_2O$ (843.28)	$(-\underline{C}H_3)$ $(-\underline{C}H_3)$ $(-\underline{C}H-C\equiv N)$ $(-CH-\underline{C}\equiv N)$	17.98 21.45 59.03 118.46

Table 6
Thermal decomposition data of the metal ion complexes

Comp.	Molecular formula	Step	Temp. range of the Decomposition °C	Suggested Formula of loss	Mass loss%	
					Cal.	Found
C_1	$]CrL_2Cl_2[Cl.3H_2O$ 753.91	1 2 3	27-113 113-171 171-374 374-800	$2H_2O$ $Cl.H_2O$ $C_{10}H_7Cl_3N_2$ $C_{10}H_8ClN_2$ Residue	4.77 7.10 34.68 25.40 28.06	4.41 7.67 34.62 25.46 27.81
C_2	$]NiL_2Cl_2[\ 1.5H_2O$ 698.14	1 2 3 4	27-149 149-306 306-444 444-800	$1.5\ H_2O$ $C_{18}H_{14}Cl_4N_4$ C_3H_2 C_9H_8 Residue	3.87 61.30 5.44 16.61 12.79	3.9 61.30 5.41 16.64 12.59
C_3	$]CuL_2Cl_2[H_2O$ 693.98	1 2 3 4	26-112 112-344 344-513 513-800	H_2O $C_{29}H_{16}N_4Cl_4$ CH_9 C_2H_5 Residue	2.59 80.98 3.02 4.17 9.24	2.54 81.12 2.99 6.42 7.1
C_4	$]ZnL_2Cl_2[2H_2O$ 713.83	1 2 3 4	25-97 97-331 331-432 432-800	H_2O $C_{20}H_{14}Cl_4N_2.H_2O$ C_2H_2 C_5H_{12} Residue	2.52 61.91 3.64 10.08 21.85	2.16 61.92 3.69 10.09 22.26
C_5	$]CdL_2Cl_2[2H_2O$ 760.86	1 2	27-310 310-800	$C_{24}H_{19}N_4CL_4.2H_2O$ C_8H_{11} Residue	71.10 14.58 14.30	71.15 18.79 10.00
C_6	$]HgL_2Cl_2[1.68H_2O$ 843.28	1 2 3 4	26-181 181-364 364-472 472-800	$1.68\ H_2O\ Cl$ $C_3H_6N_3Cl_3$ C_3H_4 $C_{24}H_{11}N$ Residue	7.79 22.59 4.74 37.11 27.63	7.80 22.50 4.69 37.17 27.79

Table 7
X-ray powder diffraction pattern of the ligand (L) and its metal ion complexes

Compound	Formula	Particle size (nm)
L	$C_{16}H_{15}ClN_2$	65
C_1	$]CrL_2Cl_2[Cl.3H_2O$	38
C_2	$]NiL_2Cl_2[1.5H_2O$	40
C_3	$]CuL_2Cl_2[H_2O$	67
C_4	$]ZnL_2Cl_2[2H_2O$	39
C_5	$]CdL_2Cl_2[2H_2O$	69
C_6	$]HgL_2Cl_2[1.68H_2O$	31

Table 8
Inhibition zones measured in (mm) of DMSO, tetracycline, ligand and metal ion complexes

Compound	Inhibition zone (mm) ***Escherichia coli***	Inhibition zone (mm) ***Pseudomonas Aeruginosa***	Inhibition zone (mm) ***Staphylococcus aureus***	Inhibition zone (mm) ***Bacillus subtilis***
Control: DMSO	----	----	----	----
Tetracycline	----	----	14.4	----
L	----	18	----	----
C_1	18	17	----	----
C_2	----	----	----	----
C_3	----	20	----	----
C_4	17	19	----	----
C_5	20	27	20	20
C_6	15	25	16	17

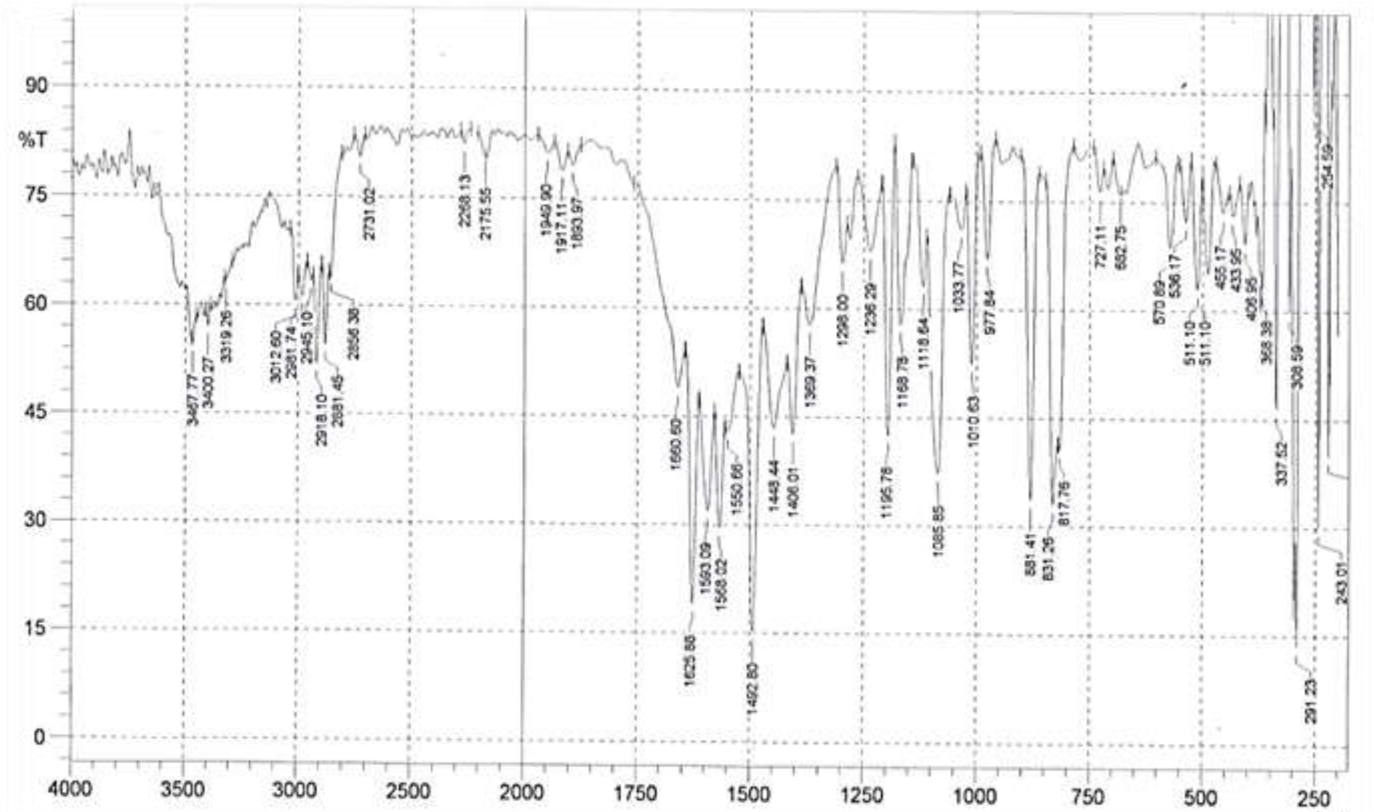


Fig. 6: FT-IR spectrum of C_5 complex

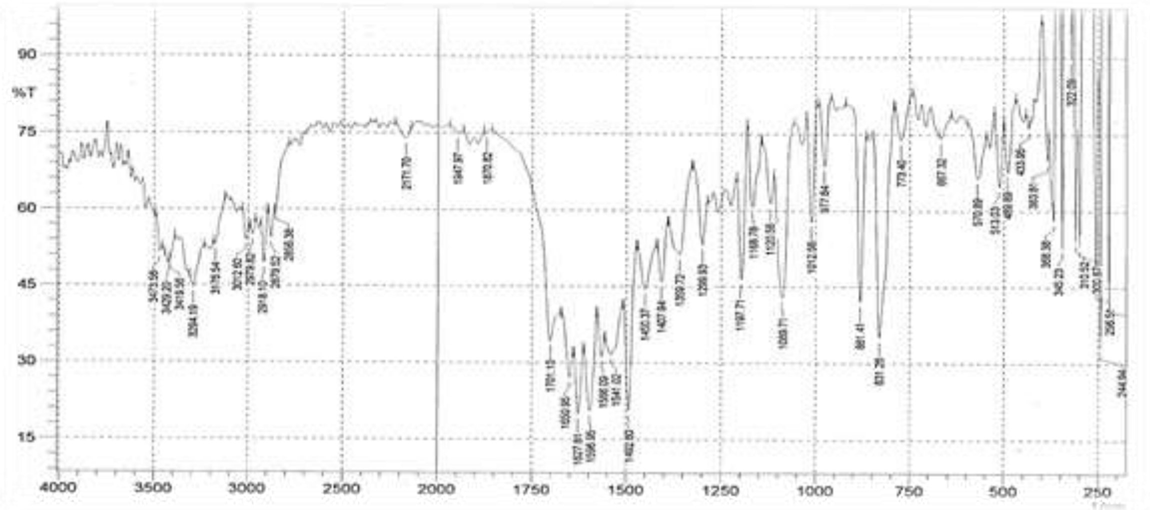


Fig. 7: FT-IR spectrum of C_6 complex

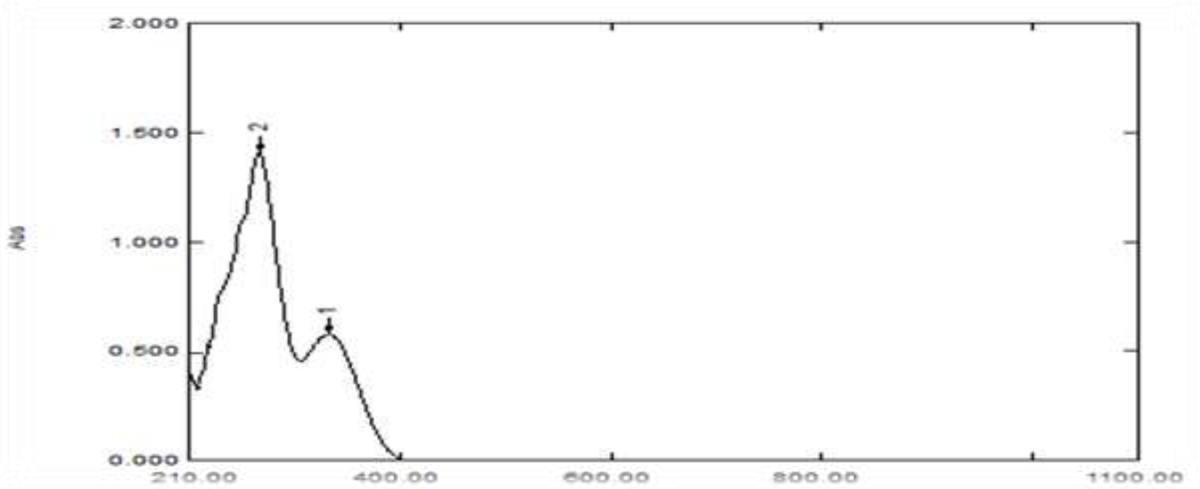


Fig. 8: UV-Vis spectrum of the ligand (L)

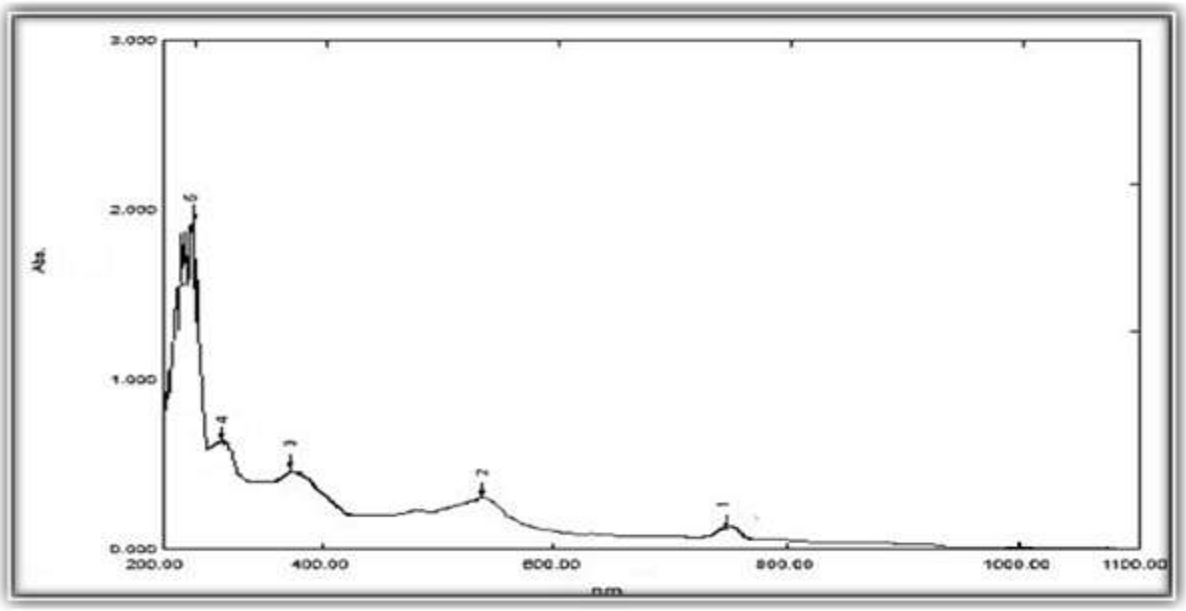


Fig. 9: UV-Vis spectrum of C_1 complex

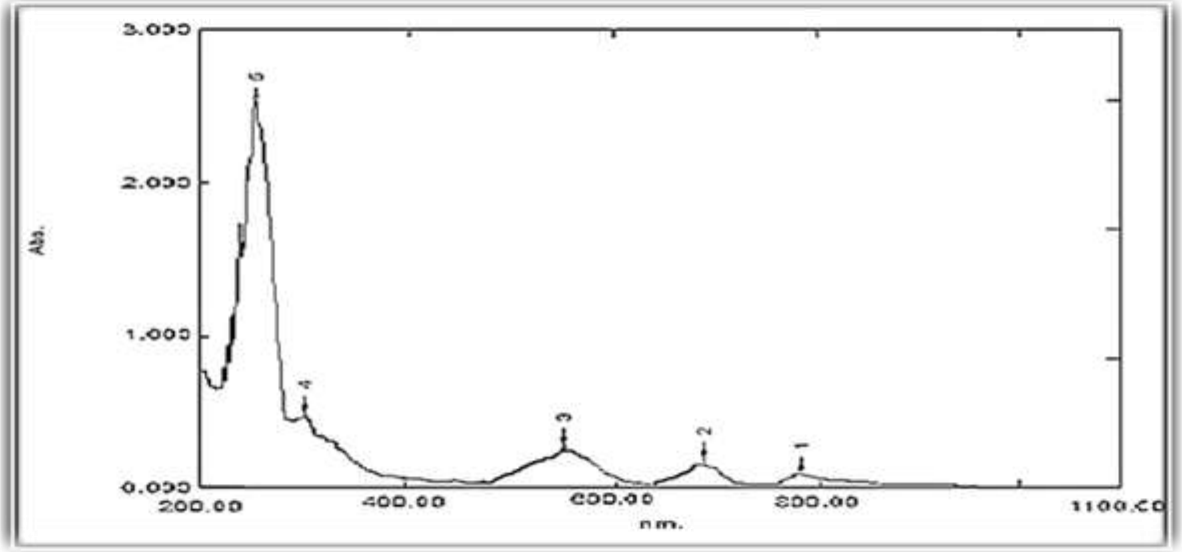


Fig. 10: UV-Vis spectrum of C_2 complex

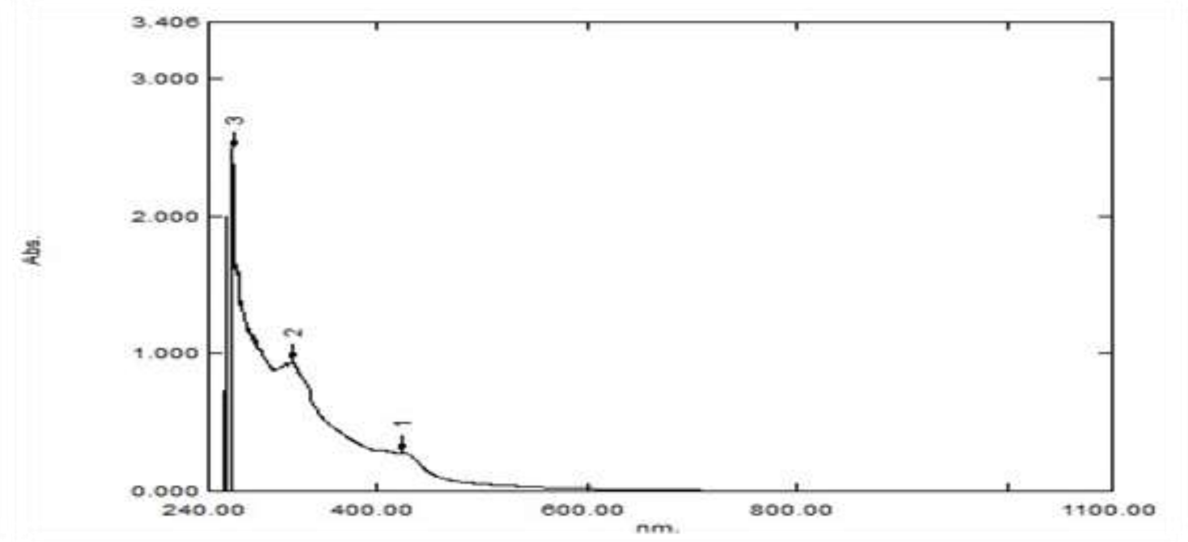


Fig. 11: UV-Vis spectrum of C_3 complex

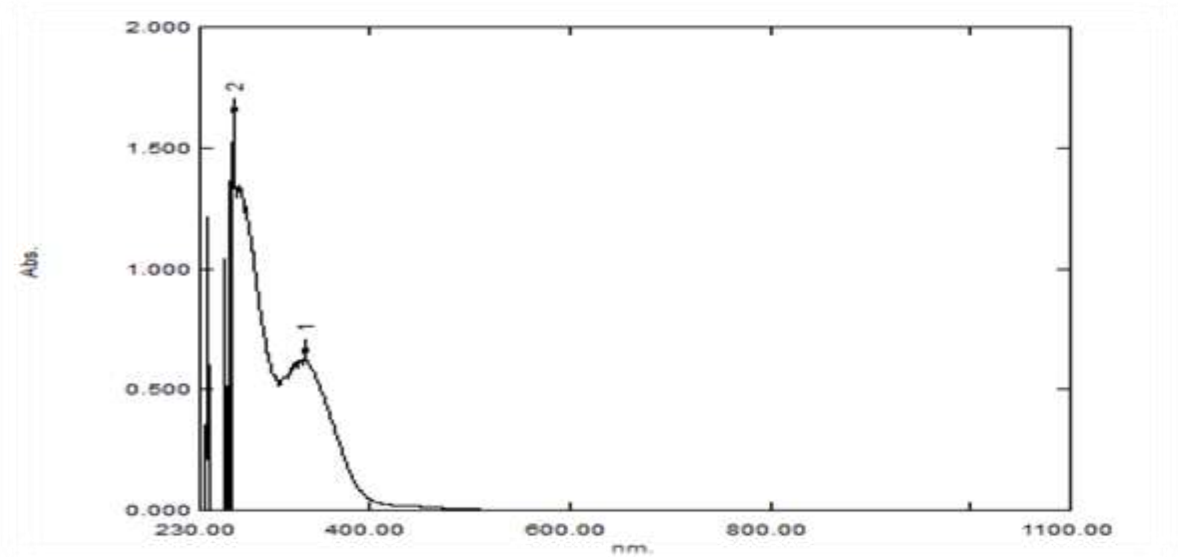


Fig. 12: UV-Vis spectrum of C_4 complex

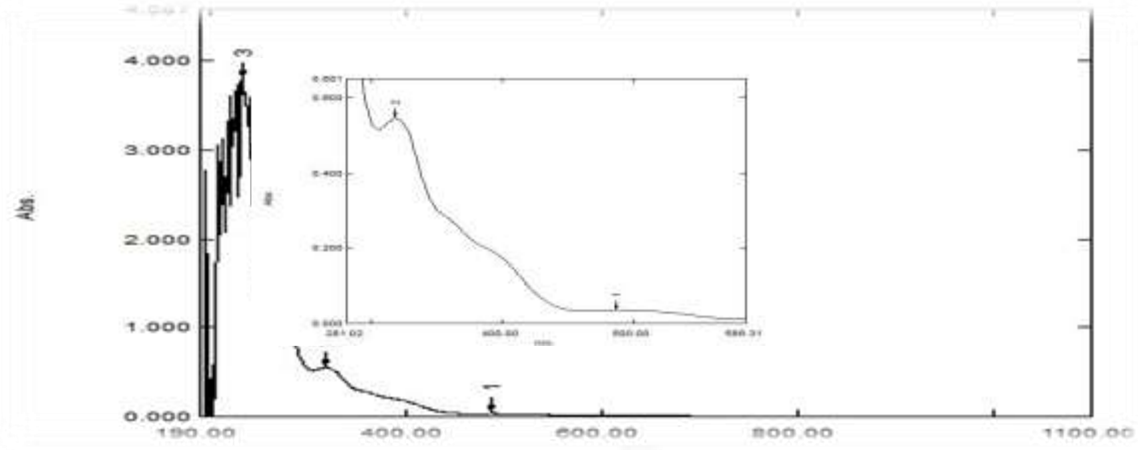


Fig. 13: UV-Vis spectrum of C_5 complex

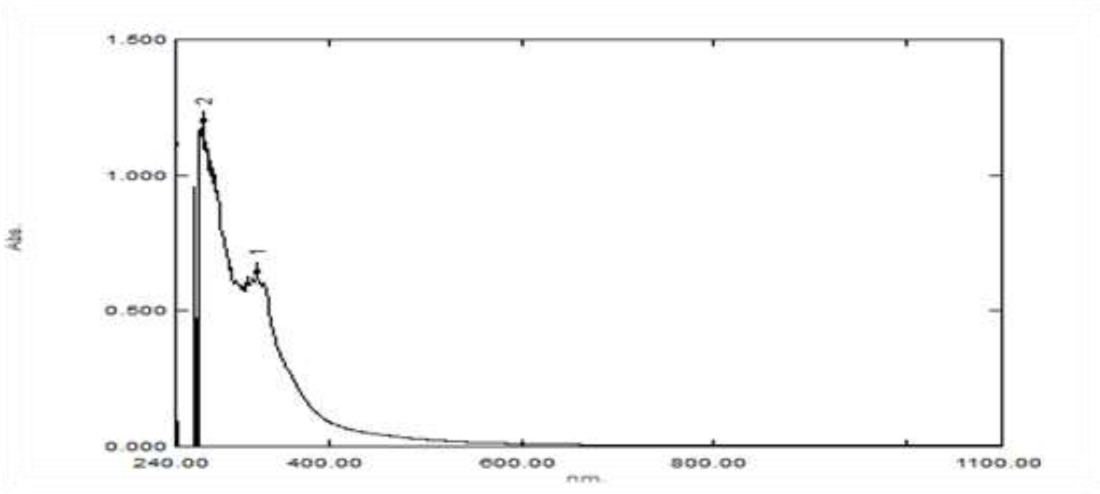


Fig. 14: UV-Vis spectrum of C_6complex

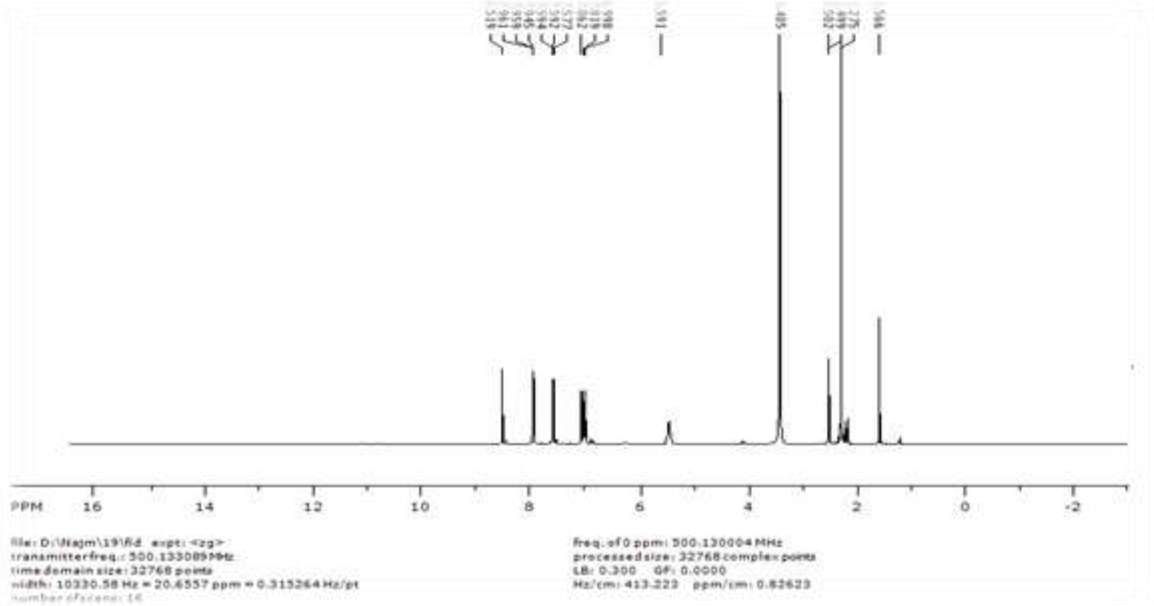


Fig. 15: ^{1}H-NMR spectrum of 2-(4-chlorophenyl)-2-[(2,4-dimethylphenyl)amino]acetonitrile (L)

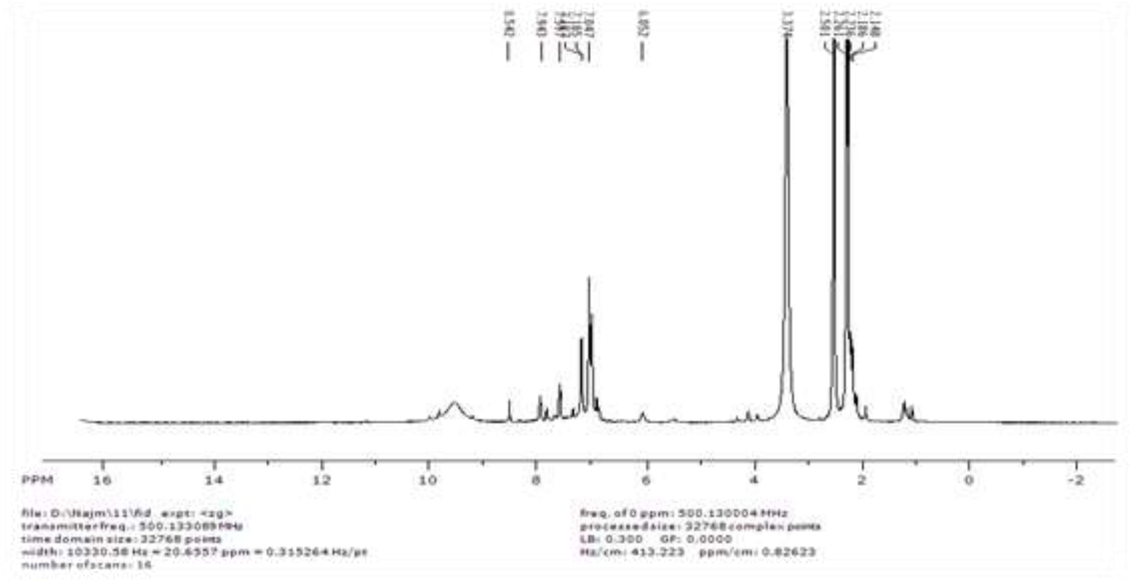


Fig. 16: ^{1}H-NMR Spectrum of C_1 Complex

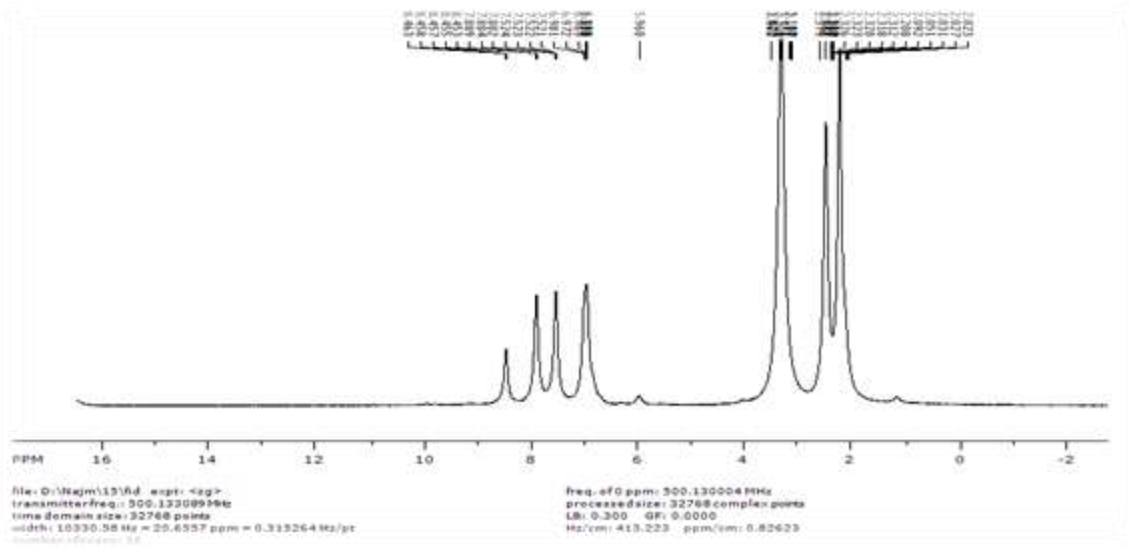


Fig. 17: ^{1}H-NMR Spectrum of C_2 Complex

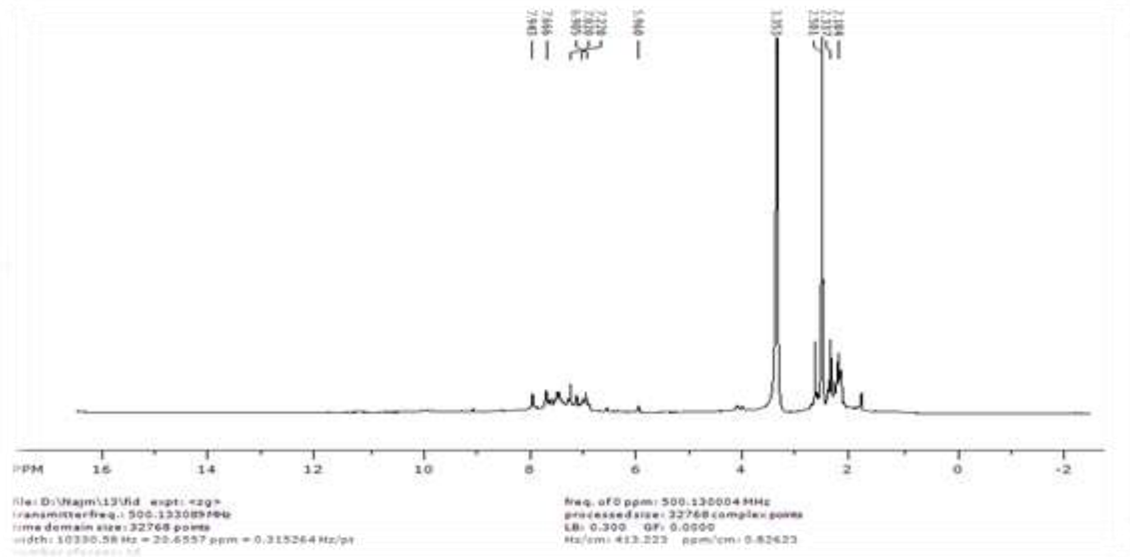


Fig. 18: ^{1}H-NMR Spectrum of C_3 Complex

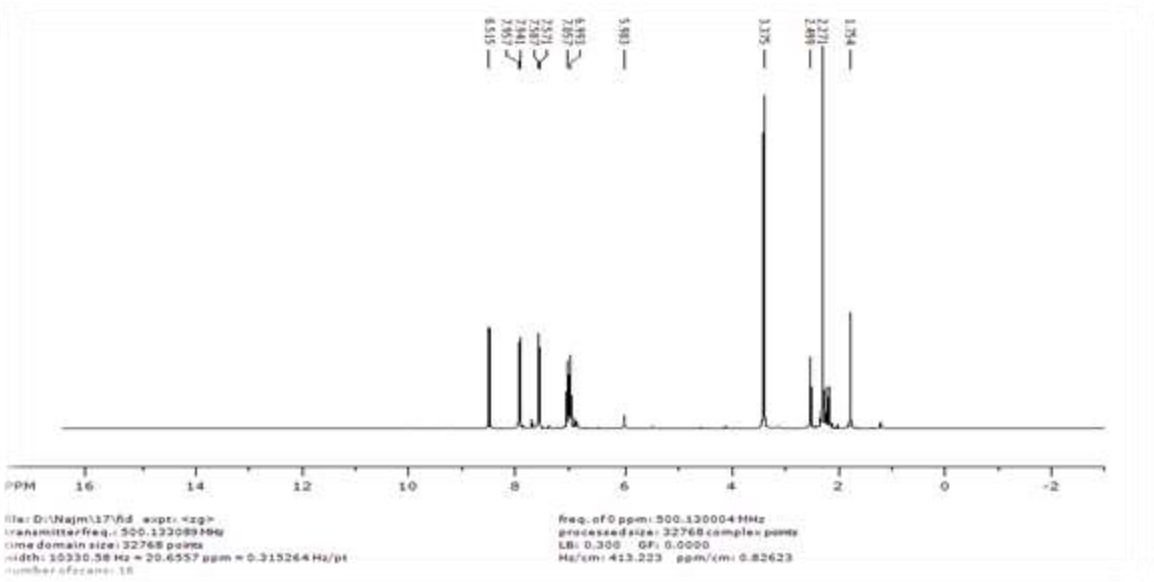


Fig. 19: ^{1}H-NMR Spectrum of C_4 Complex

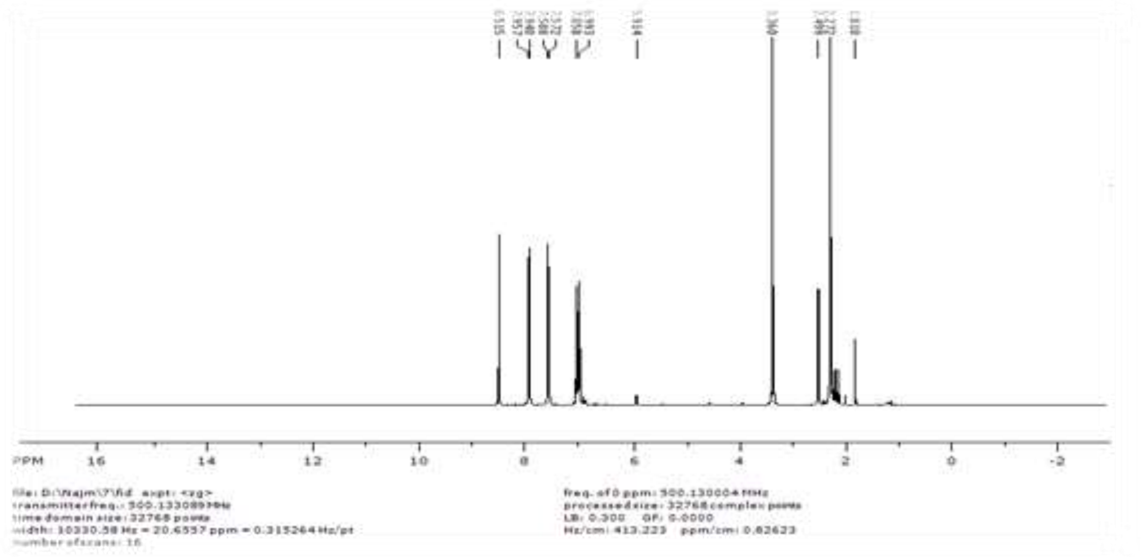


Fig. 20: ^{1}H-NMR Spectrum of C_5 Complex

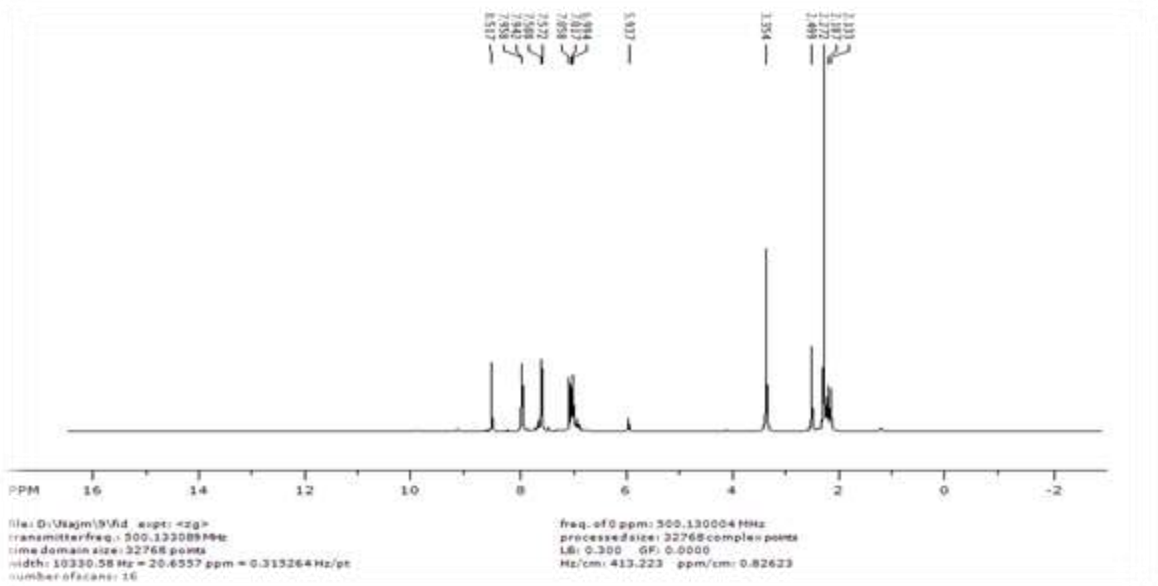


Fig. 21: ^{1}H-NMR Spectrum of C_6 Complex

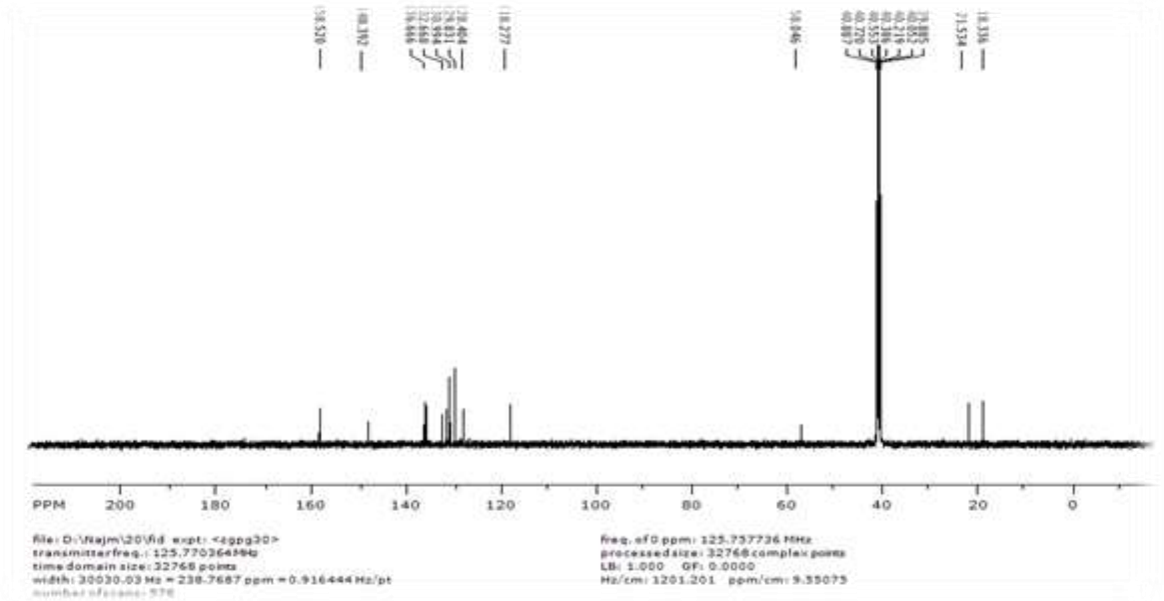


Fig. 22: ^{13}C-NMR spectrum of 2-(4-chlorophenyl)-2-[(2,4-dimethylphenyl)amino]acetonitrile (L)

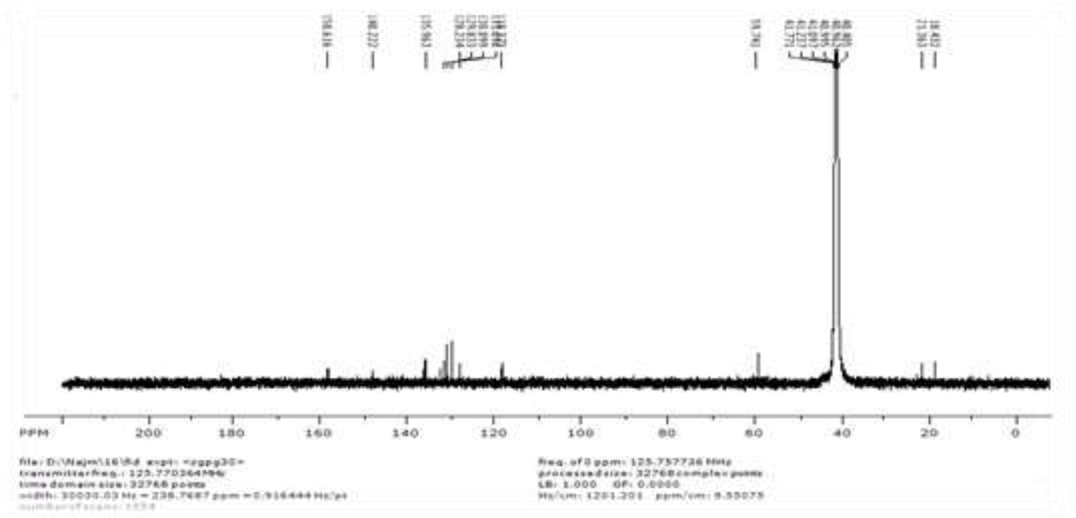


Fig. 23: ^{13}C-NMR Spectrum of C_2 Complex

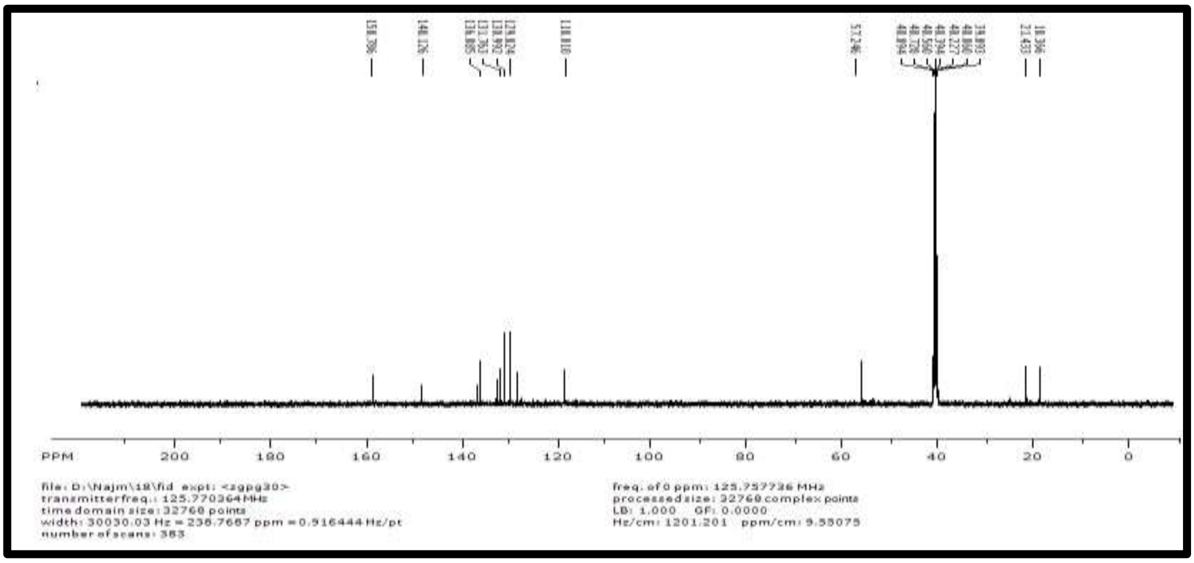


Fig. 24: ^{13}C-NMR Spectrum of C_4 Complex

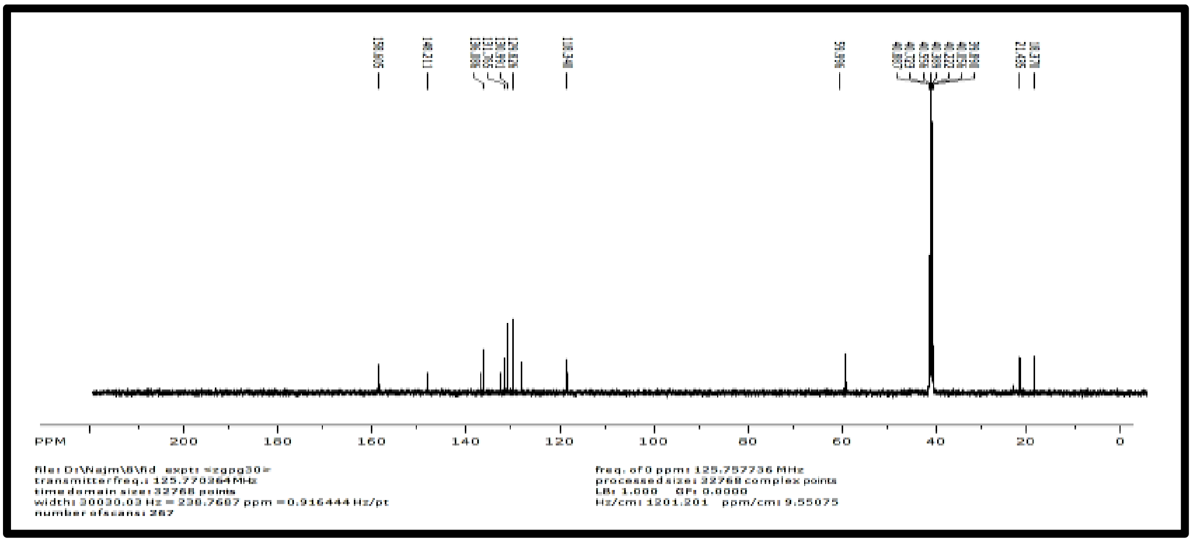


Fig. 25: ^{13}C-NMR spectrum of C_5 Complex

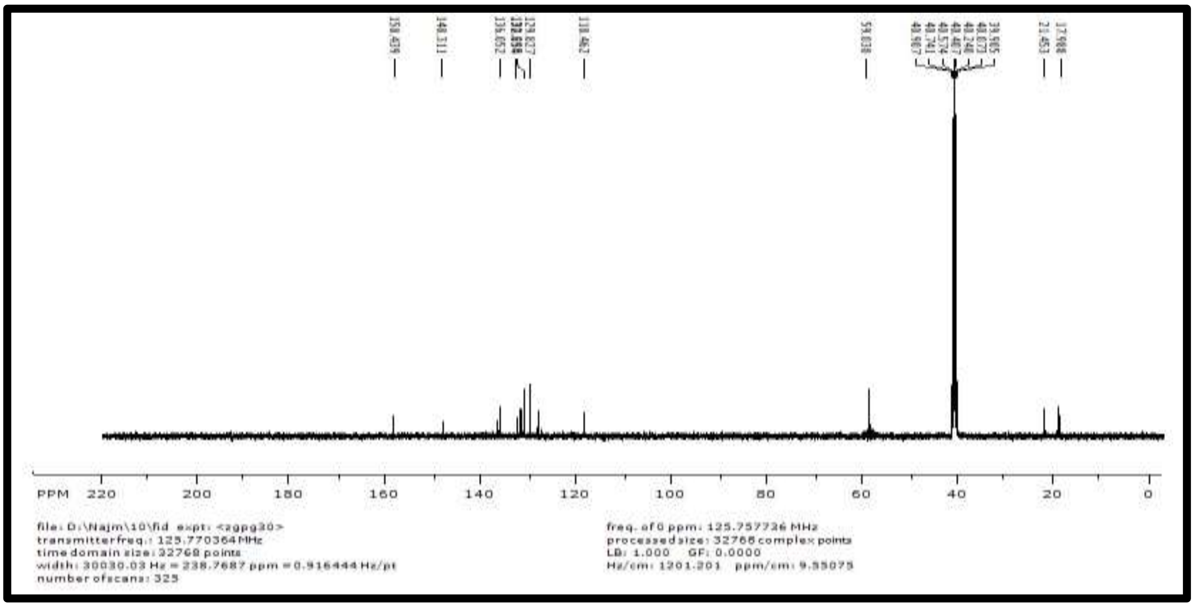


Fig. 26: ^{13}C-NMR spectrum of C_6 Complex

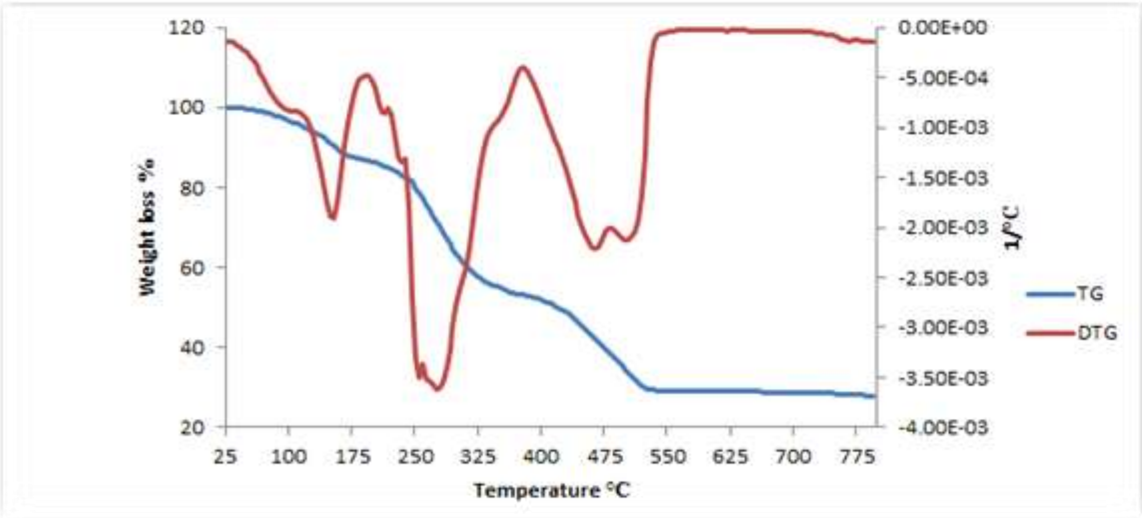


Fig. 27: The thermogram of C_1 complex

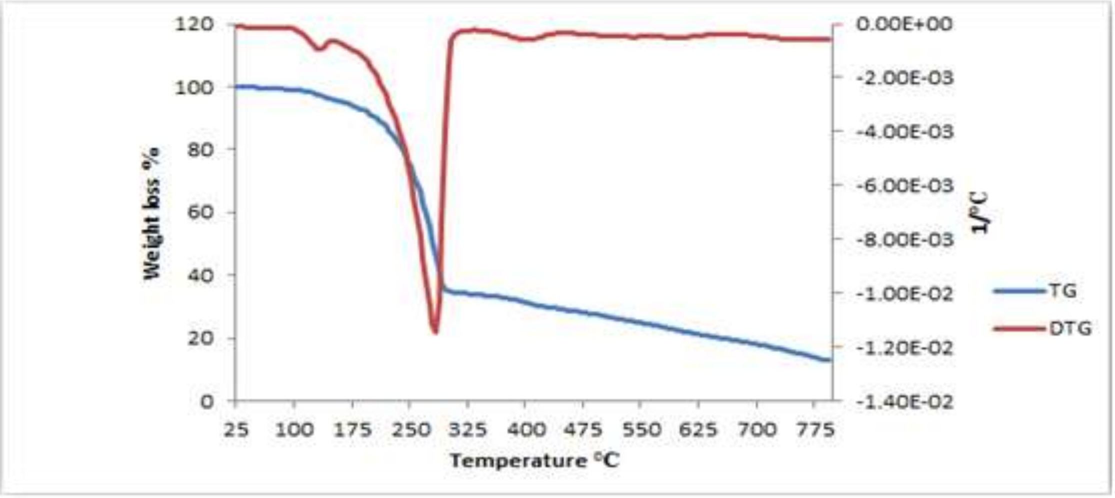


Fig. 28: The thermogram of C_2 complex

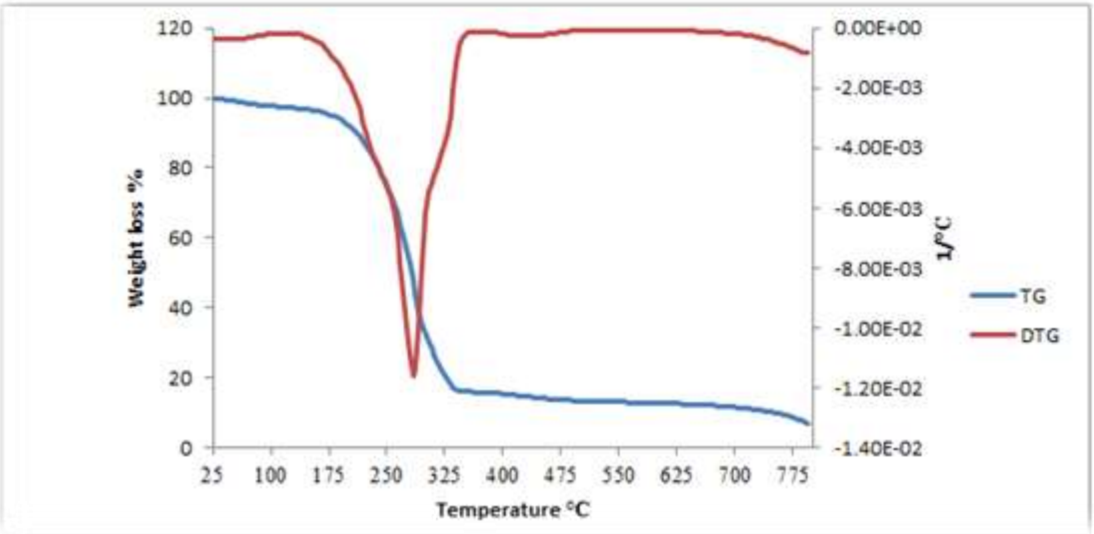


Fig. 29: The thermogram of C_3 complex

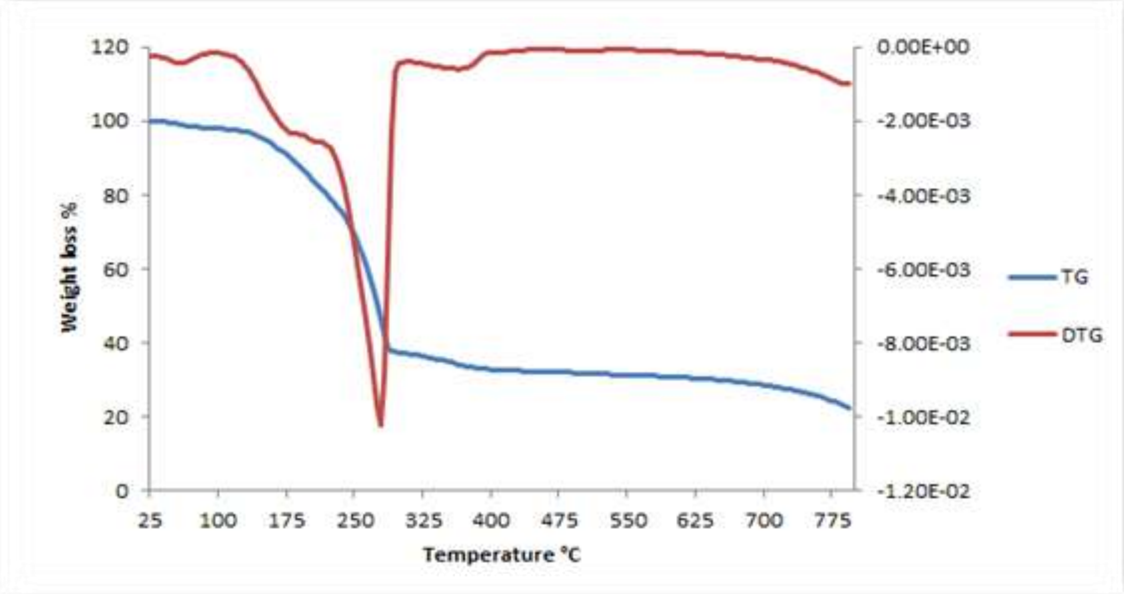


Fig. 30: The thermogram of C_4 complex

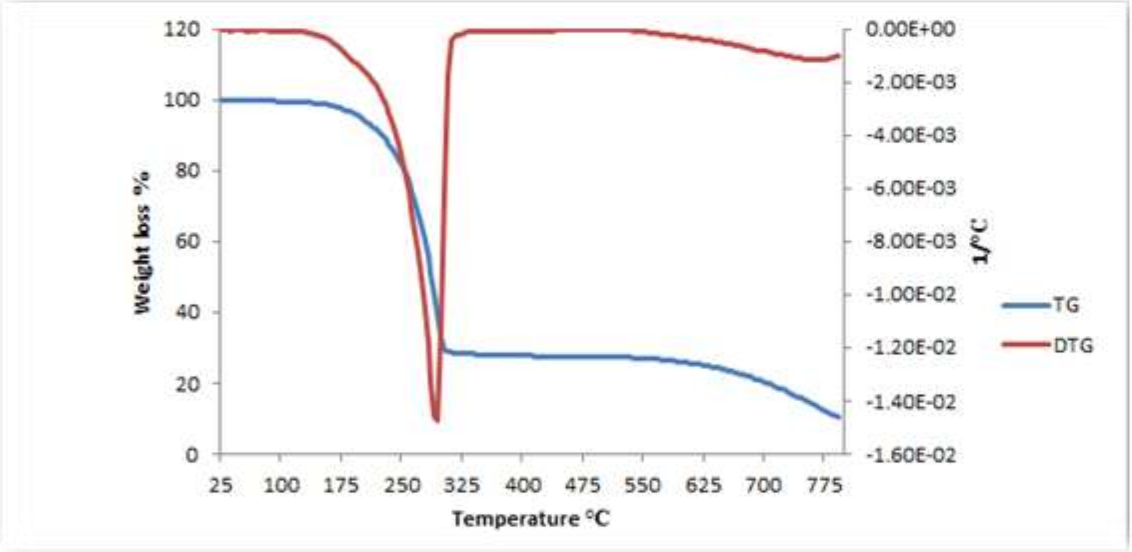


Fig. 31: The thermogram of C_5 complex

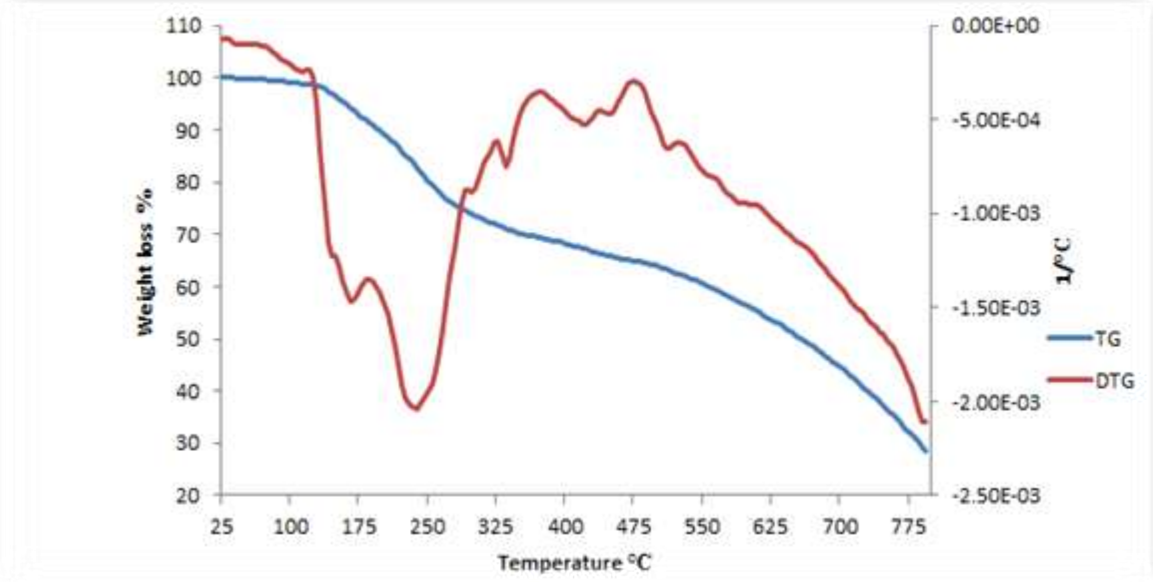


Fig. 32: The thermogram of C_6 complex

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