

Synthesis and Characterization of New (2-(((5-(3, 5-Dinitrophenyl)-1, 3, 4-Thiadiazol-2-yl)-2,5 Dihydroxy Benzalidine))) Metal Complexes

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Abstract

New complexes compounds of some metal ions such as [VO(IV)], Co(II) Ni(II), Cu(II), Zn(II) and Cd(II) are synthesized with (2-(((5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol-2-yl)-2,5dihydroxy benzalidine). The ligand Schiff base was synthesized by condensation of 2-amino -5-(3,5dinitro phenyl)1,3,4-thiadiazole with 2,5dihydroxy benzaldehyde .The suggested structures of new complexes are characterized by elemental micro analysis (C.H.N), FT-IR, UV-Vis spectra, Thermal gravimetric analysis (TGA-DTA), flame atomic absorption, molar conductivity, magnetic susceptibility and Mass Spectra. The suggested theses complexes according to the results data the probable coordination geometries are octahedral complexes excepted C₁ was pyramidal. The all complexes were found to be non-electrolyte.

Keywords: 1, 3, 4-thiadiazole, Schiff base and metal ions.

Introduction

Schiff bases was synthesized condensation primary amino with carbonyl compound are important class of ligands due to coordinate with metal ions via azomethine group [1]. 1, 3, 4-Thiadiazole was first recognized by Fischer in 1882 and then it has been developed by Bush and his team meet. In 1956, Goerdler has demonstrated the true

nature, of the ring system [2]. 1,3,4-Thiadiazole derivatives are good ligands in coordination chemistry its coordinate from exocyclic or endocyclic nitrogen or sulfur donors [3, 10]. In complex metal ion is usually show tautomerism, acid-base equilibrium, shown on Fig. (2).

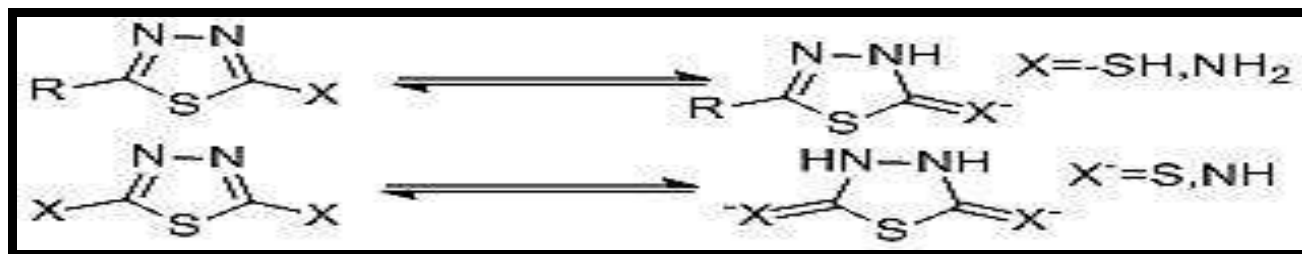


Fig.2: Tautomerism of 1, 3, 4-thiadiazole

The 2- amino substituted- 1,3,4-thiadiazoles and their Schiff bases had very important because of their biochemical properties[11]. As a ligand, it also provides many potential binding sites for complexation of diverse metal ions (such as Co(II), Ni(II), Cu(II) or Zn(II) among others) with well established biological roles[12]. In this paper we

synthesized significant heterocyclic compounds. We are synthesized of Schiff bases of 1, 3, 4-thiadiazoles derivatives and their complexes.

Materials and Methods

The following reagents, starting materials as well as solvents were purchased

commercially and used without any further purification, 3,5 dinitrobenzoic acid (Fluk), thiosemicarbazide (CDH), phosphorous oxychloride (CDH), potassium hydroxide (Fluk), 2,5-dihydroxy benzaldehyde, glacial acetic acid (BDH), vanadium sulphate hydrate ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$) (BDH) and cobalt chloride hexa hydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (Merck). Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (BDH), Nickel chloride hexa hydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (Fluk), Zinc chloride dihydrate ($\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$) and Cadmium (II) chloride dihydrate (Fluk). The melting points were measured using SMP30 melting point. Elemental C.H.N and S analysis were carried out on a (CE-440 elemental analyser).

The infra-red spectra were recorded in the frequency range ($4000\text{-}400$) cm^{-1} using KBr disc for ligand and CsI disc in the frequency range ($4000\text{-}200$) cm^{-1} for their complexes by using (8400 S-FTIR SHIMADZU spectrophotometer). The ultraviolet-visible (U.V-Vis) spectra were recorded on (1800-UV SHIMADZU spectrophotometer in the range of (200-1100) nm. Magnetic susceptibility measurements for the synthesized complexes were obtained at room temperature using (Auto Magnetic Susceptibility Balance Model Sherwood Scientific). Molar conductivity measurements were obtained using Hunts Capacitors Trade Mark British made. Thermal analyses of

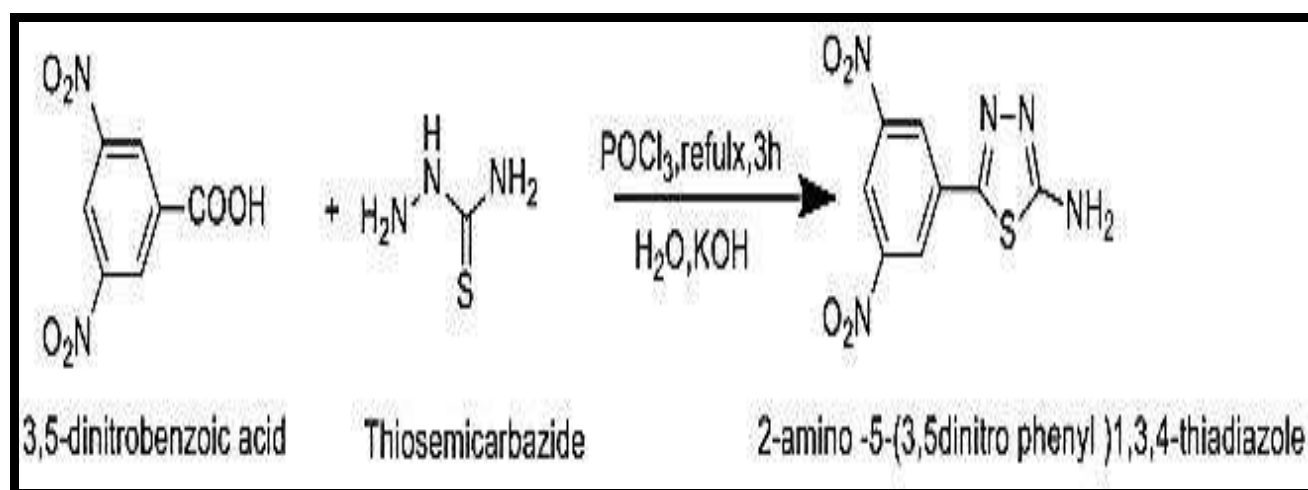
synthesized complexes were performed using (SHIMADZU 60-H Thermo Gravimetric Analyzer). Atomic absorption measurements were obtained by using (GBC Avanta Ver 1.33). The spectra of ^1H NMR and ^{13}C NMR were recorded BRUKER AV 400 Avance-III (400 MHz and 100MHz), Indian, using $\text{DMSO-}d_6$ as the solvent and Mass spectra for ligands were obtained by mass spectra were recorded by LC-MS (Perkin-Elmer, USA/Flexer SQ 300 M). Indian.

Experimental

Synthesis of the ligand (2-((5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol-2-yl)-2-hydroxy benzalidine

Preparation of 2-amino-5-(3,5-dinitro phenyl) 1, 3, 4-thiadiazole [1] [13, 15]

A mixture of 3, 5-dinitrobenzoic acid (0.01 mole, 2.212g), thiosemicarbazide (0.01 mole, 0.93g) and phosphorus oxychloride (5 mL) was heated under reflux for 3 h. Upon cooling, distilled water (50 mL) was added to the mixture and the heating under reflux was carried out for another 4 h. The obtained filtrate was neutralized with potassium hydroxide. Then the precipitate was filtered and washed with cold distilled water and finally recrystallized by using ethanol to obtain 5-(3,5-dinitrophenyl)-1,3,4-thiadiazole-2-amine as show in (Scheme 1).

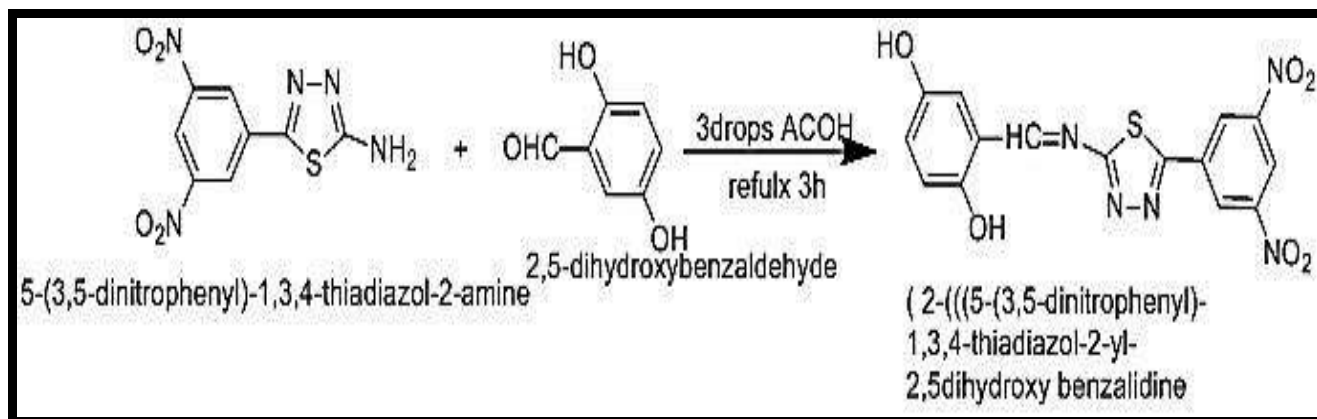


Scheme1: 2-amino -5-(3,5dinitro phenyl)1,3,4-thiadiazole

Synthesis of the ligand two (L_2) (2-((5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol-2-yl)-2,5-dihydroxy benzalidine [2]

Hot solution 5-(3,5-dinitrophenyl)-1,3,4-thiadiazole-2-amine (0.5g, 2 mmol) in 25 mL ethanol was mixed with hot alcoholic 2,5-dihydroxybenzaldehyde (0.25 g, 2 mmol) in present (3 drops) of glacial acetic acid (AcOH

) and the reaction mixture was left under reflux for 6 h. The formed solid products were separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride. The orange color Schiff base product is produced in 80% yield. Equation (1) [15,17].



Synthesis of Metal Complexes (C₁ to C₆)[3-8][15]

The complexes (C₁-C₆) were synthesis by hot ethanol solution of the metal ions [VO(II)SO₄·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O, ZnCl₂ and CdCl₂·2H₂O was added to hot ethanol solution 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2,5-dihydroxy benzalidine L in 1:2 (metal: ligand) molar ratio expected C₁ complex in 1:1(metal: ligand) Then, the mixture was heated under reflux for one hour and coloured precipitates were obtained. Later, the precipitates were filtered out, washed with distilled water and finally recrystallized from ethanol

Results and Discussion

Physical Properties and Elemental Analysis

The data of atomic absorption ,CHNS and chloride analysis as well as the physical properties of the ligands and its metal complexes are show in table (1). The molecular formulae of studied compounds were suggested depending on CHNS, chloride content, atomic absorption analysis, spectral data and conductivity measurements. The analytical data of the metal complexes are given in (Table 1). The data reveal the formation of complexes having 1:2 (ligand :metal ion)ratio . The data clearly indicate that, the ligand used acts as neutral bidentate. The complexes are insoluble in common organic solvents but all complexes completely soluble in DMF and DMSO.

Table 1: Physical properties and analytical data for L and its complexes

symbol	color	m.p °C	Yield %	M.Wt	micro elemental analysis around (calc.)				Metal content % Found (calc.)	Chloride content% Found (calc.)
					C%	H%	N%	S%		
L	Orange	210-212	80	387.33	45.54 (46.52)	2.71 (2.34)	18.73 (18.08)	8.16 (8.28)	7.00 (6.46)	7.00 (6.46)
C1	Green	183-185	67	550.32	33.11 (32.74)	1.14 (1.65)	12.51 (12.73)	11.94 (11.65)	—	—
C2	blue	193-195	75	940.52	38.56 (38.31)	2.23 (2.36)	14.54 (14.89)	7.01 (6.82)	6.12 (6.27)	7.34 (7.54)
C3	Brown	258-260	61	927.11	39.37 (38.87)	2.09 (2.17)	15.07 (15.11)	6.99 (6.92)	6.21 (6.85)	7.95 (7.65)
C4	Yellow	232-235	69	910.93	39.43 (39.56)	2.23 (1.99)	15.20 (15.38)	6.85 (7.04)	7.57 (7.18)	7.63 (7.78)
C5	Yellow	240-242	71	957.96	37.53 (37.61)	2.03 (1.89)	14.41 (14.62)	6.58 (6.69)	12.01 (11.73)	7.02 (7.40)
C6	Brown	258-260	61	927.11	39.37 (38.87)	2.09 (2.17)	15.07 (15.11)	6.99 (6.92)	6.21 (6.85)	7.95 (7.65)

FT-IR Spectrum of Ligand and its Complexes

FT-IR Spectrum of 2-amino5-(3,5-dinitrophenyl)-1,3,4-thiadiazole [1]

The structure of the prepared compound [1] was characterized by FT-IR spectrum of compound [1], showed the appearance of NH₂

stretching band at asymmetric and symmetric at (3469, 3415)cm⁻¹, band of (3090) cm⁻¹ band of (C-H) from the (C=N)_{st} appeared at (1620) cm⁻¹, (NO₂) asymmetric and symmetric at (1537) cm⁻¹ and (1348) cm⁻¹ respectively. Other bands of C=C_{st} appeared at (1508, 1419) cm⁻¹ and band of (C-S-C) at (1076) cm⁻¹ Fig. (3) [18-22]

FT-IR Spectrum of Ligand and its complexes

The spectrum of the free ligand (L), Fig.(4) showed bands at (3278, 3425) cm^{-1} assigned for $\nu(\text{O-H})_{\text{st}}$, band at (3082) cm^{-1} assigned $\nu(\text{C-H})$ aromatic[18], band at 1650 cm^{-1} for $\nu(\text{C=N})$ of the Schiff base[23, 24] and the band at (1593) cm^{-1} assigned to $\nu(\text{C=N})$ cyclic ring stretching [25]. Also the spectrum shows (1575 and 1483) cm^{-1} , (1544 and 1348) cm^{-1} , (1274), (1085), and cm^{-1} attributed to the $\nu(\text{C=C})$ aromatic, $\nu(\text{NO}_2)$ asymmetric and

symmetric), $\nu(\text{C-O})$ and $\nu(\text{C-S-C})$ stretches frequencies respectively. The shift of $\nu(\text{O-H})$ and $\nu(\text{C=N})$ imine for azomethane group in their positions and change the shape or intensity of band compared with the ligand (L) attributable to the coordination of this ligand with the metal ions, and gave an indication that the complexes were formed. The range (200-600) cm^{-1} appeared stretching band for $\nu(\text{M-N})$, $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$ [18, 19, 26-28]. IR spectra data of compounds L and its complexes were shown in Table (2) and Figures (5-10).

Table 2: IR spectra data of compounds L and its complexes

Symbol of compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$ ring	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	M-Cl
L	3425,3278	1593	1650	—	—	—
C ₁	3431,3269	1596	1627	350	295	—
C ₂	3429,3267	1591	1654	410	319	310
C ₃	3429,3280	1591	1627	495	410	365
C ₄	3244,3433	1596	1656	485	404	340
C ₅	3431,3282	1612	1656	430	405	340
C ₆	3431,3271	1589	1654	310	295	280

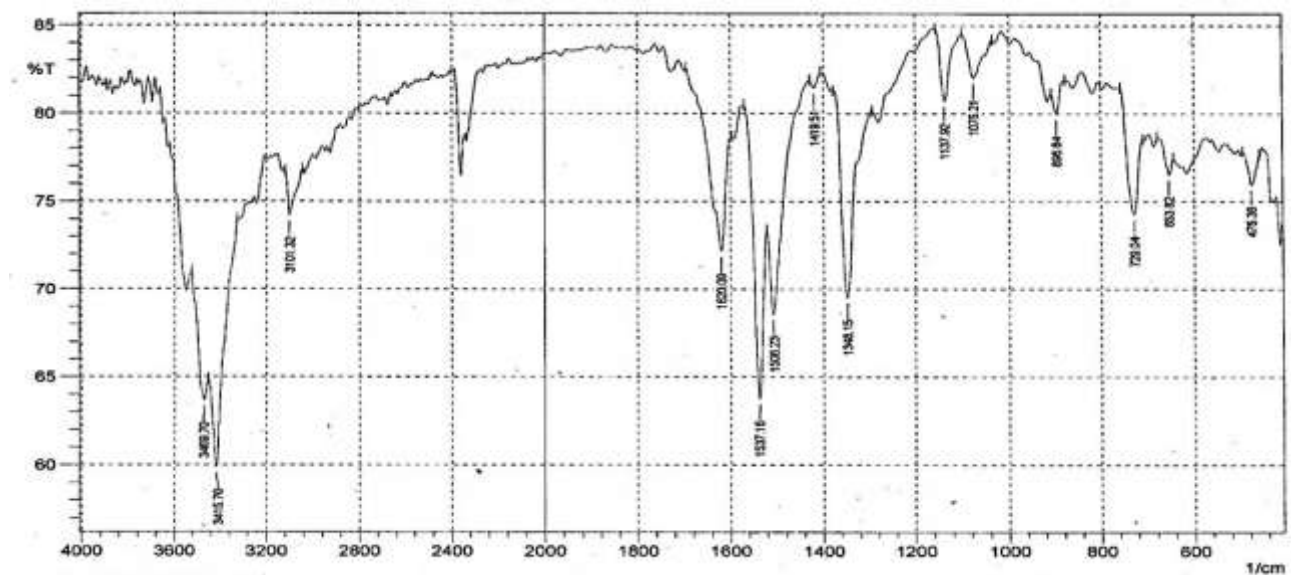


Fig.3: 2-amino-5-(3,5-dinitrophenyl)-1,3,4-thiadiazole

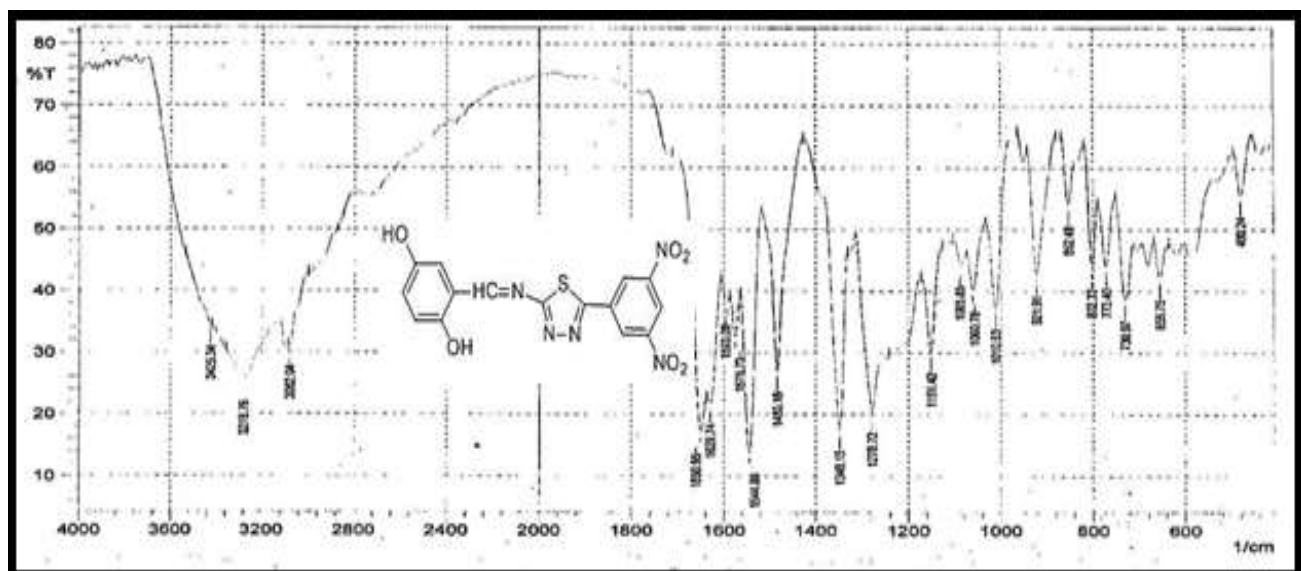


Fig.4 FT-IR spectrum 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2,5-dihydroxy-benzaldehyde

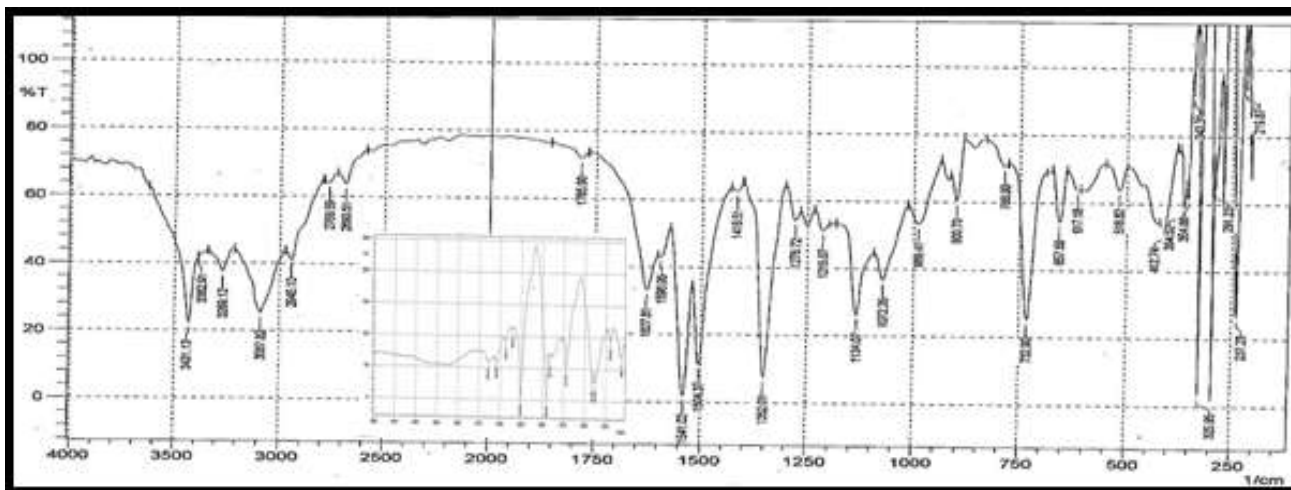


Fig. 5: FT-IR spectrum of C1 complex

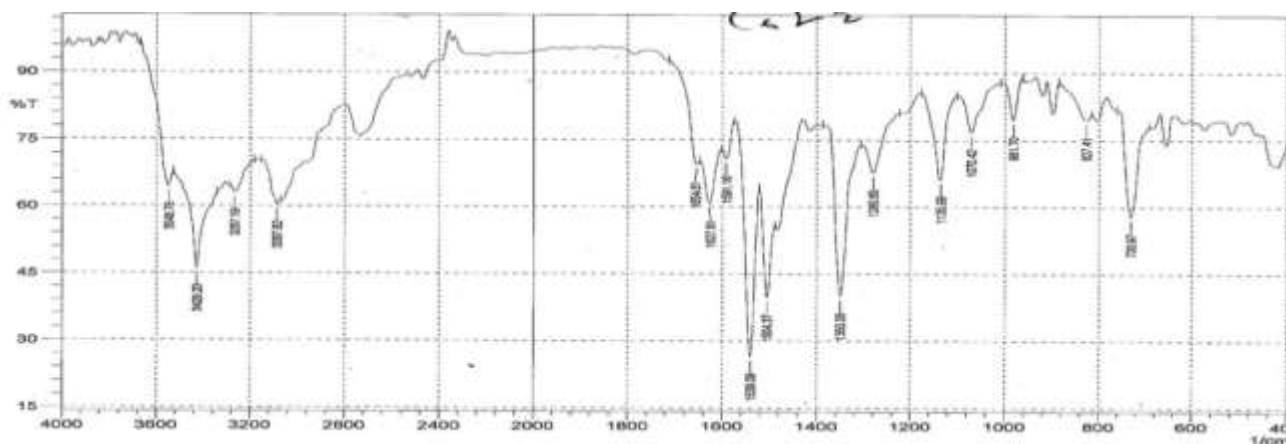


Fig. 6: FT-IR spectrum of C2 complex

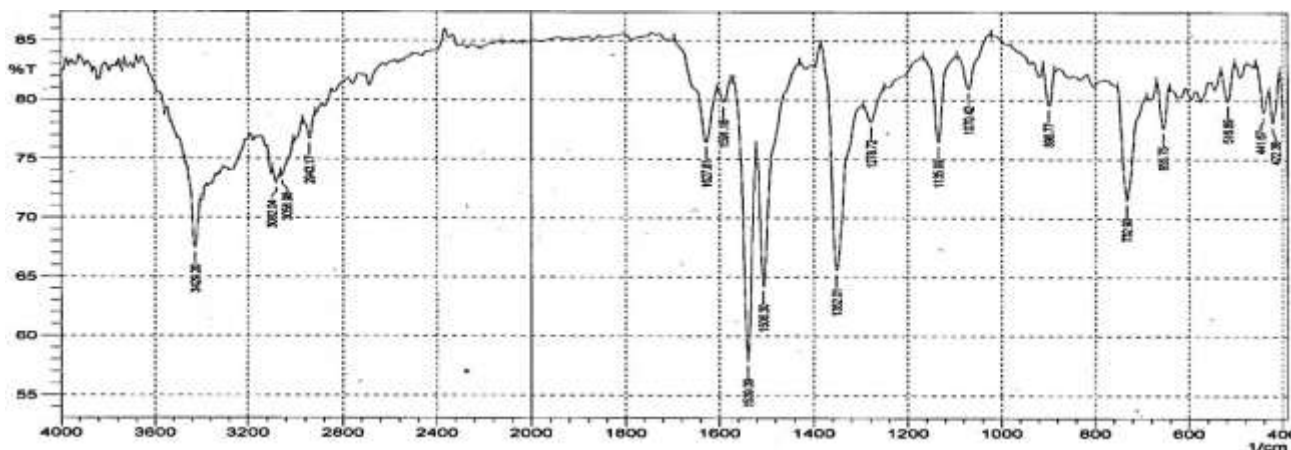


Fig. 7: FT-IR spectrum of C3 complex

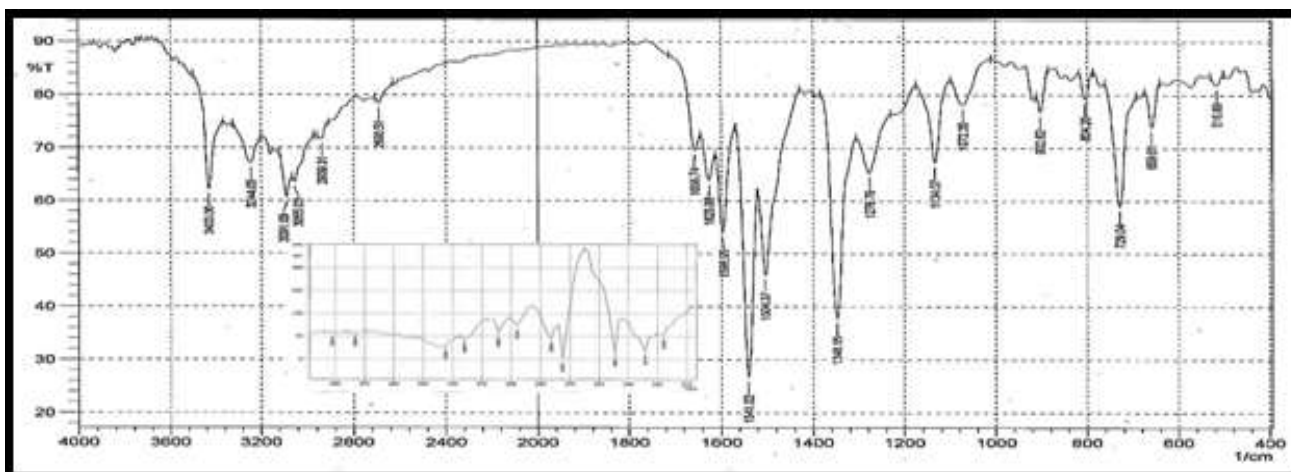


Fig. 8: FT-IR spectrum of C4 complex

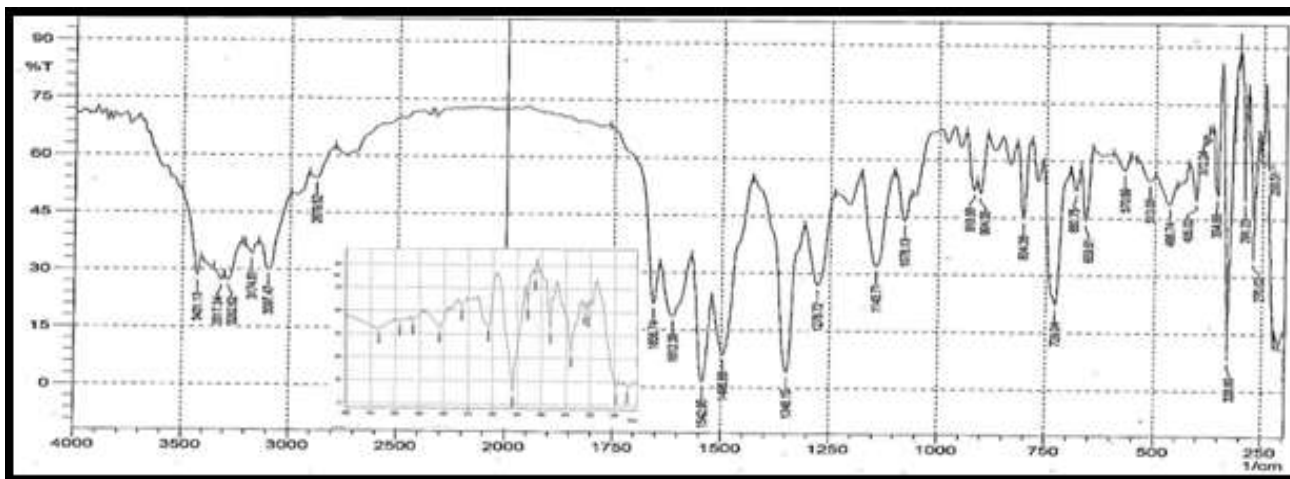


Fig. 9: FT-IR spectrum of C₅ complex

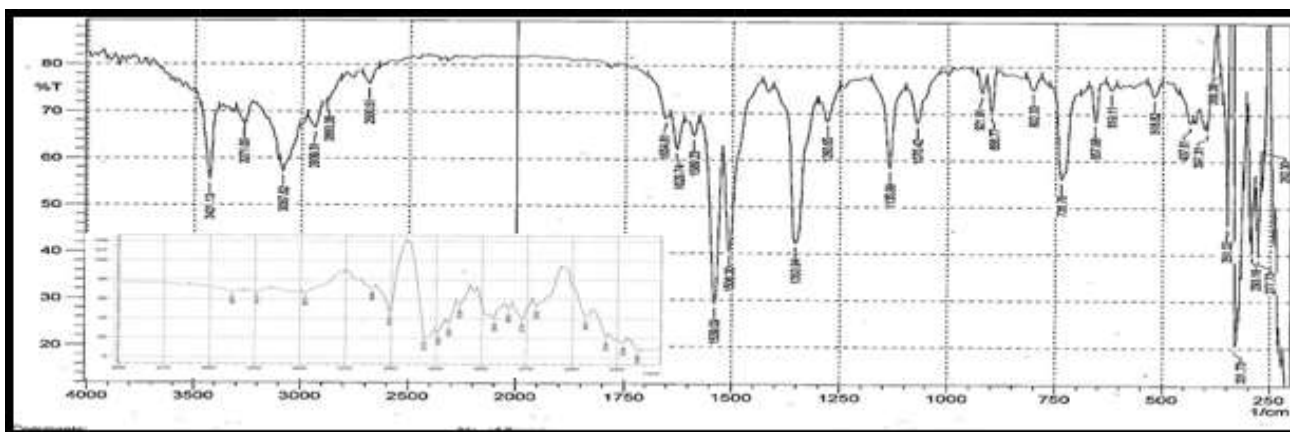


Fig. 10: FT-IR spectrum of C₆ complex

¹H-NMR spectrum of 2-amino5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol

The ¹H-NMR spectrum showed three signals at δ 7.86ppm (2 H) that could be assigned NH₂[29, 30] and two signals at δ 8.89,8.79ppm multiplet for benzene ring Fig. (11)

¹H-NMR Spectrum of Prepared Ligand One and its Complex

The ¹H-NMR spectrum of the ligand(L), Fig (12) in DMSO-d₆ showed four signals, the

first two signals at (δ=10.5,10.18ppm, 1H) due to two(OH) group and two signals in the range (δ=6.8.-9.185ppm, 2H) due to aromatic protons. The other one signal at (δ= 9.12 ppm, 1H) due to -N=CH- group[23].The ¹H-NMR spectrum for metal complex C₆, Fig.(13) in DMSO-d₆ showed lower chemical shift for -OH at 9.21 and, -N=CH- at 8.8 and other signal for OH group at 10.05, the range of (6.83-9.03) due to aromatic protons, 3.37 for H₂O[15, 31, 32].

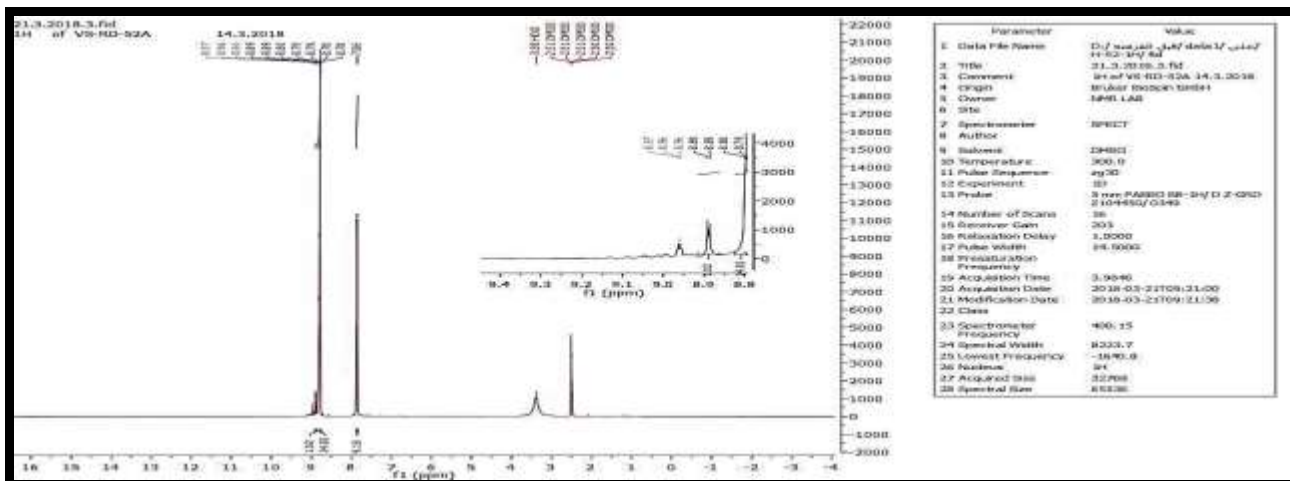


Fig.11: ¹H-NMR spectrum for 2-amino5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol

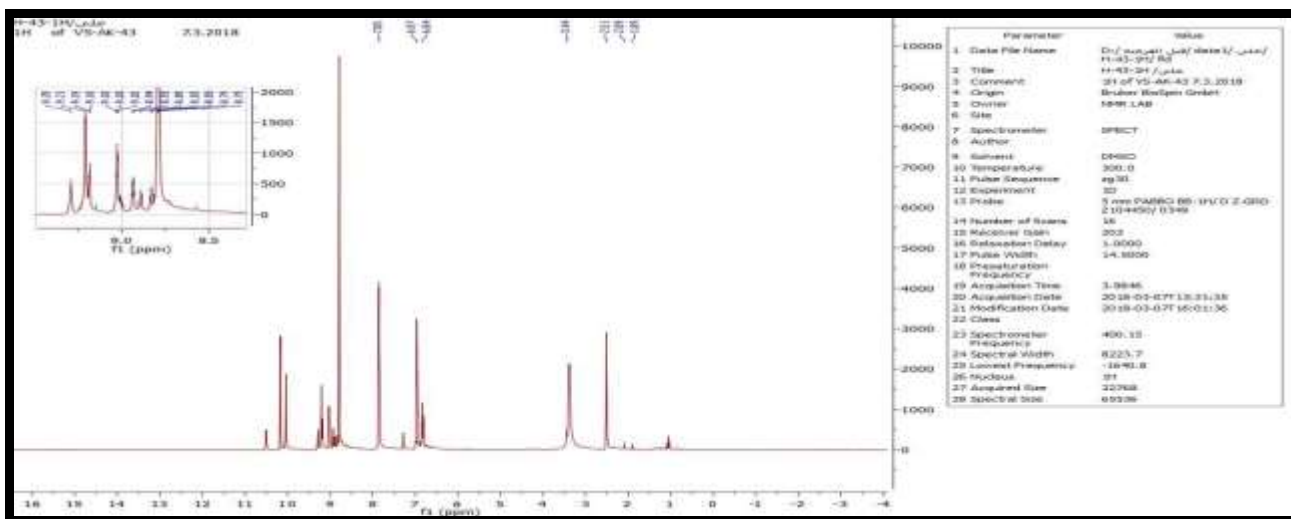


Fig.12: H-NMR spectrum for (L) 2-(((5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol-2-yl)-2,5-dihydroxy-benzalidine

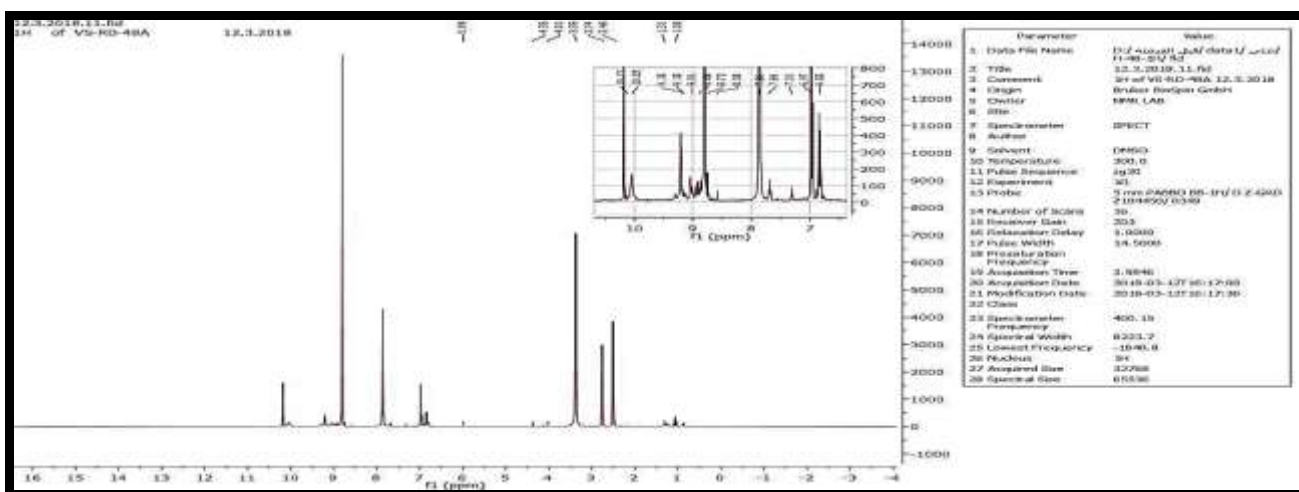


Fig.13: 1H-NMR spectrum for C5complex

¹³C-NMR Spectrum of Prepared Ligand (L) and its Complex

The ¹³CNMR spectrum of the ligand L is shown in Fig.(14).The spectrum of (L) is characterized by the presence of (N=CH) of azomethine group which appeared as a signal at δ=(149) ppm[26]. Chemical shift of (C-aromatic ring) appeared at δ =113-125 ppm[18, 19]The spectrum appearance at low fields at δ = (177) ppm which was assigned to

CH=N of thiazol ring [25]. The ¹³CNMR spectrum of C₆ is shown in Fig (15) The spectrum of C₆ is characterized by the presence of (N=CH) of azomethine group which appeared as a signal at δ=(154) ppm[15]. Chemical shift of (C-aromatic ring) appeared at δ =113-134 ppm[18, 19]The spectrum appearance at low fields at δ = (170) ppm which was assigned to CH=N of thiazol ring[15].

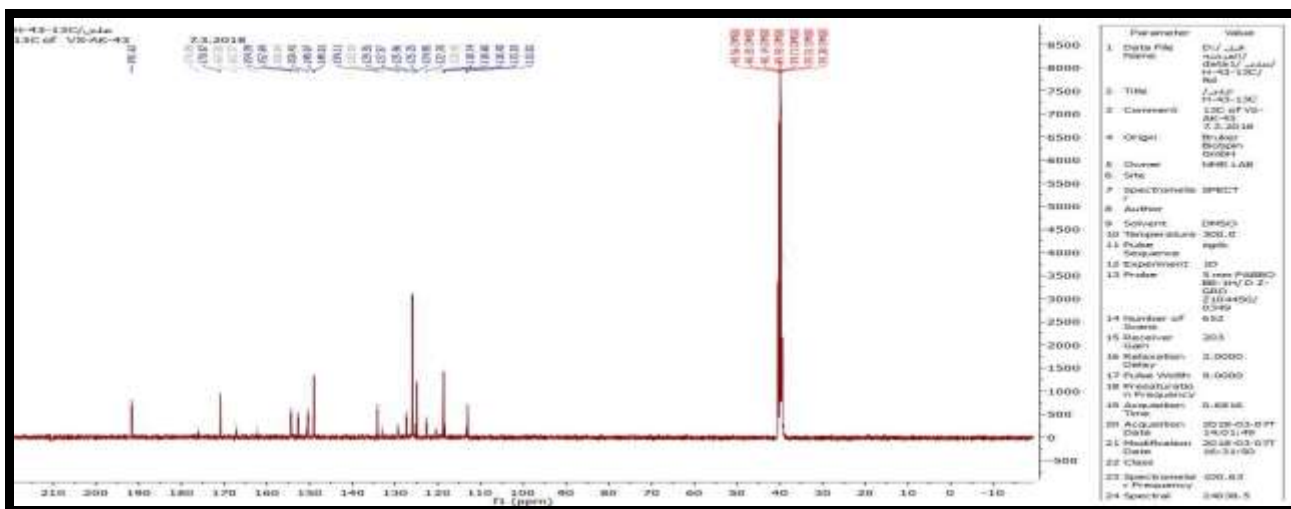


Fig.14: ¹³C-NMR spectrum for ligand (L) 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2,5-dihydroxy-benzalidine

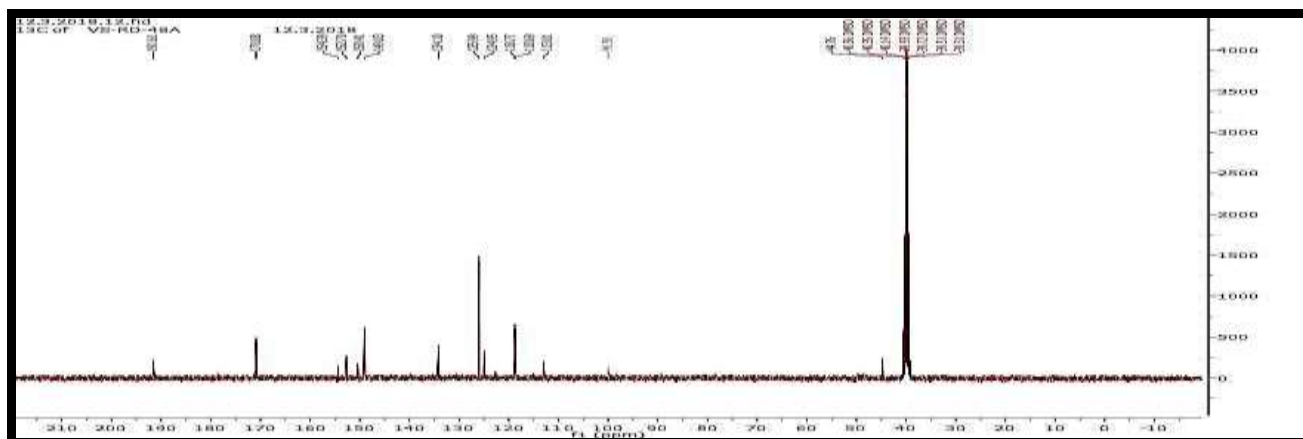


Fig. 15: ¹³C-NMR spectrum for C6 complex

Magnetic Susceptibility

The magnetic susceptibility measurements were contributed in the determination of complexes structure. These measurements provide information about the type of bonding and strength of the ligand field of complexes and also give information about the number of unpaired electrons. The effective magnetic spin of the complexes were measured by using only a spin magnetic moment ($\mu_{s.o}$) according to the following equation[33].

$$\mu_{s.o} = 2\sqrt{S} \quad (\text{B.M}) \quad \text{where } S = n/2 \quad (n = \text{number of UN paired electrons}).$$

The results obtained from this equation were compared with the actual values obtained through the magnetic measurements as in Table (3). These values were corrected for diamagnetic effects using the following relationship[34, 35].

Molar Conductance

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.

Table 3: Magnetic susceptibility and Molar conductance for metal complexes (C₁-C₆)

compound	Malar conductivity Ohm ⁻¹ ,cm ² ,mole ⁻¹	Magnetic susceptibility(B.M)	
		Cal.	found
C ₁	45.01	1.73	1.32
C ₂	50.88	3.87	3.73
C ₃	56.35	2.82	2.78
C ₄	34.21	1.73	1.84
C ₅	23.87	diamagnetic	
C ₆	10.65	diamagnetic	

Electronic Spectra of ligands (L) and their Metal ion Complexes

The electronic spectrum of the ligand (L) was exhibited a high intensity bands appeared as a singlet due to intra-ligand transitions, the band which appeared at (304.39 nm, 32852.59 cm⁻¹) is assigned to ($\pi \rightarrow \pi^*$) transition of the conjugated system. A lower intensity band appeared in the near U.V. region at (326.06 nm, 30669.20cm⁻¹) was assigned to ($n \rightarrow \pi^*$) [15,23]which is shown in Fig (16) the complexes (C1-C6) of this ligand were showed the following:

Electronic Spectrum of Vanadium (IV) Complex (C1)

The electronic spectrum of V(IV) complex, exhibited absorption band at (418 nm, 23052.10 cm⁻¹)assignable to ${}^2B_2 \rightarrow {}^2A_1$ (d-d)

transition as shown in Fig (17).Indicating square pyramidal geometry and bands at (347) nm, (28818.44) cm⁻¹ due to charge transfer from (M→L) [15, 36].

Electronic Spectrum of Cobalt (II) complex (C2):

The electronic spectrum of Co(II) complex, exhibited absorption bands at, (572nm, 17482.52cm⁻¹),(409nm, 24449.88 cm⁻¹) assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$,(d-d) transition as shown in Fig (18). Indicating distorted octahedral geometry and band at (343nm, 29154.52cm⁻¹) due to charge transfer from (M→L)[37].

Electronic Spectrum of Nickel (II) complex (C3)

The spectrum of the Ni (II) complex showed as Fig (19). a peak in the d-d region at (1062nm, 9416.20cm,401nm, 24937.66cm) assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(p)$ transition respectively, confirming a distorted octahedral geometry and bands at (329nm, 30395.14cm⁻¹) due to charge transfer from (M→L) [38, 39].

Electronic Spectrum of Cu (II) Complex (C₄)

The spectrum of the Cu (II) complex showed Fig (20). a peaks in the d-d region at (610nm, 16393.44cm⁻¹)nm assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ respectively. The band at (366nm, 27322.40 cm⁻¹) due to charge transfer from (M→L).[40]

Electronic spectra of Zn (II) Complex (C₅)

The electronic spectrum of complex (C₅) was showed no d-d transition as it belongs to (d¹⁰). The ultraviolet-visible spectra of this complex was appeared in Fig (21) (331,361 nm, 30211.48, 27700.83cm⁻¹) due to charge transfer from (M→L). The octahedral structure can be suggested for this complex[41].

Electronic Spectra of Cd (II) Complex (C₆)

The electronic spectrum of complex (C₆) was showed no d-d transition as it belongs to (d¹⁰). The ultraviolet-visible spectrum of this complex was appeared in Fig (22). (336nm, 27548.21cm⁻¹) due to charge transfer from (M→L).The octahedral structure can be suggested for this complex[16].

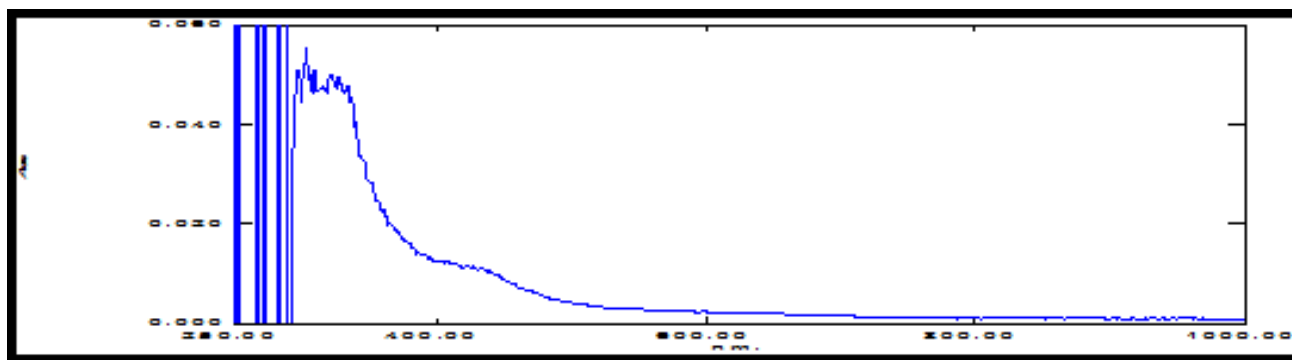


Fig.16: UV-Vis spectrum of the ligand (L)

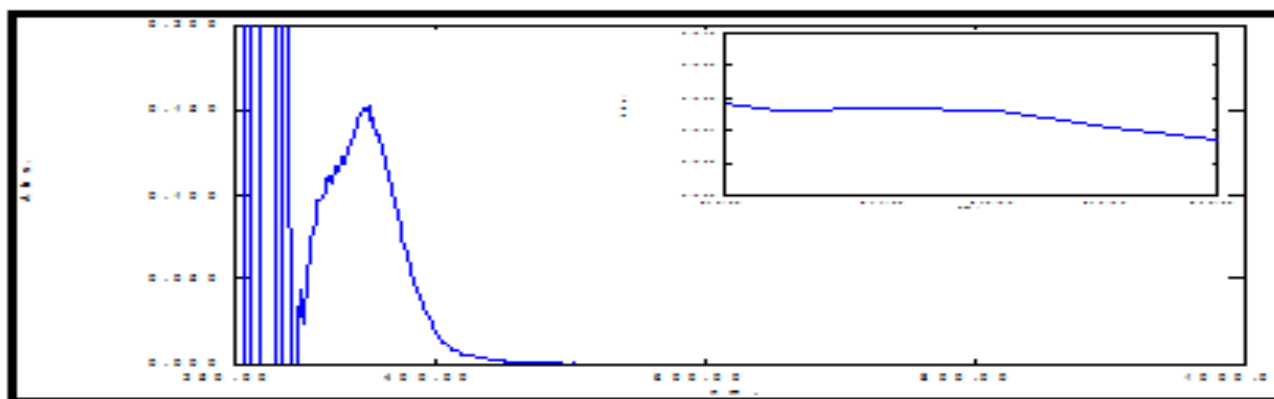


Fig.18: UV-Vis spectrum of C2 complex

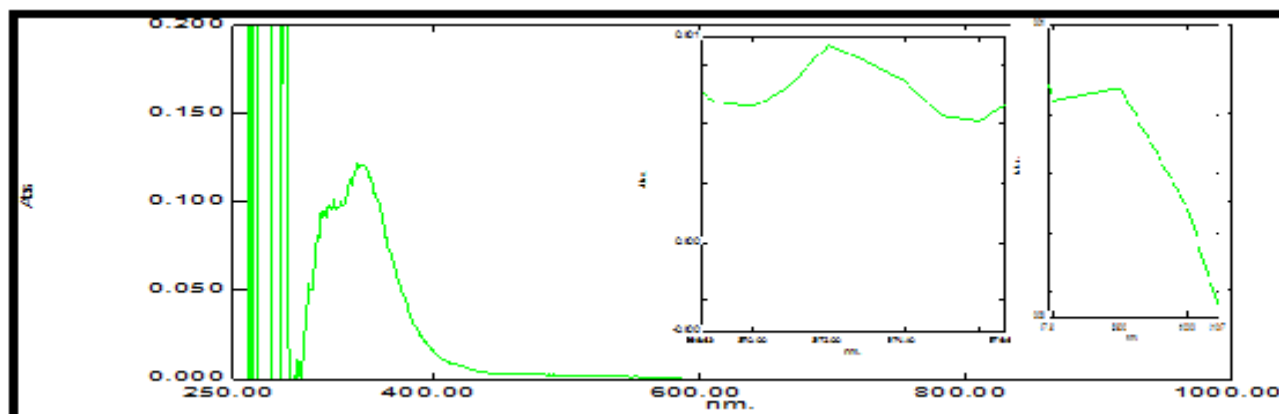


Fig.17: UV-Vis spectrum of C1 complex

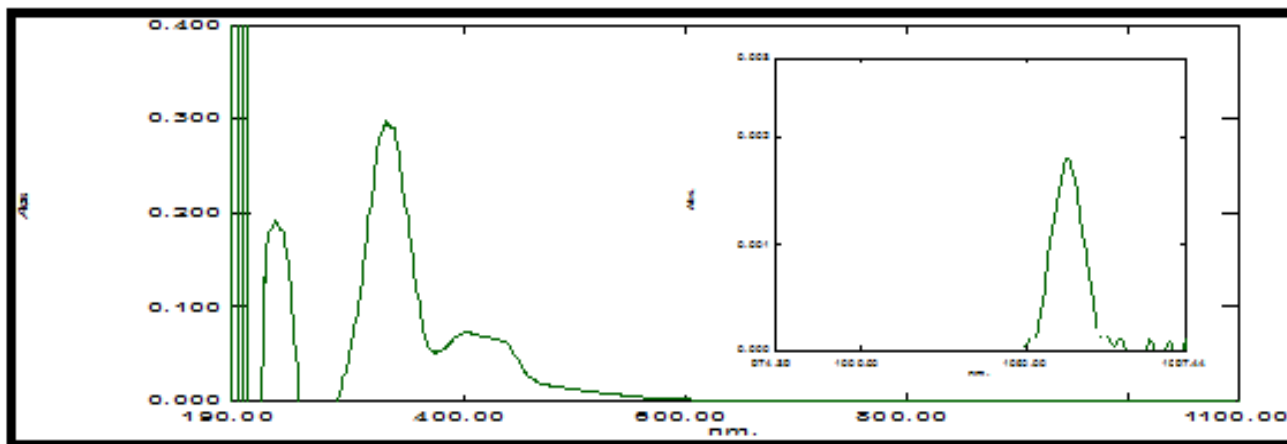


Fig.19: UV-Vis spectrum of C3 complex

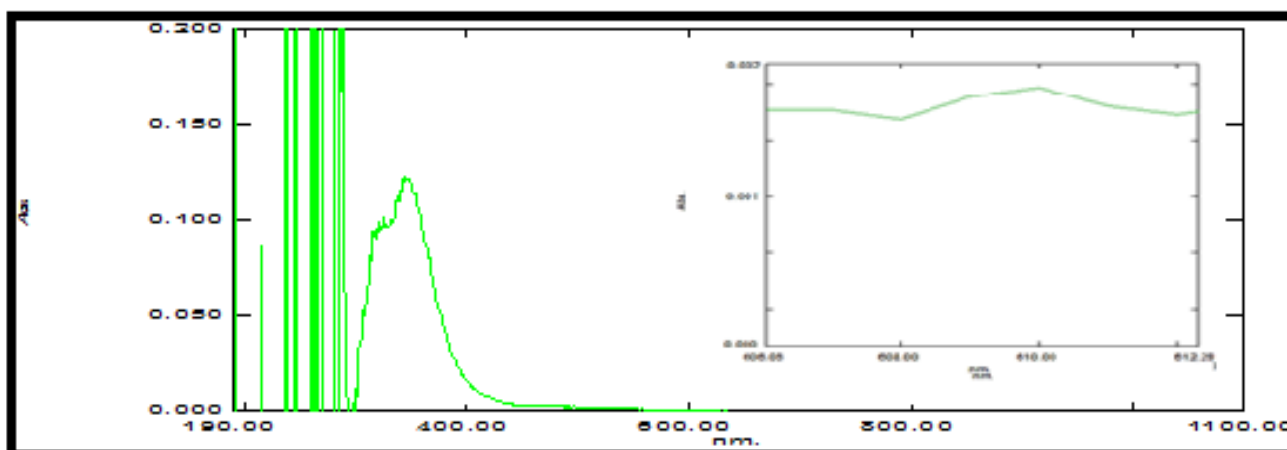


Fig.20: UV-Vis spectrum of C4 complex

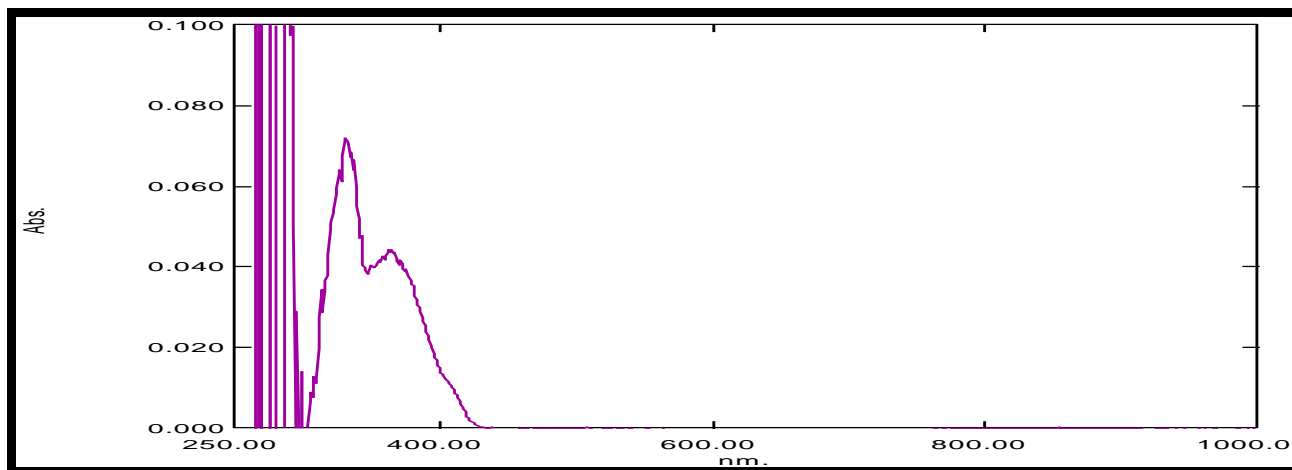


Fig21: UV-Vis spectrum of C5 complex

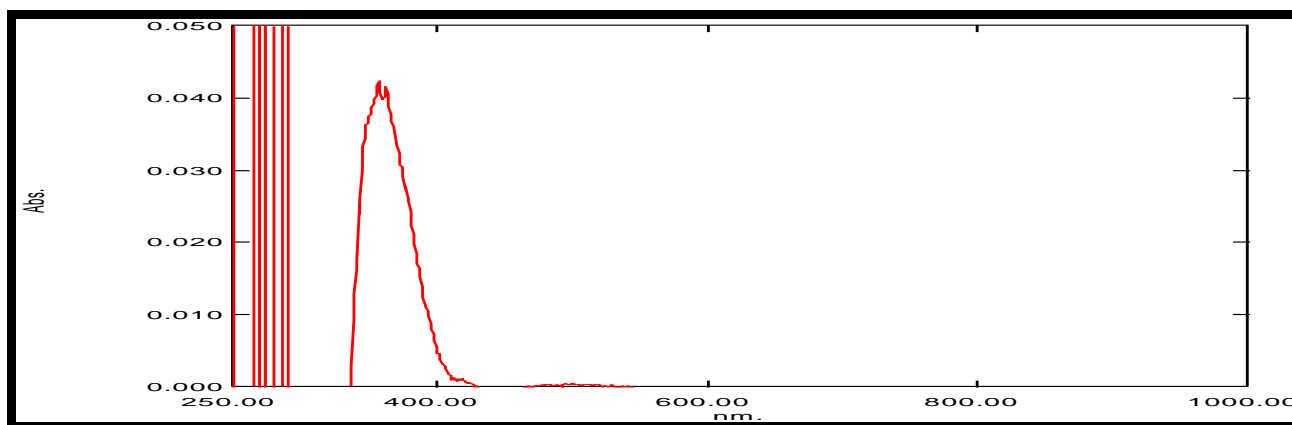


Fig22: UV-Vis spectrum of C6 complex

Thermal Analysis of the ligand and their Metal ion Complexes

Thermal analysis TG and DTA of complexes were studied under Nitrogen gas at heating range (25-800) °C and heating rate

(10°C/min). The thermal analysis was performed to proof the suggested structures and studied the thermal stability of the complexes. The results were listed in (table 4) and shown in Figures (23-31).

Table4: Thermal decomposition data of the ligand and complexes

Compound	Molecular formula M.Wt	step	Temp. range of the decomposition (TG) °C	Suggested Formula of loss	Mass loss%	
					Cal.	found
L	$C_{15}H_9N_5O_6S$ (387.33)	1	30-200	-NO ₂ , -OH	16.26	16.64
		2	200-300	-NO ₂	11.61	11.61
		3	300-450	-C ₄ H ₃	16.00	15.91
		4	450-800	-C ₆ H ₅	19.62	19.28
		5	> 800	-C ₄ H ₅ N ₃ OS	36.96	36.58
C1	[VO(L)SO ₄] (550.32)	1	30-200	-NO ₂	8.35	7.00
		2	200-300	-SO ₄	17.44	17.68
		3	300-500	-C ₇ H ₆ N ₂ O ₃	30.18	30.81
		4	500-800	-C ₂ H ₃ N ₂ S	15.83	14.86
		5	> 800	-C ₆ H ₆ O ₂ V	29.26	29.59
C2	[Co(L) ₂ Cl ₂] 2H ₂ O (940.59)	1	150-292.23	2H ₂ O, C ₆ H ₃ (NO ₂) ₂	21.58	20.67
		2	292.23-462.62	2NO ₂	9.78	9.42
		3	462.62-684.81	2Cl, C ₆ H ₃	15.52	16.01
		4	684-800	Residual C ₆ H ₃ (OH) ₂ CNC ₂ HN ₂ SCoC ₆ H ₃ OHCN	53.04	53.09
C3	[Ni(L) ₂ Cl ₂] 2H ₂ O (904.35)	1	150-292.23	2H ₂ O, 2Cl	11.37	10.9
		2	292.23-462.62	C ₆ H ₃ (NO ₂) ₂ , C ₆ H ₃ (NO ₂) ₂ C ₂ HN ₂ S	52.10	51.70
		3	462.62-684.81	C ₆ H ₃ (NO ₂) ₂ CN ₂ S		
		4	684-800	2OH, CHNC Residual C ₆ H ₃ OHCHNHNiC ₆ H ₃ OH	7.76 28.67	7.45 29.95
C4	Cu(L) ₂ Cl ₂]H ₂ O (927.11)	1	30-200	-H ₂ O, -Cl	5.76	6.47
		2	200-320	-C ₆ H ₃ N ₂ O ₄ , -Cl	21.84	21.90
		3	320-450	-C ₆ H ₄ N ₂ O ₅	19.85	18.90
		4	450-800	-C ₃ H ₄ N ₄ S ₂	16.82	16.15
		5	> 800	-C ₁₅ H ₁₃ CuN ₂ O ₃	35.89	36.60
C6	[Cd(L) ₂ Cl ₂] 2H ₂ O (994.06)	1	30-192.21	2H ₂ O	3.62	4.14
		2	192.21-311.32	C ₆ H ₃ (NO ₂) ₂ , C ₂ HN ₂ S C ₆ H ₃ (NO ₂) ₂ , CN ₂ , 2Cl	51.60	52.00
		3	311.32-539.00	C ₆ H ₃ OH, C ₆ H ₃ (OH) ₂ CHNCS	27.36	26.91
		4	>539.00	OH Cd CHN	15.73	16.95

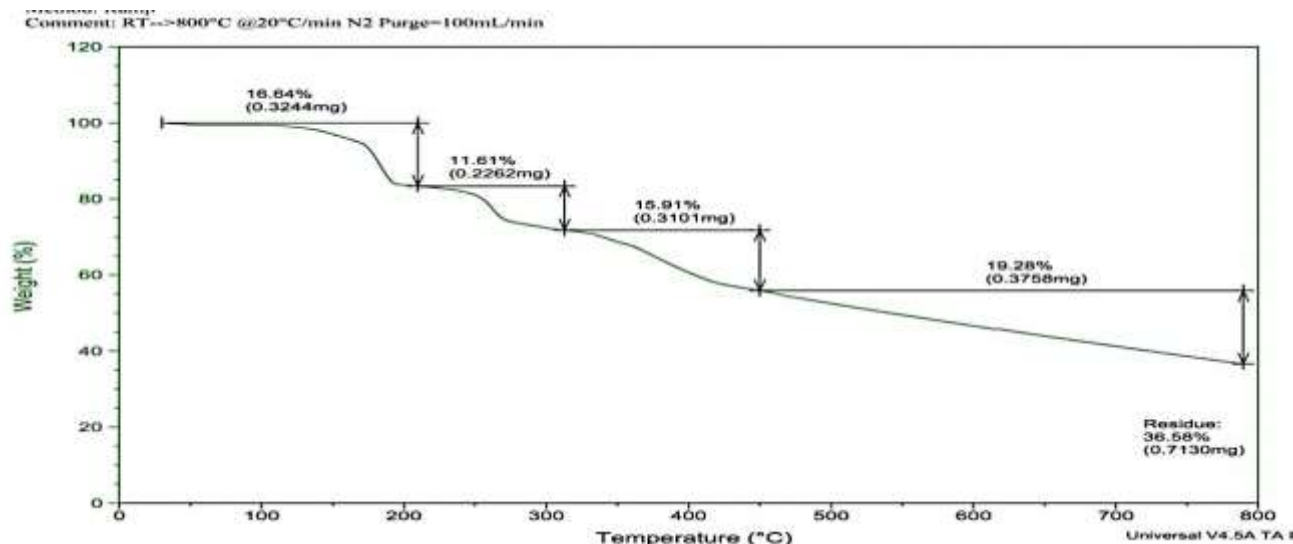


Fig23: Thermographs (TGA) of Ligand (L)

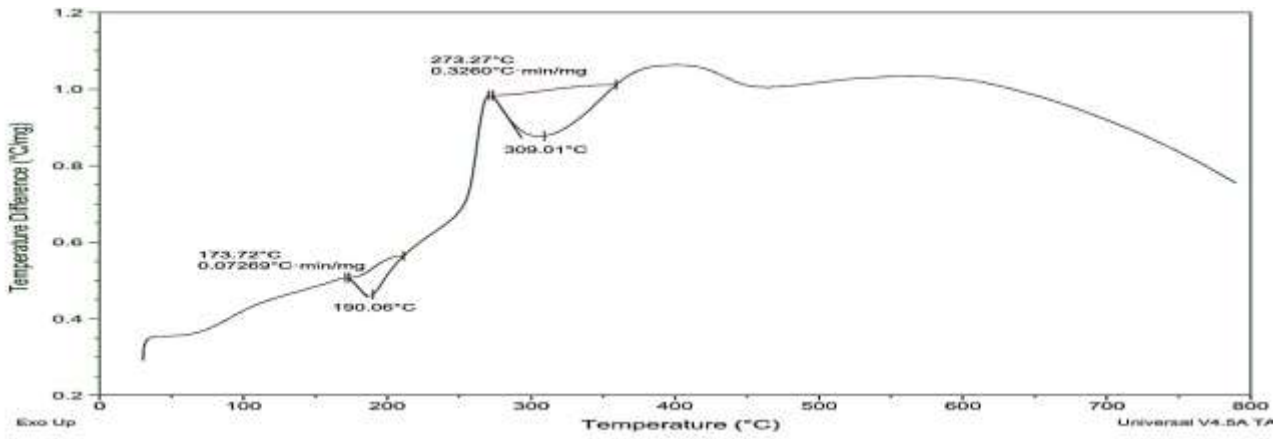


Fig24: Thermographs (DTA)of Ligand (L)

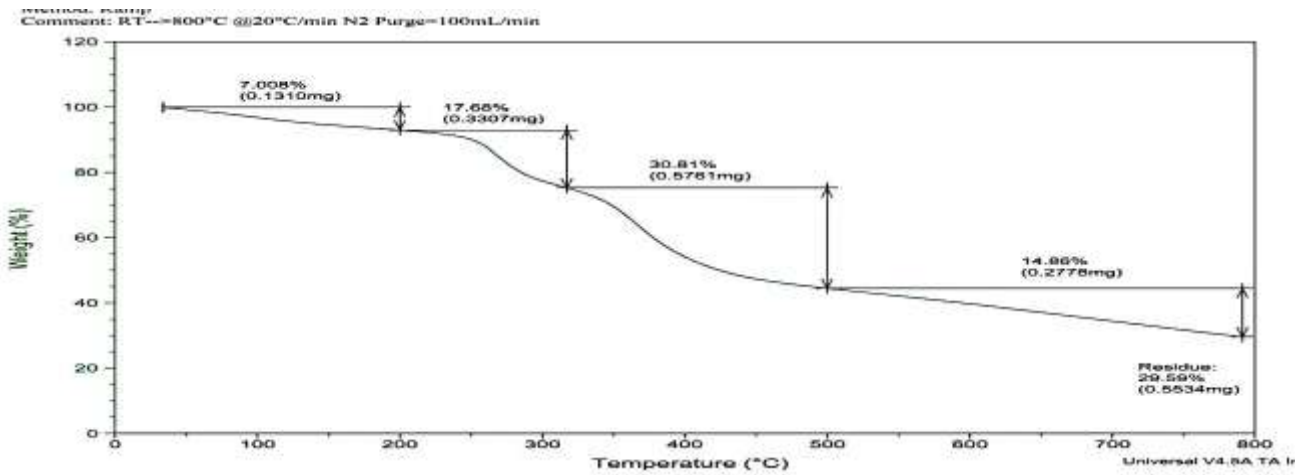


Fig25: Thermographs (TGA)of C1 complex

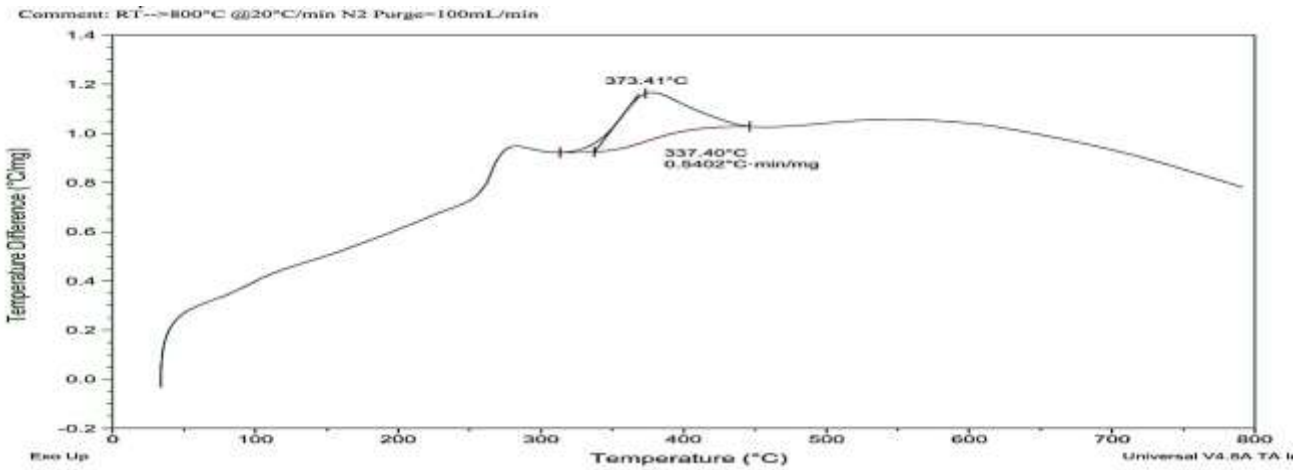


Fig26: Thermographs (DTA)of C1 complex

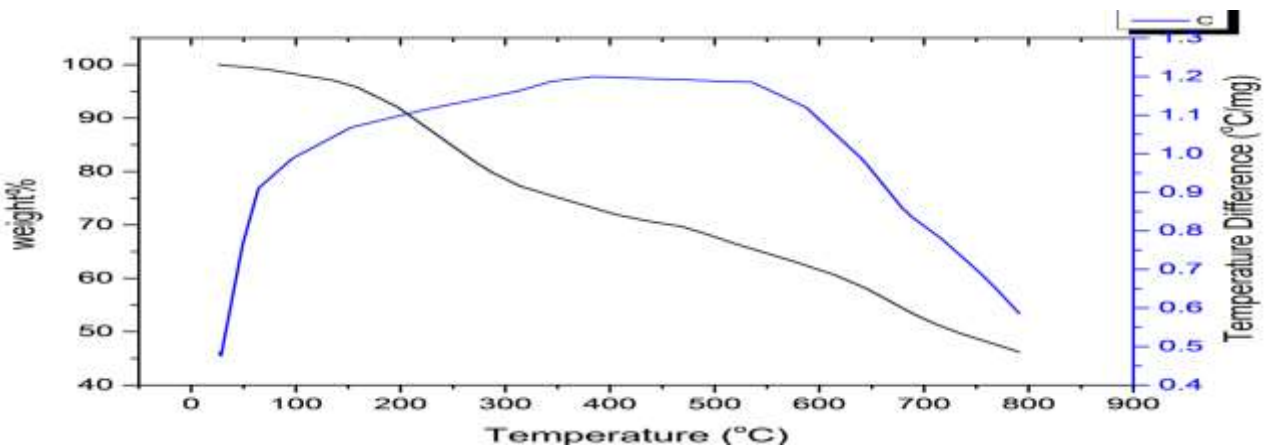


Fig27: Thermographs (TGA and DTA)of C2 complex

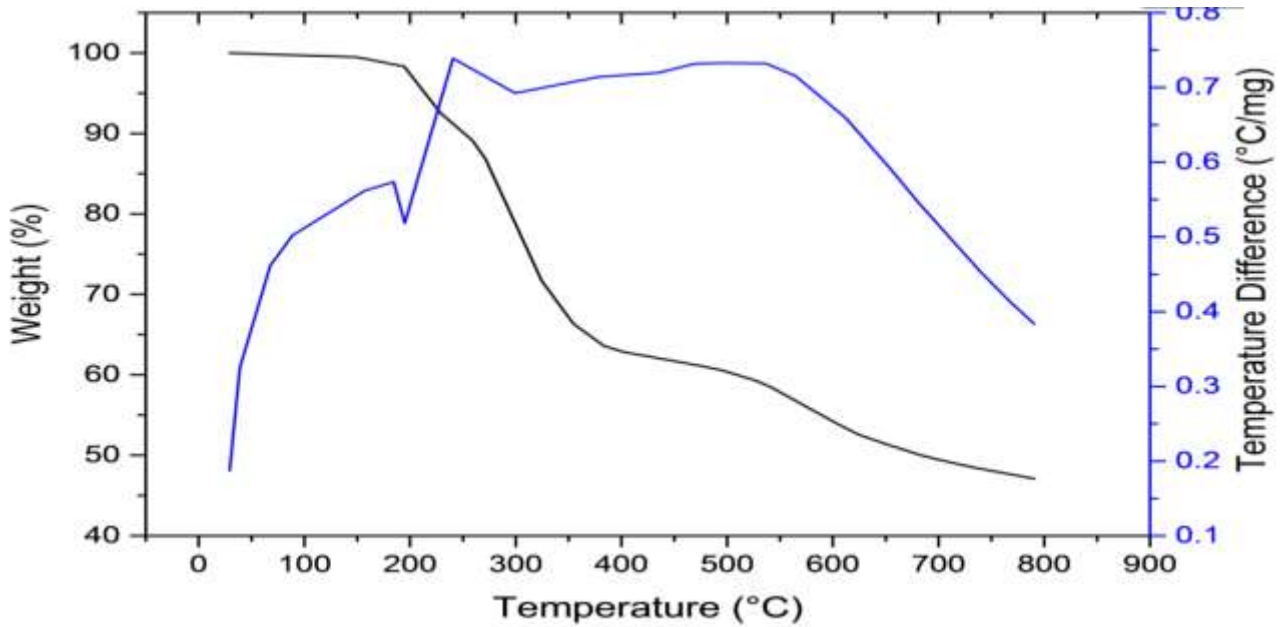


Fig28: Thermographs (TGA andDTA)of C3 complex

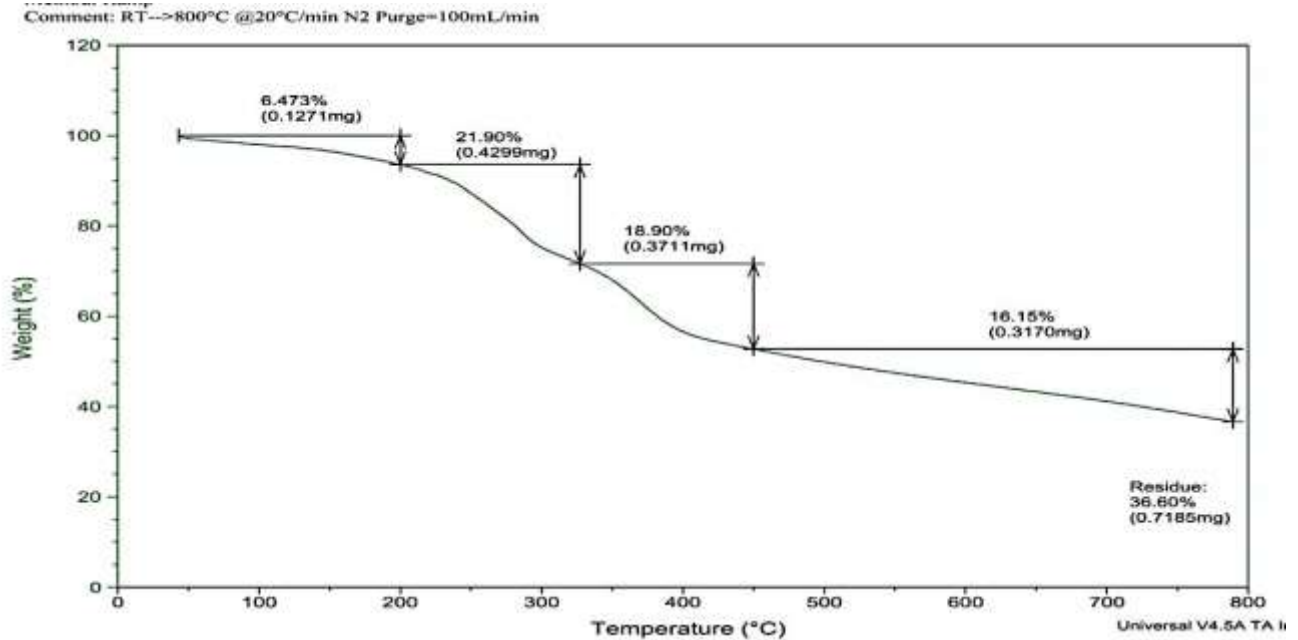


Fig29: Thermographs (TGA)of C4 complex

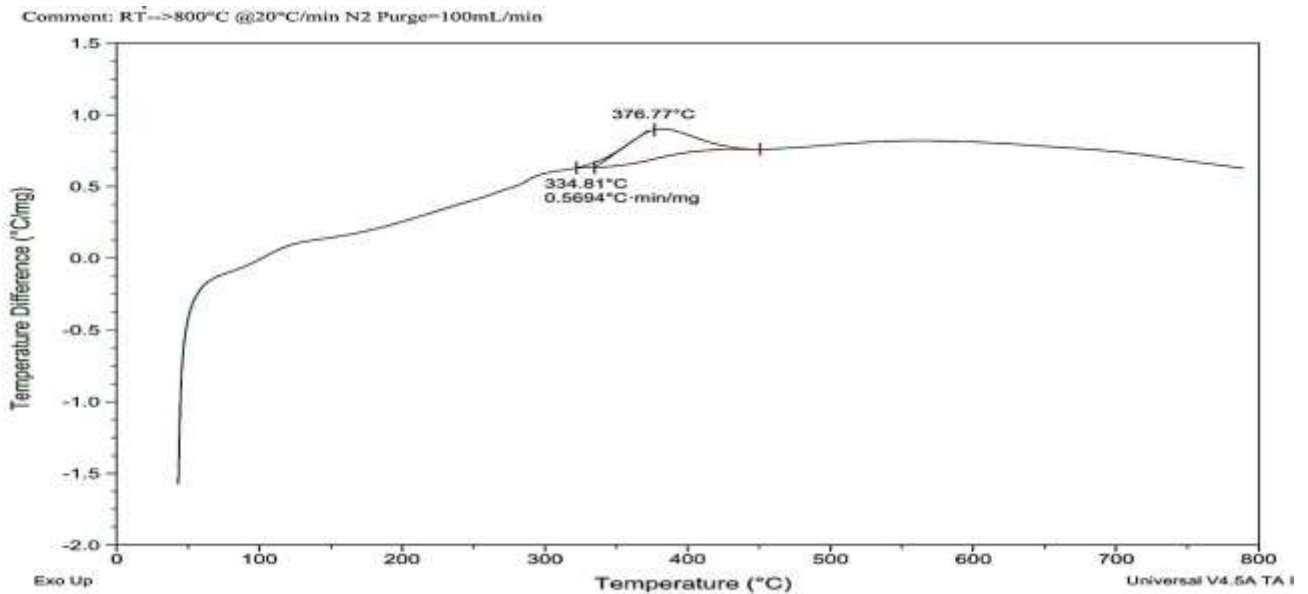


Fig30: Thermographs (DTA)of C4 complex

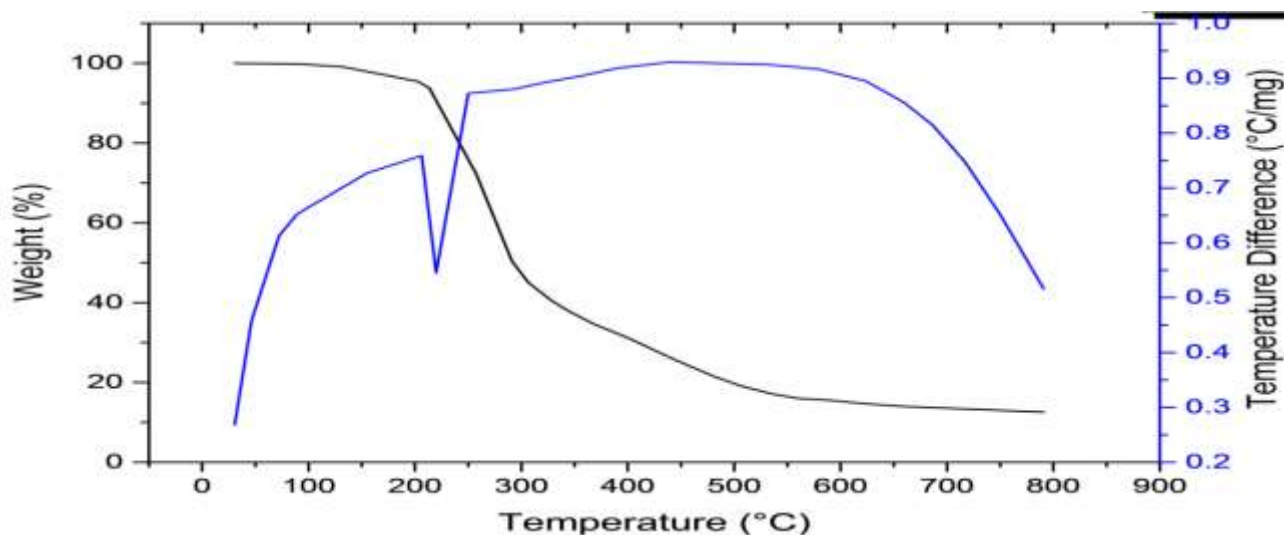


Fig31: Thermographs (TGA and DTA)of C6 complex

Mass Spectra

Mass spectrometry has been successfully used to investigate molecular[42] The ligand

(L) was compared with their molecular formula weight. The mass spectra of ligands (L) was Shown a molecular ion mother peak at $m/z = (384.46)$ as show in Fig(32).

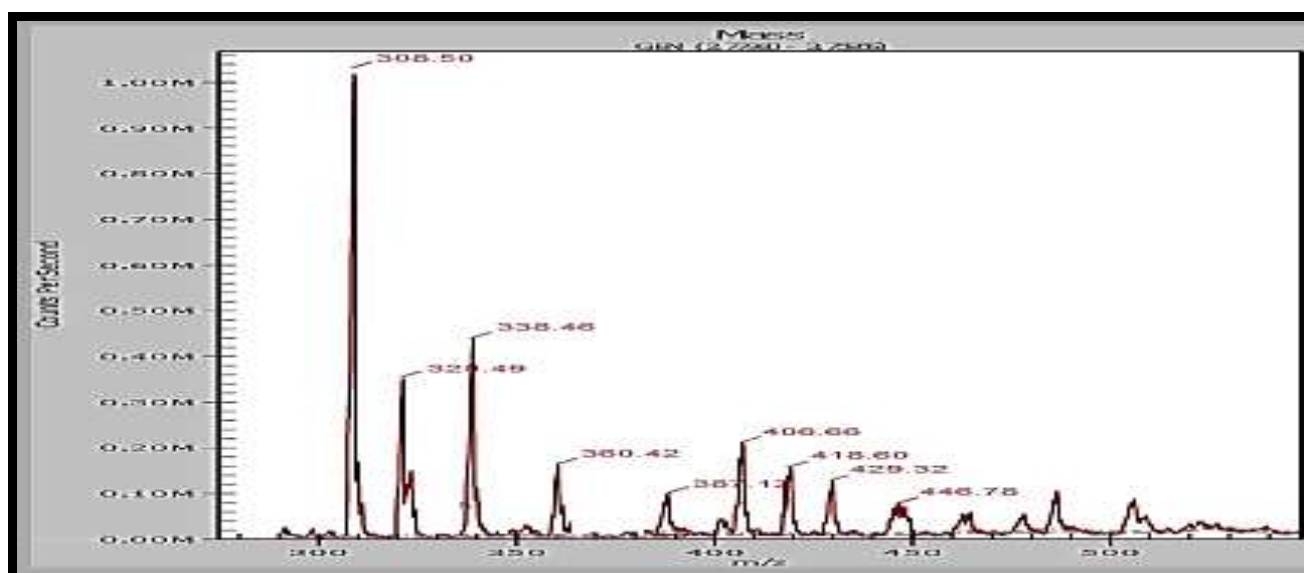


Fig. 32: Mass spectra of the ligand (L)

Conclusion

The ligand were synthesized by condensation of substituted aldehyde with 2-amino5-(3,5-dinitrophenyl)-1,3,4-thiadiazol with reflux as reported in literature , six metal complexes had been prepared with new ligand. These complexes have molar ratio of 1:2) where the order is metal: ligand ,excepted C₁ complex has (1:1)ratio.The ligand and there complexes were identified structures by elemental micro analysis (CHNS), FT-IR, UV-Vis ¹H-NMR, and ¹³C-NMR,spectra ,atomic absorption, thermal analysis (TG, DTG), magnetic susceptibility molar conductance and. The ligand synthesized is bidentate of Schiff-bases good type for chelation.

The coordinated complexes take place through nitrogen of isomathane group and hydroxyl group.

Nomenclature and Suggested Structures of the Complexes

The synthesized complexes are suggested structures of had been investigated and confirmed via using infrared (FT-IR¹H-NMR, ¹³C-NMR UV-Visible and mass spectroscopy), micro elemental analysis (C.H.N.S), spectroscopy, molar conductance, thermal analysis, magnetic susceptibility, and atomic absorption According to the observations obtained the structures of the complexes were suggested as in Fig. (33).

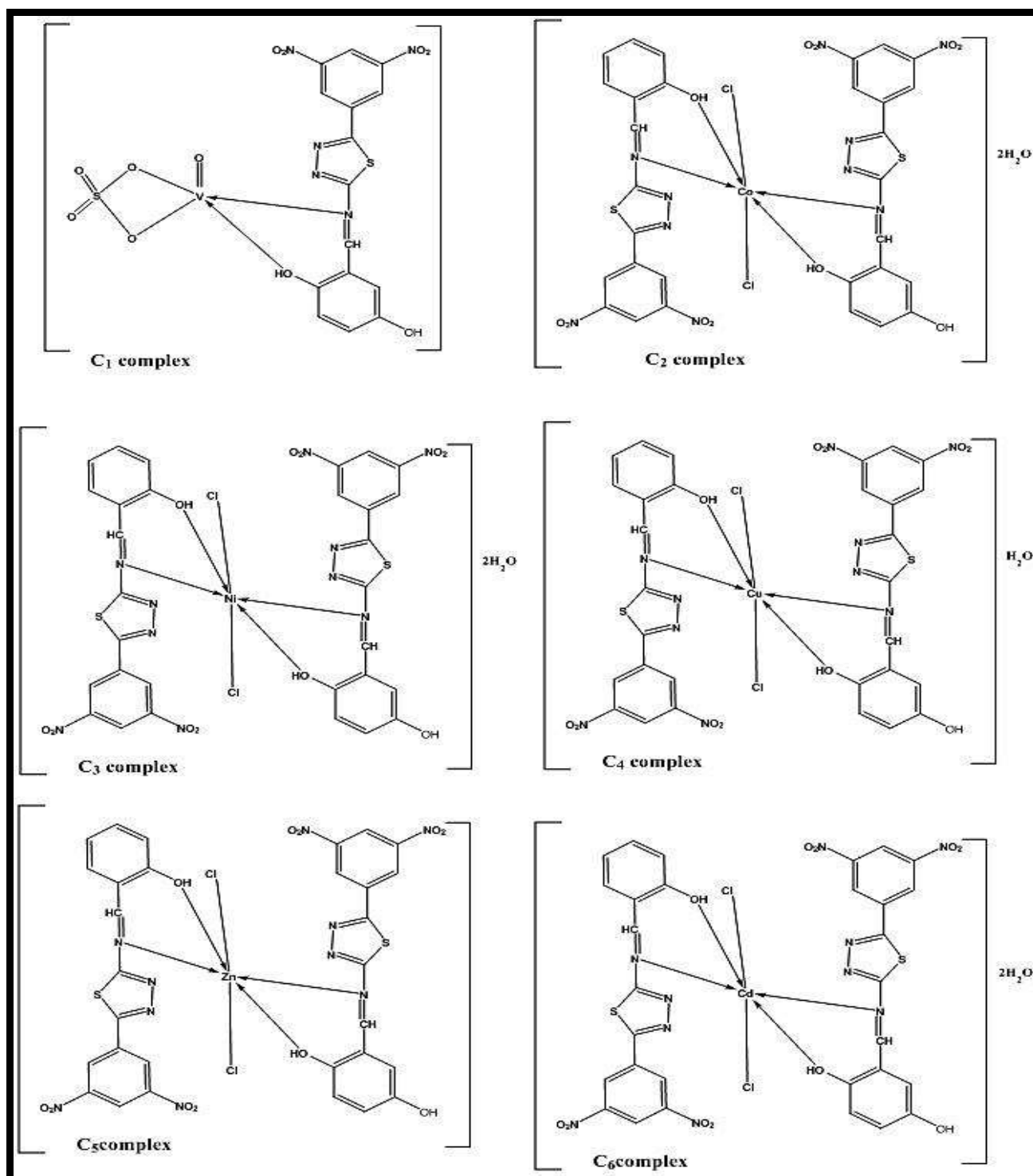


Fig33:Suggestion of structures for all complexes (C1-C6)

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