

# Synthesis and Characterization new metal complexes of heterocyclic units and study antibacterial and antifungal

Ali T.Bader<sup>1\*</sup>, Basim I. Al-Abdaly<sup>2</sup> and Ibtisam k. Jassim<sup>3</sup>

1- Department of Chemistry, College of science for Women , Babylon University, Hilla, Iraq

2- Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

3-Department of Chemistry, College of Education-Ibn-Alhathim, University of Baghdad, Baghdad,Iraq

## Abstract :

New series coordination compounds of some transition metal ions [VO(IV)), Co(II) Ni(II),Cu(II),Zn(II) and Cd(II)] of synthesized of the ligand (2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine). The ligand was prepared by Schiff bases by reaction from 2-amino -5-(3,5dinitro phenyl )1,3,4-thiadiazole with salicylaldehyde. The structures of the new metal ion complexes were characterized elemental micro analysis (CHNS), FT-IR, UV-Vis <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy, atomic absorption, thermal analysis (TG, DTG), magnetic susceptibility and molar conductance. The According to the obtained data the probable coordination geometries of these complexes were suggested as octahedral excepted C<sub>1</sub> was pyramidal. All complexes were found to be non-electrolyte. The biological activity (antibacterial and antifungal) in-vitro are investigated for the complexes at prepared concentration (1\*10<sup>-3</sup> M) and showed inhibition ability against growth of the four types of pathogenic bacteria: [*Staphylococcus aureus*.] as gram positive and [*Escherichia coli* and *Pseudomonas aeruginosa*] as gram negative and showed inhibition ability against fungi (*Candida albicans*). The most of these complexes are effective against both types of bacteria in varying degree, with high activity for Cd (II) complexes and some the complexes are showed good inhibition zones against the type of fungi.

**Keywords:** Biological activity , 1,3,4-thiadiazole , Schiff base and Transition metal ions,

## INTRODUCTION:

Schiff bases synthesized from an amino and carbonyl compound are signification class of ligands that coordinate to metal ions by azomethine group and had been studied extensively[1]. In azomethine derivatives, the C=N linkage is fundamental for biological activity, several azomethine had been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities[2] 1,3,4-Thiadiazole was first described in 1882 by Fischer and further 1,3,4-Thiadiazole was first recognized by Fischer in 1882 and than it has been developed by Bush and his team meet .In 1956, Goerdler has demonstrated the true nature, of the ring system [3].however , thiadiazole ring could be divided in to three major sub classes :

a-aromatic systems that include the neutral thiadiazole

b- Mesoionic systems which contain five-membered heterocycles in which they are not a covalent or a polar and also have a sextet of electrons combined with the five atoms that comprising the ring;

c-Nonaromatic systems like the tetrahydro 1,3,4-thiadiazoles and the 1,3,4-thiadiazoles

d- the prefix Δ, with being a Δ<sup>2</sup>-1,3,4-thiadiazole (Structures 6-8).

1,3,4-Thiadiazole derivatives have interesting biological activity probably conferred to them by the strong aromaticity of this ring system, which leads to great in vivo stability and generally, a lack of toxicity for higher vertebrates, including humans. When diverse functional groups that interact with biological receptors are attached to this ring, compounds possessing outstanding properties are obtained. Except for some antibacterial sulfonamides (albucid and globucid), no longer used clinically, but which possessed historical importance, the most interesting examples are constituted by 5-amino-1,3,4-thiadiazole-derivatives[4]. In addition, the chemistry and the applications of these new Schiff base thiadiazole derivatives could be extensively studied by coordinating to various metal ion moieties. As a result, the structural-activity relationship study of 1,3,4-thiadiazoles could be expanded in the near future [5-7], As the continuation interest of our study of transition metal complexes[1, 8] here we presence the synthesis and characterization of new complex derivatives of (2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine.. Moreover, the preliminary *in vitro*antibacterial screening activities of the complexes obtained are carried out and the results are reported here in.

## 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 (fluka), Salicylaldehyde , Glacial acetic acid(BDH), VOSO<sub>4</sub>.5H<sub>2</sub>O (BDH) and CoCl<sub>2</sub>.6H<sub>2</sub>O (Merck). copper (II) chloride dihydrate (BDH), Nickel chloride hex hydrate(Fluk), copper (II) chloride dihydrate (BDH), Zinic chloride di hydrate and Cadmium (II) chloride dihydrate (FLUKA).

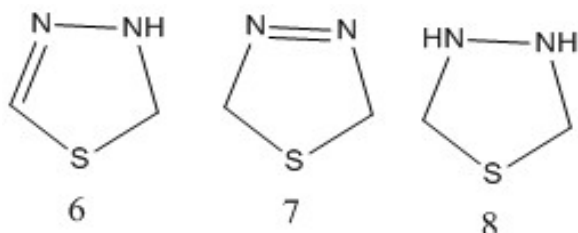


Fig. (1)structure of 1,3,4-thiadiazole

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 (4000-400)  $\text{cm}^{-1}$  using KBr disc for ligands and CsI disc in the frequency range (4000-200)  $\text{cm}^{-1}$  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 analysis 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  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR were recorded BRUKER AV 400 Avance-III (400 MHz and 100MHz), Indian, using 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

##### 1- Preparation of 2-amino-5-(3,5-dinitro phenyl)1,3,4-thiadiazole.[1] [9-11]

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

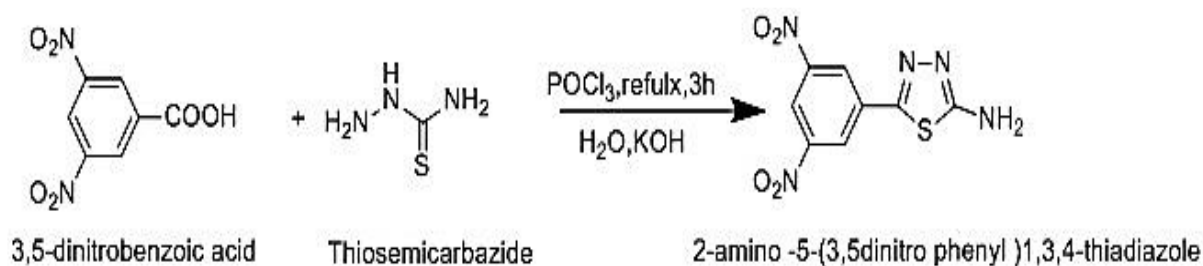
cooling, distilled water (50 mL) was added to the mixture and the heating under reflux was carried out for another 4 h. The obtained filtrate was neutralized with potassium hydroxide. Then, the precipitate was filtered and washed with cold distilled water and finally recrystallized by using ethanol to obtain 5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-amine as show in (scheme 1).

##### 2-Synthesis of ligand one (2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine ))) [2][11-13].

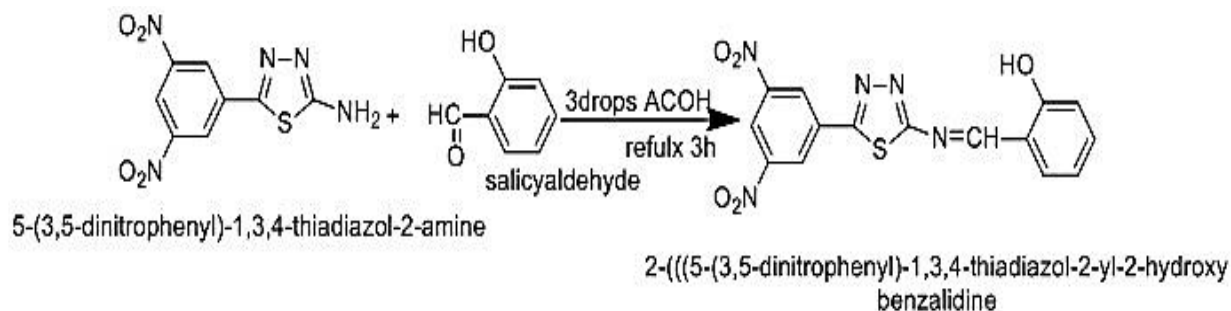
A hot solution of 5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-amine. (0.002 mole, 0.5g) in 15 mL of EtOH was added slowly and dropwise into a solution of salicylaldehyde (0.002, 0.24g), in presence (3) drops of glacial acetic acid (AcOH) and the mixture was refluxed for 3 h. A pale-yellow colored precipitate was filtered and washed with EtOH, then dried in air to obtain ligand one 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine) as show in the equation (1)

##### 3-Synthesis of metal complexes ( $C_1$ to $C_6$ ) [3-8][11]

The complexes ( $C_1$ - $C_6$ ) were synthesis by hot ethanol solution of the metal ions [ $\text{VO}(\text{II})\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  was added to hot ethanol solution 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)imino)methyl)phenol L1 in 1:2 (metal:ligand) molar ratio expected  $C_1$  complex in 1:1 (metal:ligand) as show a table (1.2). Then, the mixture was heated under reflux for one an hour and coloured precipitates were obtained. Later, the precipitates were filtered out, washed with distilled water and finally recrystallized from ethanol



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



Equation (2) 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine)

Table (1) : Physical properties and analytical data for L and their complexes

symbol	color	m.p °C	Yield %	M.Wt	Micro Elemental Analysis Found (calc.)				Metal content % Found (calc.)	Chloride content % Found (calc.)
					C%	H%	N%	S%		
L	Yellow	270-272	75	371.33	48.82 (48.52)	2.20 (2.44)	18.54 (18.86)	8.55 (8.63)	-----	-----
C1	green	263-265	60	588.37	30.80 (30.62)	2.77 (2.57)	10.80 (11.90)	10.55 (10.90)	----	----
C2	Blue	251-253	65	908.52	40.11 (39.66)	2.54 (2.44)	15.23 (15.42)	7.20 (7.06)	7.50 (7.80)	
C3	yellow	258-260	55	908.28	39.54 (39.67)	1.98 (2.44)	15.58 (15.42)	6.88 (7.06)	7.00 (6.46)	7.77 (7.81)
C4	Brown	250-252	67	895.12	40.11 (40.26)	2.23 (2.25)	15.83 (15.65)	7.03 (7.16)	6.90 (7.10)	7.72 (7.92)
C5	Yellow	287-290	53	878.93	42.33 (41.00)	2.11 (2.06)	15.53 (15.94)	7.35 (7.30)	7.33 (7.44)	7.89 (8.07)
C6	Yellow	244-246	64	943.98	38.64 (38.71)	2.51 (2.14)	15.10 (14.84)	6.39 (6.79)	11.43 (11.91)	7.22 (7.51)

Table (2) FT-IR data of L and its complexes

Symbol of compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	M-Cl
L <sub>1</sub>	3200-3400	1625	-	---	---
C1	3200-3600	1625	480	325	---
C2	3100-3600	1625	447	319	270
C3	3300-3600	1627	450	430	350
C4	3300-3600	1625	410	400	370
C5	3300-3550	1625	405	360	291
C6	3300-3450	1624	410	310	227

## 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 their metal complexes are shown 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 act as neutral bidentate. The complexes are insoluble in common organic solvents but all complexes completely soluble in DMF and DMSO

### 2. -FT-IR spectrum of Ligand and their complexes:

#### FT-IR spectrum of 2-amino5-(3,5-dinitrophenyl)-1,3,4-thiadiazol[1]

The structure of the prepared compound [1] was characterized by FT-IR spectrum of compound [1], showed the appearance of NH<sub>2</sub> stretching band at asymmetric and symmetric at (3469,3415.)cm<sup>-1</sup>, band of (3090) cm<sup>-1</sup> band of (C-H)arom from the (C=N)<sub>st</sub> appeared at (1620)cm<sup>-1</sup>, (NO<sub>2</sub>) asymmetric and symmetric at (1537) cm<sup>-1</sup> and (1348) cm<sup>-1</sup> respectively. Other bands of C=C<sub>st</sub> appeared at (1508,1419)cm<sup>-1</sup> and band of (C-S-C) at (1076) cm<sup>-1</sup> Fig. (2) [14-17]

#### FT-IR spectrum of Ligand and their complexes:

The spectrum of the free ligand (L), Fig. (3) table (2) showed bands at (3200-3400) cm<sup>-1</sup> assigned for  $\nu(\text{O-H})$  stretching, the band at (3085) assigned for  $\nu(\text{C-H})$  aromatic

[18] and the band at 1625cm<sup>-1</sup> due to  $\nu(\text{C=N})$  of the Schiff base. Also the spectrum shows bands at (1589)cm<sup>-1</sup> assigned to  $\nu(\text{C=N})$  cyclic ring stretching and the bands at (1539 and 1355)cm<sup>-1</sup>, (1506 and 1352)cm<sup>-1</sup>, (1260)cm<sup>-1</sup> and (1072)cm<sup>-1</sup> attributed to the  $\nu(\text{NO}_2)$  asymmetric and symmetric),  $\nu(\text{C=C})$ ,  $\nu(\text{C-O})$ ,  $\nu(\text{C-S-C})$ , stretches frequencies, respectively.[15] The shift of  $\nu(\text{O-H})$  and (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 (200-500) cm<sup>-1</sup> appeared stretching band for  $\nu(\text{M-N})$ , (M-O) and (M-Cl) as showed in Fig(4-8). [14, 15, 19-21].

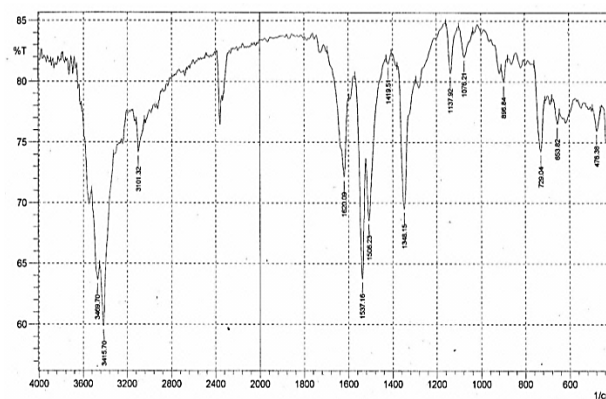


Fig.(2) FT-IR spectra 2-amino5-(3,5-dinitrophenyl)-1,3,4-thiadiazol

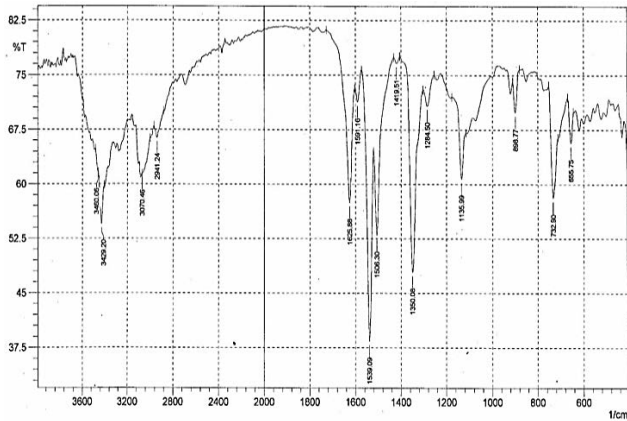


Fig.(3) FT-IR spectrum 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzaldehyde)

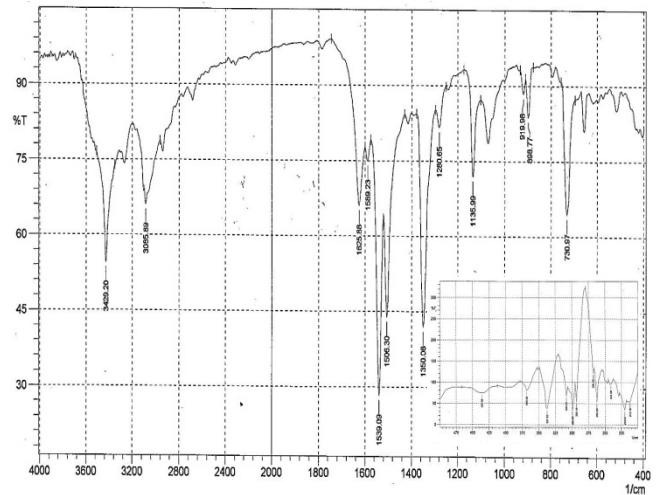


Fig. (7) FT-IR spectrum of C<sub>4</sub> complex

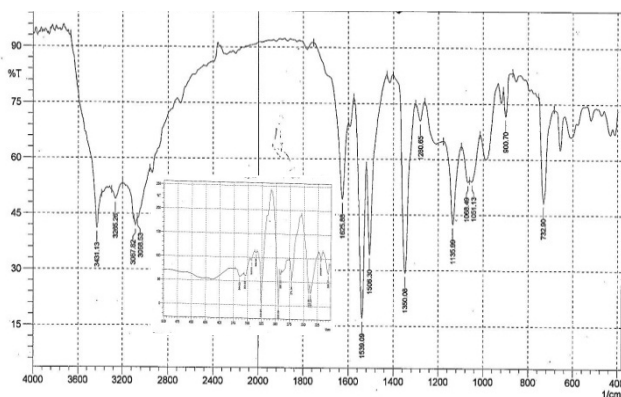


Fig. (4) FT-IR spectrum of C<sub>1</sub> complex

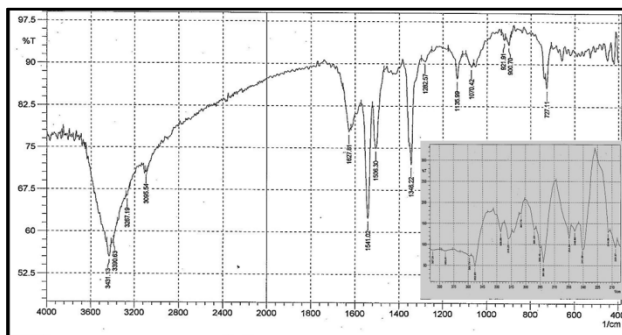


Fig. (5) FT-IR spectrum of C<sub>3</sub> complex

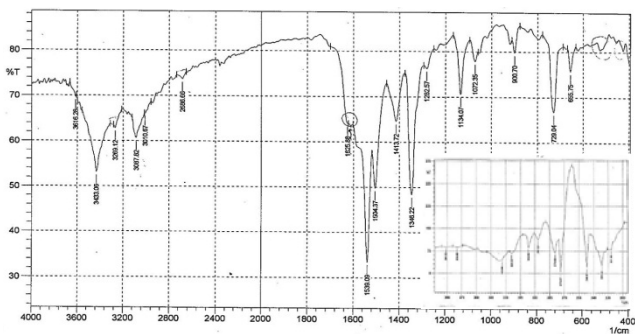


Fig. (6) FT-IR spectrum of C<sub>4</sub> complex

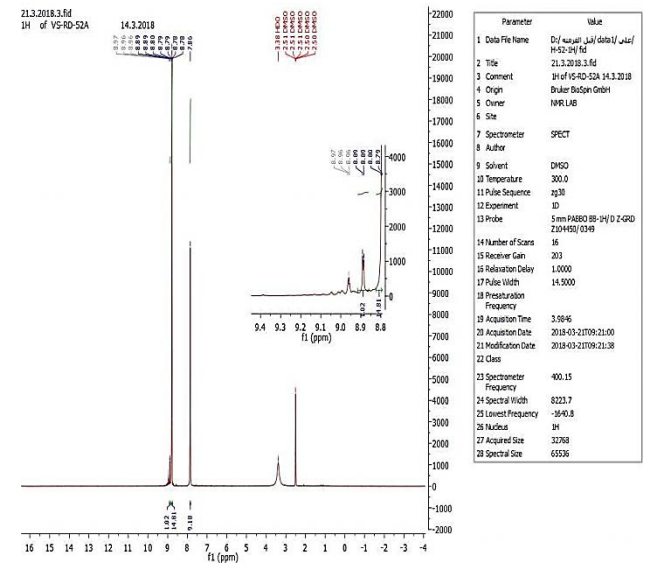


Fig. (8) <sup>1</sup>H-NMR spectrum for 2-amino5-(3,5-dinitrophenyl)-1,3,4-thiadiazol

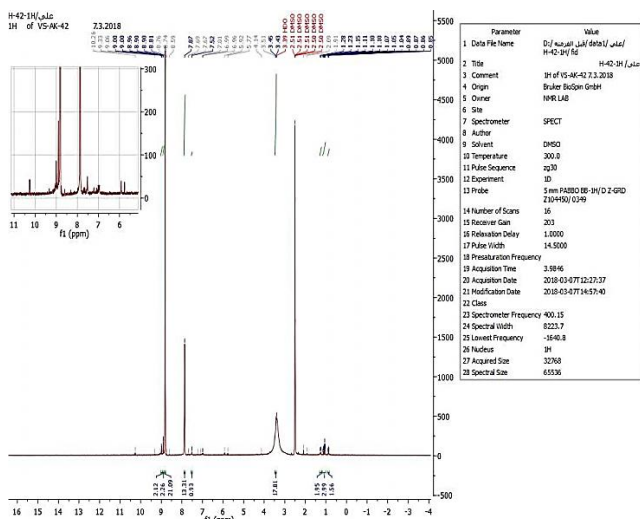


Fig. (9) <sup>1</sup>H-NMR spectrum for(L) 2-(((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)-2-hydroxy benzalidine )

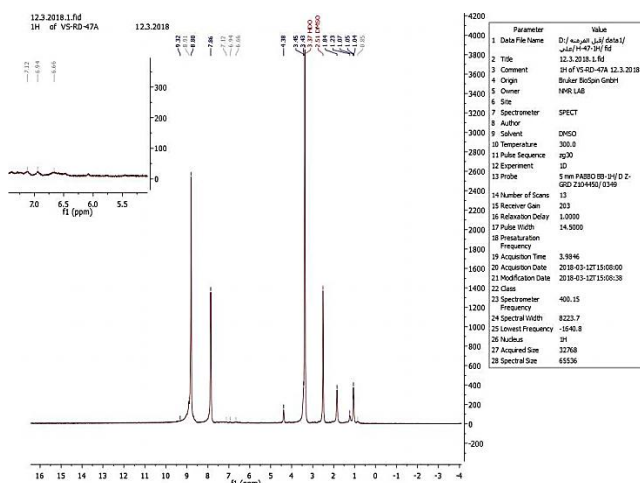


Fig. (10) <sup>1</sup>H-NMR spectrum for C6 complex complex

<sup>13</sup>C-NMR spectrum of prepared ligand one and its complex

The <sup>13</sup>CNMR spectrum of the ligand L is shown in Fig (11). The spectrum of L is characterized by the presence of (N=CH) of azomethine group which appeared as a signal at δ=(152) ppm[19]. Chemical shift of (C-aromatic ring) appeared at δ =116-134 ppm[14]. The spectrum appearance at low fields at δ = (170) ppm which was assigned to CH=N of thiazol ring as Fig (13) show [26].

The <sup>13</sup>CNMR spectrum of C<sub>6</sub> complex is shown in Fig (12). The spectrum of C<sub>6</sub> complex is characterized by the presence of (N=CH) of azomethine group which appeared as a signal at δ=(1542) ppm[11]. Chemical shift of (C-aromatic ring) appeared at δ =118-134 ppm[14]. The spectrum appearance at low fields at δ = (170) ppm which was assigned to CH=N of thiazol ring ([26]

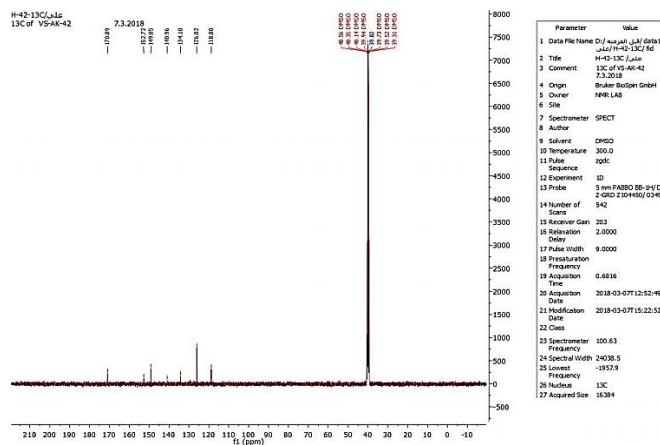


Fig.(11) <sup>13</sup>C-NMR spectrum for ligand one (L)

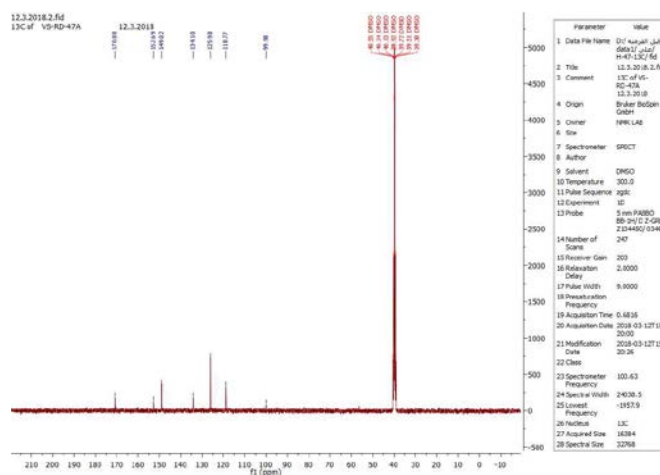


Fig.(12) <sup>13</sup>C-NMR spectrum for C<sub>5</sub> complex

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 (μ<sub>s.o</sub>) according to the following equation[27]

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

The results obtained from this equation were compared with the actual values obtained through the magnetic measurements as in Table (3.5). These values were corrected for diamagnetic effects using the following relationship[28, 29].

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(C<sub>1</sub>-C<sub>6</sub>)**

Compound	Malar conductivity Ohm <sup>-1</sup> .cm <sup>2</sup> .mole <sup>-1</sup>	Magnetic susceptibility(B.M)	
		Cal.	found
C <sub>1</sub>	45.01	1.73	1.32
C <sub>2</sub>	50.88	3.87	3.73
C <sub>3</sub>	56.35	2.82	2.78
C <sub>4</sub>	34.21	1.73	1.84
C <sub>5</sub>	23.87	diamagnetic	
C <sub>6</sub>	10.65	diamagnetic	

**Electronic Spectra of ligands L1 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 293.27 nm (34098.27 cm<sup>-1</sup>) is assigned to ( $\pi \rightarrow \pi^*$ ) transition of the conjugated system. A lower intensity band appeared in the near U.V. region at 328.45nm (30446.03 cm<sup>-1</sup>) was assigned to ( $n \rightarrow \pi^*$ ) which are shown in Fig(13)[15]. The complexes (C1-C6) of this ligand were showed the following:

**A-Electronic Spectrum of vanadium (IV) complex (C1):**

The electronic spectrum of V(IV) complex, exhibited absorption band at 402 nm (24875.62cm<sup>-1</sup>) assignable to  ${}^2B_2 \rightarrow {}^2A_1$  (d-d) transition as shown in Fig (14). Indicating square pyramidal geometry and bands at (335,292.13)nm (29850.75, 34211.43) cm<sup>-1</sup> due to charge transfer from (M→L) [ [11, 30]. The V(IV) complex was shown magnetic moment (2.47)B.M. corresponds to one unpaired electron [144].

**B-Electronic Spectrum of Co (II) complex (C2):**

The electronic spectrum of Co(II) complex, exhibited absorption bands at, (610nm,16393.44cm<sup>-1</sup>), (669nm,14947.68 cm<sup>-1</sup>) assignable to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$ , (d-d) transition as shown in Fig (15). Indicating distorted octahedral geometry and band at (354nm,28248.59cm<sup>-1</sup>) due to charge transfer from (M→L).[31]

**C-Electronic Spectrum of Ni (II) complex (C3)**

The spectrum of the Ni(II) complex showed as Fig (16). a peak in the d-d region at 775 nm(12903.23) cm<sup>-1</sup> assigned to  ${}^3A_2g(F) \rightarrow {}^3T_{1g}(F)$  transition, confirming a distorted octahedral geometry and bands at (325,380)nm (30769.23, 26315.79) cm<sup>-1</sup> due to charge transfer from (M→L)[32].

**D-Electronic Spectrum of Cu (II) complex (C4)**

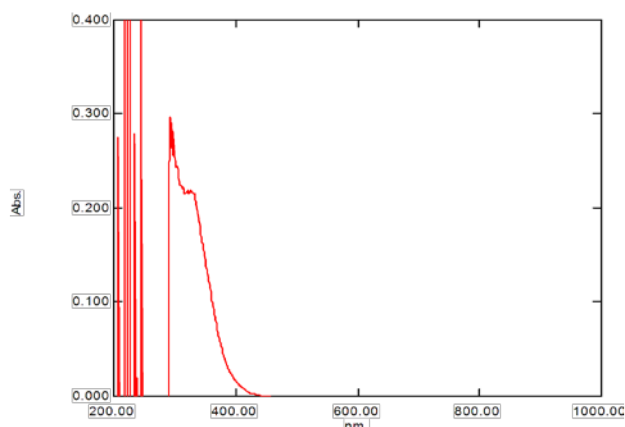
The spectrum of the Cu(II) complex showed Fig (17). a peaks in the d-d region at (754 nm,13262.60 cm<sup>-1</sup>), (800nm,12500cm<sup>-1</sup>) assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  respectively. The bands at (436,331,291)nm due to charge transfer from (M→L)[33-35].

**E) Electronic spectra of Zn(II) complex (C5)**

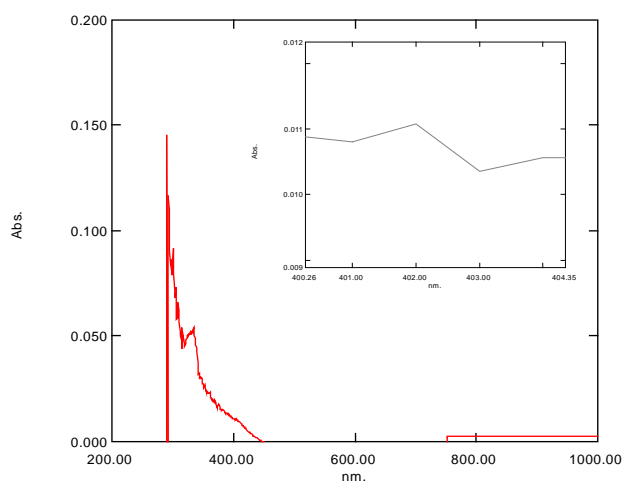
The electronic spectrum of complex (C<sub>5</sub>), was showed no d-d transition as it belong to (d<sup>10</sup>). The ultraviolet-visible spectra of this complex was appeared in Fig (18). (314 nm, 22271cm<sup>-1</sup>,296.9nm, 33681.37 cm<sup>-1</sup>) due to charge transfer from (M→L). The octahedral structure can be suggested for this complex[33, 36].

**D) Electronic spectra of Cd(II) complex (C6)**

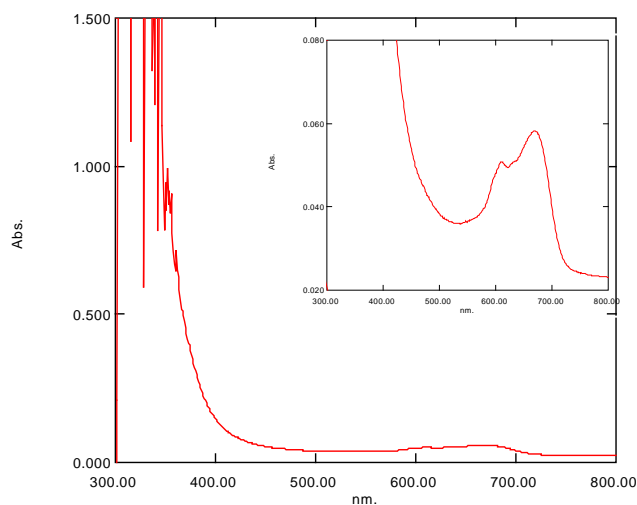
The electronic spectrum of complex (C<sub>6</sub>), was showed no d-d transition as it belong to (d<sup>10</sup>). The ultraviolet-visible spectra of this complex was appeared in Fig (19). (326.2nm, 30656.04 cm<sup>-1</sup> and 296.9nm, 33681.37) due to charge transfer from (M→L). The octahedral structure can be suggested for this complex[37, 38]



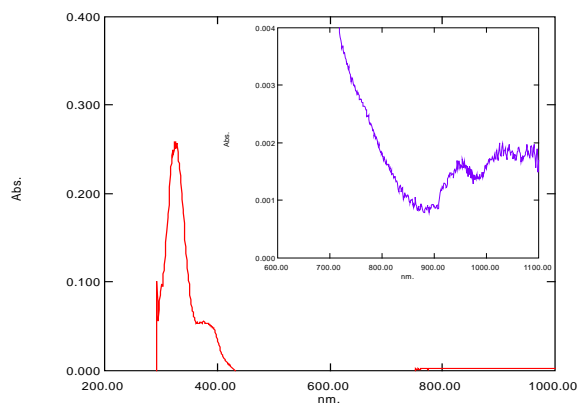
Fig(13) UV-Vis spectrum of the ligand (L)



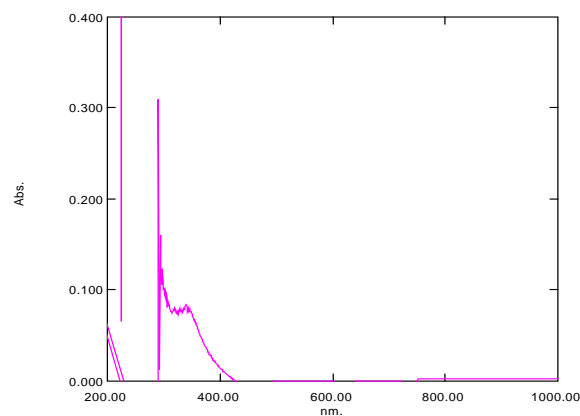
Fig(14): UV-Vis spectrum of C1



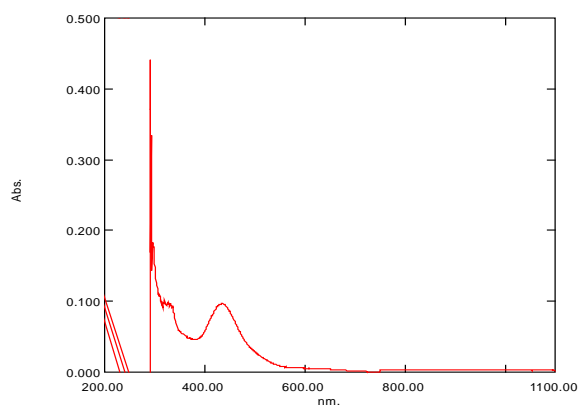
Fig(15): UV-Vis spectrum of C2 complex



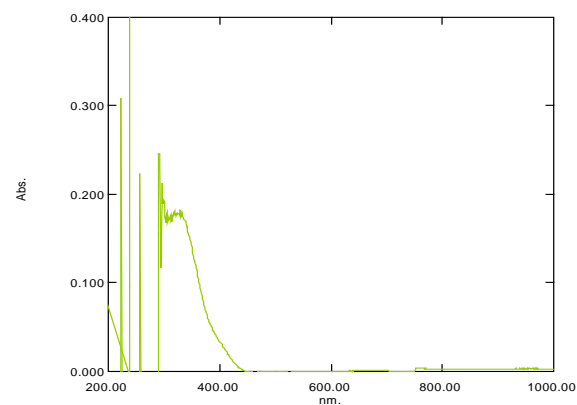
Fig(16): UV-Vis spectrum of C3 complex



Fig(18): UV-Vis spectrum of C5 complex



Fig(17): UV-Vis spectrum of C4 complex



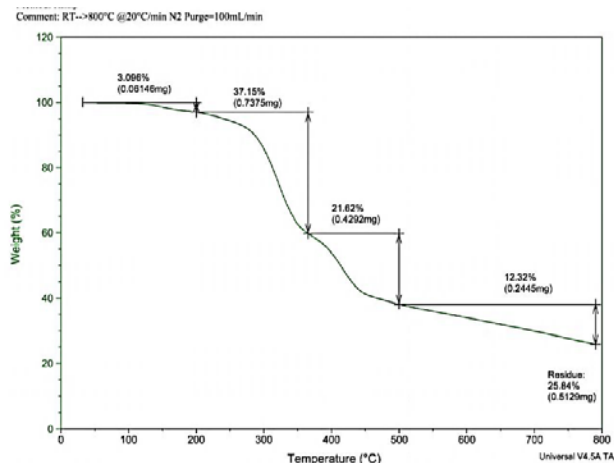
Fig(19): UV-Vis spectrum of C6 complex

Table 4 Thermal decomposition data of the ligand and complexes

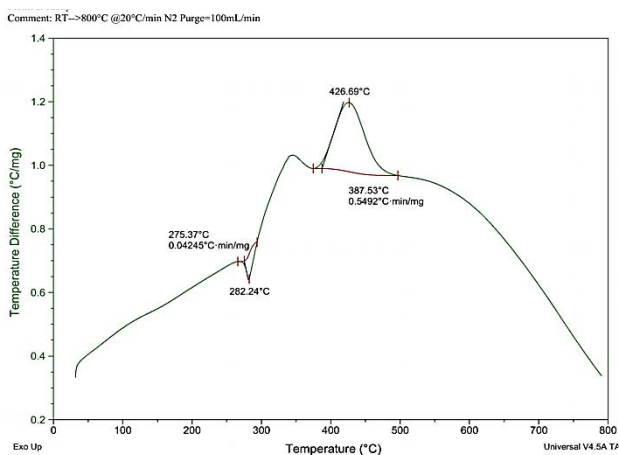
Compound	Molecular formula M.Wt	step	Temp. range of the decomposition (TG) °C	Suggested Formula of loss	Mass loss%	
					Cal.	found
L1	C <sub>15</sub> H <sub>9</sub> N <sub>5</sub> O <sub>5</sub> S (371.33)	1	30-210	-OH	4.57	3.09
		2	210-350	C <sub>7</sub> H <sub>7</sub> ,-NO <sub>2</sub>	36.35	37.15
		3	350-500	CN <sub>3</sub> O <sub>2</sub>	21.62	23.15
		4	500-800	NS	12.38	12.32
		5	> 800	C <sub>7</sub> H <sub>5</sub>	23.43	25.84
C1	C <sub>15</sub> H <sub>15</sub> N <sub>5</sub> O <sub>12</sub> S <sub>2</sub> V	1	30-200	-3H <sub>2</sub> O	9.17	9.39
		2	200-500	C <sub>10</sub> H <sub>8</sub> N <sub>5</sub> O <sub>5</sub> S	53.03	54.08
		3	500-800			
C2	C <sub>30</sub> H <sub>22</sub> Cl <sub>2</sub> CoN <sub>10</sub> O <sub>12</sub> S <sub>2</sub> (908.52)	1	30-200	-2H <sub>2</sub> O, -Cl	7.86	8.13
		2	200-350	-Cl,-4NO <sub>2</sub>	24.15	24.01
		3	350-450	-C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> S	25.75	24.75
		4	350-800	C <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub> S	18.92	18.83
		5	> 800	2C <sub>6</sub> H <sub>4</sub> ,Co	23.20	24.45
C3	C <sub>30</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>10</sub> NiO <sub>12</sub> S <sub>2</sub> (908.28)	1	30-150	-2H <sub>2</sub> O	3.96	3.70
		2	150-500	2C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub> ,2Cl	44.58	44.87
		3	500-800	C <sub>2</sub> HN <sub>2</sub> S	18.50	17.24
		4	> 800	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> NiO <sub>2</sub>	32.88	
C4	[Cu(L1) <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	1	30-150	-H <sub>2</sub> O	2.01	1.84
		2	150-350	-4NO <sub>2</sub> ,2Cl	28.48	28.23
		3	350-500	-C <sub>13</sub> H <sub>4</sub> S	21.47	20.28
		4	500-800	-C <sub>2</sub> N <sub>3</sub> S	10.96	10.84
		5	> 800	-C <sub>15</sub> H <sub>15</sub> CuN <sub>3</sub> O <sub>2</sub>	37.18	38.81
C5	[Zn(L1) <sub>2</sub> Cl <sub>2</sub> ] (878.93)	1	30-200	-Cl	4.03	3.07
		2	200-350	-C <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub> S	28.69	28.52
		3	350-500	-C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	20.72	20.24
		4	500-800	-C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> S	11.71	11.97
		5	> 800	C <sub>13</sub> H <sub>13</sub> ClNO <sub>2</sub> Zn	35.96	36.20
C6	[Cd(L1) <sub>2</sub> Cl <sub>2</sub> ]	1	30-200	-H <sub>2</sub> O	1.90	2.19
		2	200-350	C <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub> S	26.71	26.53
		3	350-500	-2NO <sub>2</sub> ,-2Cl	17.26	17.01
		4	500-800	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> S	15.80	15.78
		5	> 800	C <sub>15</sub> H <sub>13</sub> CdN <sub>2</sub> O <sub>2</sub>	38.73	38.52

**Thermal analysis of the ligand and their metal ion complexes:**

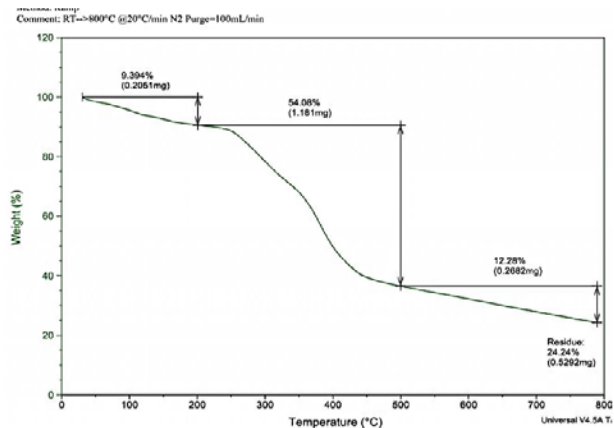
Thermal analysis TG and DTA of complexes were studied under Nitrogen gas at heating range (25-800)°C and heating rate(10°C/min).The thermal analysis was performed to proof the suggested structures and studied the thermal stability of the complexes. The results were listed in (Table 4) and shown in Figures (20-32).



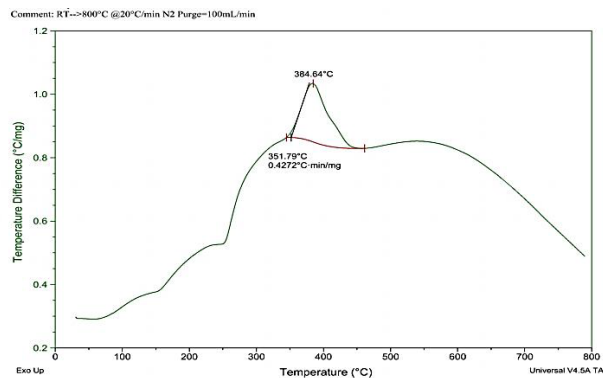
**Fig(20)Thermographs (TGA)of Ligand (L1)**



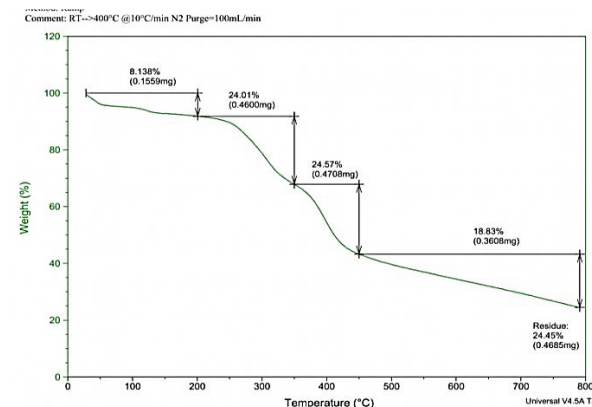
**Fig(21)Thermographs (DTA)of Ligand one(L1)**



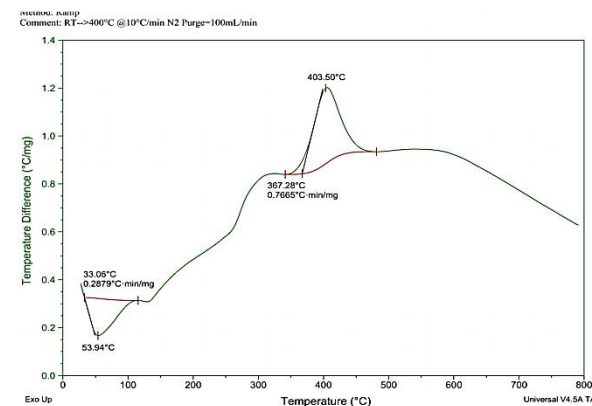
**Fig(22)Thermographs (TGA)of Ligand C<sub>1</sub> complex**



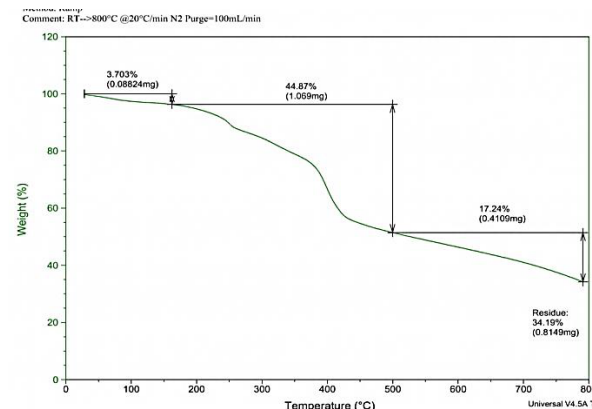
**Fig(23)Thermographs (DTA)of Ligand C<sub>1</sub> complex**



**Fig(24)Thermographs (TGA)of Ligand C<sub>2</sub> complex**

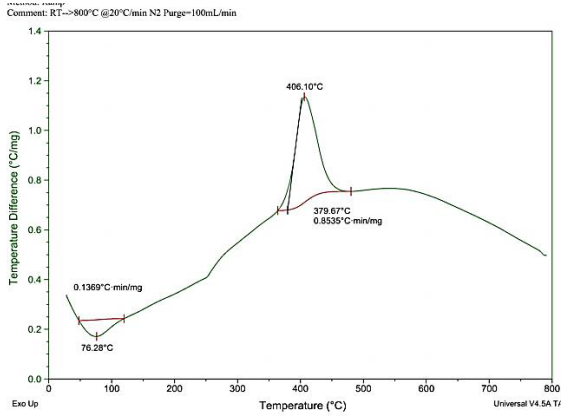


**Fig(25)Thermographs (DTA)of C<sub>2</sub> complex**

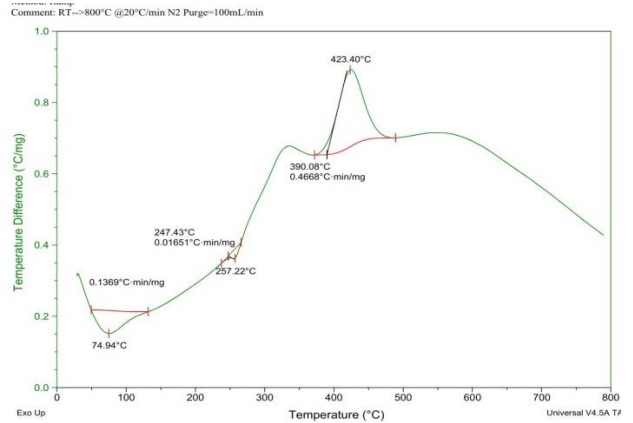


**Fig(26)Thermographs (TGA)of C<sub>3</sub> complex**

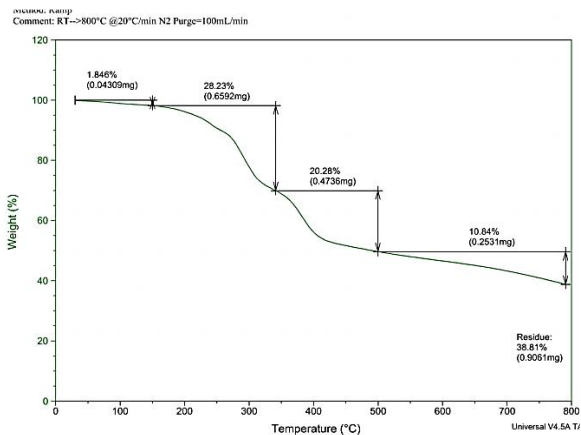




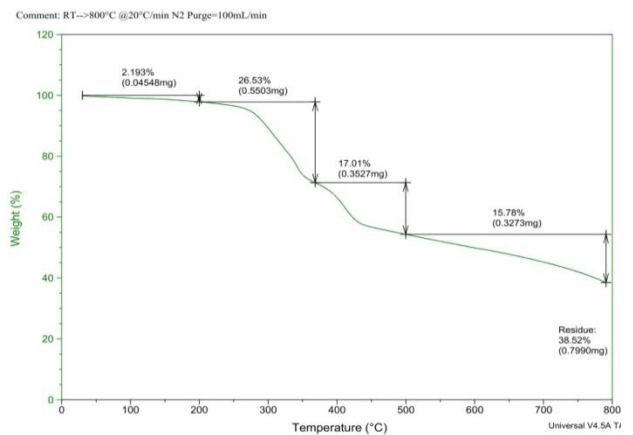
**Fig(27) Thermographs (DTA) of C<sub>3</sub> complex**



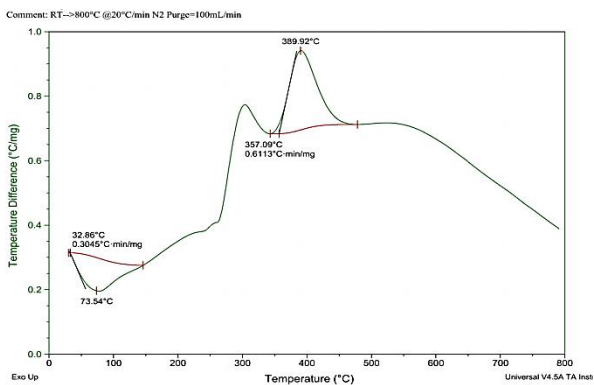
**Fig(30) Thermographs (DTA) of C<sub>5</sub> complex**



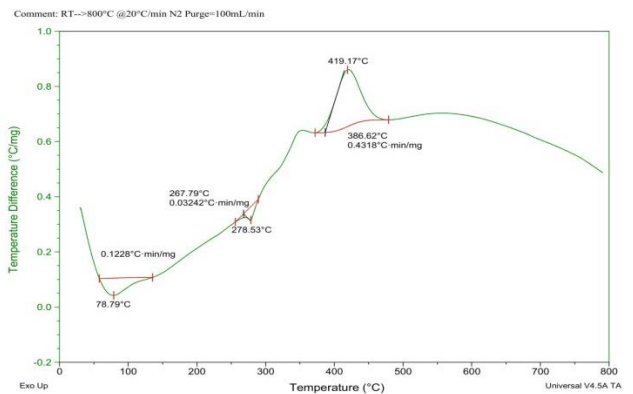
**Fig(28) Thermographs (TGA) of C<sub>4</sub> complex**



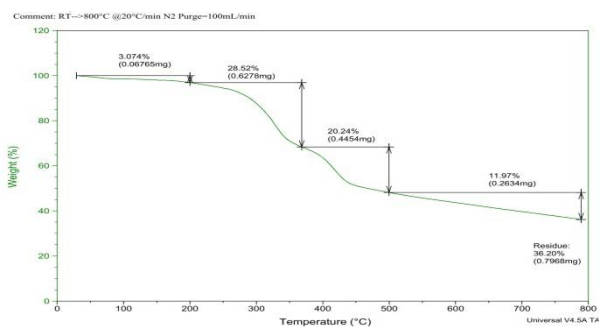
**Fig(31) Thermographs (TGA) of C<sub>6</sub> complex**



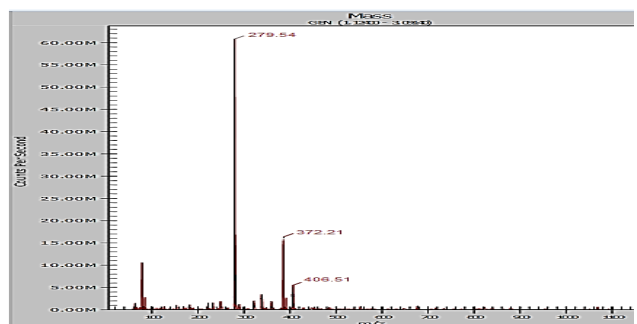
**Fig(29) Thermographs (DTA) of C<sub>4</sub> complex**



**Fig(32) Thermographs (DTA) of C<sub>6</sub> complex**



**Fig(30) Thermographs (TGA) of C<sub>5</sub> complex**



**Fig (33): Mass spectra of the ligand (L)**

**Mass spectra:**

Mass spectrometry has been successfully used to investigate molecular[39] The ligand (L) was compared with their molecular formula weight. The mass spectra of ligands (L<sub>1</sub>) was Shown a molecular ion mother peak at m/z = (372.21) as show in Fig(33).

**Biological activity:**

They are many factors influence on the biological activities of ligands and metal complexes such as type of ligand, type of metal ion ,electron configuration of metal ion, the transition series and geometry of complexes[40].

**In vitro antibacterial activity :**

The compounds were evaluated for their biological activity against one fungus is Candida albicans, one Gram positive bacteria is Staphylococcus aureus and two Gram negative bacteria are Escherichia coli and Pseudomonas aeruginosa via disc diffusion assay. Amoxicillin was used as standard drug to compare the tested compounds and DSMO was also used in a control experiment which didn't show effect in the experiment The results of antibacterial activity as shown in (table 5) Fig (34-35)indicated that the compounds L showed moderate activity against Escherichia coli but didn't show any activity against

Staphylococcus aureus and Pseudomonas aeruginosa. The compounds C<sub>1</sub>and C<sub>6</sub> showed moderate activity against Staphylococcus aureus and Pseudomonas aeruginosa while it didn't show any activity against Escherichia coli. The compound C<sub>3</sub> showed moderate activity against Pseudomonas aeruginosa but didn't show any activity against Escherichia coli and Staphylococcus aureus. the compounds C<sub>5</sub> didn't show any activity against all tested bacteria.

**Antifungal Activity of the synthesized complexes**

The compounds were evaluated for their biological activity against one fungus is Candida albicans .The solvent was DMSO .The inhibition zones of the complexes were measured in (mm) and their results are listed in Table(6).

The results of antifungal activity as shown in (table 6) indicated that compounds L,C<sub>1</sub>,C<sub>5</sub> and C<sub>6</sub> showed potent antifungal activity against Candida albicans as showed in fig(36). The showed moderate activity against Candida albicans as while the compounds C<sub>2</sub>,C<sub>3</sub> and C<sub>4</sub> didn't show any activity against the tested fungus .

Table (5):Evaluation of antibacterial activity of the compounds.

Compound	Gram Positive	Gram negative	
	<i>Staphylococcus Aureus</i>	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>
DMSO	7(R)	7(R)	7(R)
Amox	36mm	24mm	R
L1	R	S(+)	R
C1	S(+)	R	S(+)
C3	R	R	S(+)
C5	R	R	R
C6	S(+)	R	S(+)

Table (6):Evaluation of antifungus activity of the compounds

Compounds	Sensitivity <i>candida albicans</i>
Nystatine (100mg)	S(+)
DMSO	R
L1	S
C1	S(++)
C2	R
C3	R
C4	R
C5	S
C6	S



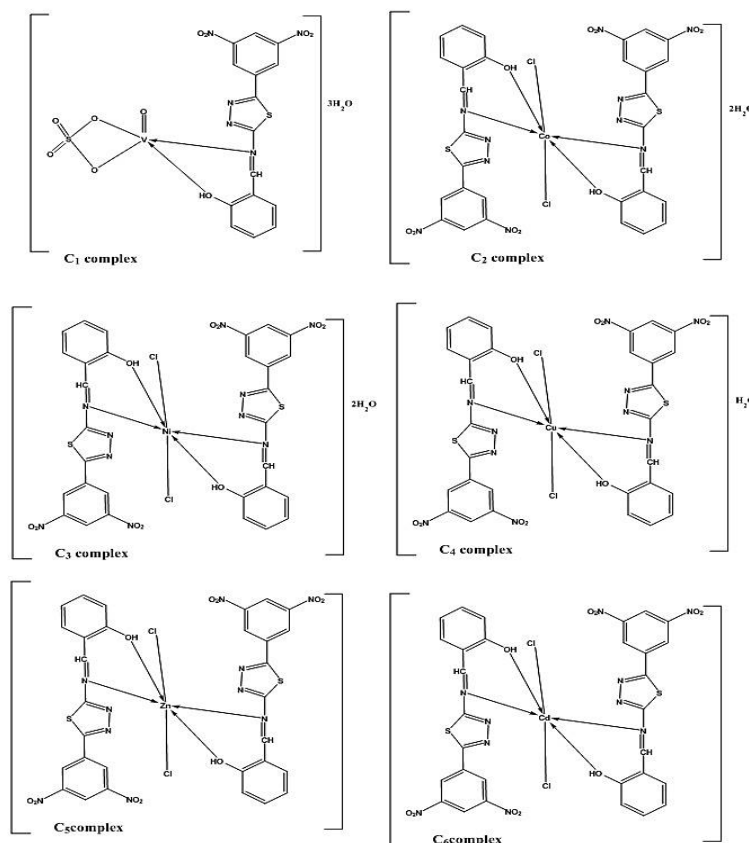
Fig.(34): Inhibition zones for Amox.and DMSO against *E.coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.



Fig.(35): Inhibition zones L<sub>1</sub>,C<sub>2</sub>,C<sub>5</sub> and C<sub>6</sub> against *E.coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.



Fig.(36): Inhibition zones L<sub>1</sub>,C<sub>2</sub>,C<sub>3</sub>,C<sub>4</sub>,C<sub>5</sub> and C<sub>6</sub> against against *Candida albicans*



Fig(37):Suggestion structures for all complexes (C<sub>1</sub>-C<sub>6</sub>)

**CONCLUSION :**

The ligand were synthesized by condensation of substituted aldehyde with 2-amino-5-(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 C<sub>1</sub> complex has (1:1)ratio . The ligand and there complexes were identified structures by elemental micro analysis (CHNS), FT-IR, UV-Vis <sup>1</sup>H-NMR, and <sup>13</sup>C-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 . The ligand and complexes are evaluation anti bacteria such as *in-vitro* against some gram positive and gram negative bacteria and their results were compared with standard antibiotic (Amoxicillin). The

ligand( L) showed moderate activity against *Escherichia coli* but didn't show any activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa* and the complexes showed some activity against the tested bacteria

The Ligand and their complexes are evaluation antifungi such as *candida albicans* and were compared with standard antibiotic (Nystatine). The ligand and Some of complexes showed activity against the tested fungi.

**Nomenclature and suggested structures of the complexes**

The synthesized complexes are suggested structures of had been investigated and confirmed via using infrared (FT-IR)<sup>1</sup>H-NMR, <sup>13</sup>C-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. (37):

## REFERENCES:

- Mahdi S.M. and Ali A.M., *Preparation & identification of new azo-schiff ligand with its complexes*. Iraqi National Journal Of Chemistry, **2015**. 15(2): p. 214-236.
- Annapoorani S. and Krishnan C., *Synthesis and spectroscopic studies of trinuclear N4 Schiff base complexes*. Synthesis, **2013**. 5(1): p. 180-185.
- Goerdeler J., Ohm J. and Tegtmeier O., *Darstellung und Eigenschaften des 1.2. 4- und des 1.3. 4-Thiadiazols*. European Journal of Inorganic Chemistry, **1956**. 89(6): p. 1534-1543.
- Kornis G., *1, 3, 4-Thiadiazoles*. **1984**.
- Elzahany E.A., Hegab K.H., Khalil S.K. and Youssef N.S., *Synthesis, characterization and biological activity of some transition metal complexes with schiff bases derived from 2-formylindole, salicylaldehyde and N-amino rhodanine*. Aust. J. Basic. Appl. Sci., **2008**. 2: p. 210-220.
- Gaber M., Mabrouk H. and Al-Shihry S.S., *Complexing behaviour of naphthylidene sulfamethazine Schiff base ligand towards some metal ions*. Egyptian journal of chemistry, **2001**. 44(4-6): p. 191-200.
- Hadizadeh F. and Vosoghi R., *Synthesis of  $\alpha$ -[5-(5-amino-1, 3, 4-thiadiazol-2-yl)-2-imidazolylthio] acetic acids*. Journal of Heterocyclic Chemistry, **2008**. 45(5): p. 1477-1479.
- Ahmed A., Adel H. and Ibraheem H., *SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME METAL IONS WITH 2-THIOACETIC-5-PHENYL-1, 3, 4-OXADIAZOLE*. Journal of Al-Nahrain University-Science, **2010**. 13(1): p. 43-47.
- Mahmoud M.A., Jassim I.K. and Mahmoud M.J., *Synthesis and Characterization of Five, Seve Heterocyclic Membered Rings*. Baghdad Science Journal, **2013**. 10(عدد خاص بمؤتمر الكيمياء 3): p. 803-817.
- Keerthi Kumar C.T., Keshavayya J., Rajesh T.N., Peethambar S.K. and Shoukat Ali A.R., *Synthesis, characterization, and biological activity of 5-phenyl-1, 3, 4-thiadiazole-2-amine incorporated azo dye derivatives*. Organic Chemistry International, **2013**. 2013.
- Yousif E., Majeed A., Al-Sammarrae K., Salih N., Salimon J. and Abdullah B., *Metal complexes of Schiff base: Preparation, characterization and antibacterial activity*. Arabian Journal of Chemistry, **2017**. 10: p. S1639-S1644.
- Turan N. and Şekerci M., *Synthesis and Spectral Studies of Novel Co(II), Ni(II), Cu(II), Cd(II), and Fe(II) Metal Complexes with N-[5'-Amino-2,2'-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL)*. Spectroscopy Letters, **2009**. 42(5): p. 258-267.
- Waaled A., Jabbar S.A. and Jassim I.K., *Synthesis and study the biological activity of some new heterocyclic compounds*. karbala journal of pharmaceutical sciences, **2015**(10).
- Silverstein R.M., Webster F.X., Kiemle D.J. and Bryce D.L., *Spectrometric identification of organic compounds*. **2014**: John Wiley & sons.
- Pavia D.L., Lampman G.M., Kriz G.S. and Vyvyan J.A., *Introduction to spectroscopy*. **2014**: Cengage Learning.
- Muğlu H., Şener N., Mohammad Emsaed H.A., Özkınalı S., Özkan O.E. and Gür M., *Synthesis and characterization of 1,3,4-thiadiazole compounds derived from 4-phenoxybutyric acid for antimicrobial activities*. Journal of Molecular Structure, **2018**.
- Barot K.P., Manna K.S. and Ghate M.D., *Design, synthesis and antimicrobial activities of some novel 1,3,4-thiadiazole, 1,2,4-triazole-5-thione and 1,3-thiazolan-4-one derivatives of benzimidazole*. Journal of Saudi Chemical Society, **2017**. 21: p. S35-S43.
- Silverstein R.M., Webster F.X., Kiemle D.J. and Bryce D.L., *Spectrometric identification of organic compounds* **2014**: John Wiley & sons.
- Abdulghani A.J. and Khaleel A.M.N., *Preparation and characterization of Di-, Tri-, and tetranuclear Schiff base complexes derived from diamines and 3, 4-dihydroxybenzaldehyde*. Bioinorganic chemistry and applications. Vol. 2013. **2013**.
- Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Handbook of Vibrational Spectroscopy, **2006**.
- Al-Azawi K.F., Mohammed I.M., Al-Baghdadi S.B., Salman T.A., Issa H.A., Al-Amiery A.A., Gaaz T.S. and Kadhum A.A.H., *Experimental and quantum chemical simulations on the corrosion inhibition of mild steel by 3-((5-(3, 5-dinitrophenyl)-1, 3, 4-thiadiazol-2-yl) imino) indolin-2-one*. Results in Physics, **2018**. 9: p. 278-283.
- Hwang H.J. and Kim J.-G., *Regiospecific alkylation of 5-substituted 2-acylamino-1, 3, 4-thiadiazoles*. Heterocycles, **2001**. 55(3): p. 579-587.
- Alan R. Katritzky ; editors-in-chief C.A.R., Eric F.V. Scriven, Richard J.K. Taylor., *Comprehensive heterocyclic chemistry III*. **2008**: Elsevier.
- Omar Y.M., Abdu-Allah H.H. and Abdel-Moty S.G., *Synthesis, biological evaluation and docking study of 1, 3, 4-thiadiazole-thiazolidinone hybrids as anti-inflammatory agents with dual inhibition of COX-2 and 15-LOX*. Bioorganic chemistry, **2018**.
- Srivastava A., Pandey O. and Sengupta S., *Synthesis, spectral and antimicrobial studies of Bis (cyclopentadienyl) titanium (IV) derivatives with schiff bases derived from 2-Amino-5-phenyl-1, 3, 4-thiadiazole*. Bioinorganic chemistry and applications, **2005**. 3(3-4): p. 289-297.
- Katritzky A.R., Ramsden C.A., Scriven E. and Taylor R., *Comprehensive heterocyclic chemistry III*. Vol. 4. **2008**: Elsevier Amsterdam.
- Bain G.A. and Berry J.F., *Diamagnetic Corrections and Pascal's Constants*. Journal of Chemical Education, **2008**. 85(4): p. 532.
- Burger K., *Coordination chemistry: experimental methods*. **1973**.
- Mehandjiev D. and Bontchev P., *Application of magnetic methods to the study of 3d transition metal complexes*. Journal of the University of Chemical Technology and Metallurgy, **2010**. 45(4): p. 415-420.
- Maurya R.C., Chourasia J., Rajak D., Malik B.A., Mir J.M., Jain N. and Batalia S., *Oxovanadium(IV) complexes of bioinorganic and medicinal relevance: Synthesis, characterization and 3D molecular modeling of some oxovanadium(IV) complexes involving O, N-donor environment of salicylaldehyde-based sulfa drug Schiff bases*. Arabian Journal of Chemistry, **2016**. 9: p. S1084-S1100.
- Gopalan R., *Concise Coordination Chemistry, 1E*. **2001**: Vikas Publishing House Pvt Ltd. p.104.
- Chandra S., Gautam S., Rajor H.K. and Bhatia R., *Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel Schiff's base benzil bis(5-amino-1,3,4-thiadiazole-2-thiol) with Ni(II), and Cu(II) metal complexes*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2015**. 137: p. 749-760.
- Chohan Z.H., Pervez H., Rauf A., Khan K.M. and Supuran C.T., *Antibacterial cobalt (II), copper (II), nickel (II) and zinc (II) complexes of mercaptothiadiazole-derived furanyl, thienyl, pyrrolyl, salicylyl and pyridinyl Schiff bases*. Journal of Enzyme Inhibition and Medicinal Chemistry, **2006**. 21(2): p. 193-201.
- Kharadi G.J., *Effect of the Thermal Decomposition and In Vitro Antimicrobial Activity of Mixed Ligand Copper(II) Complexes*. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, **2012**. 42(3): p. 424-431.
- Gopalan R., *Concise Coordination Chemistry*. 1 ed. **2001**: Vikas Publishing House Pvt Ltd. . p.109.
- Chohan Z.H., Jaffery M.F. and Supuran C.T., *antibacterial Co (II), Cu (II), Ni (II) and Zn (II) complexes of thiadiazoles Schiff bases*. Metal-based drugs, **2001**. 8(2): p. 95-101.
- Manju, Kishore D. and Kumar D., *Cadmium and tin complexes of Schiff-base ligands*. Journal of Coordination Chemistry, **2011**. 64(12): p. 2130-2156.
- Numan A.T., Atiyah E.M., Al-Shemary R.K. and Abd\_Ulrazzaq S.S. *Composition, Characterization and Antibacterial activity of Mn (II), Co (II), Ni (II), Cu (II) Zn (II) and Cd (II) mixed ligand complexes Schiff base derived from Trimethoprim with 8-Hydroxy quinoline*. in *Journal of Physics: Conference Series*. 2018. IOP Publishing.
- Prakash A., Singh B.K., Bhojak N. and Adhikari D., *Synthesis and characterization of bioactive zinc (II) and cadmium (II) complexes with new Schiff bases derived from 4-nitrobenzaldehyde and acetophenone with ethylenediamine*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2010**. 76(3-4): p. 356-362.
- Alias M., Kassum H. and Shakir C., *Synthesis, physical characterization and biological evaluation of Schiff base M(II) complexes*. Journal of the Association of Arab Universities for Basic and Applied Sciences, **2014**. 15: p. 28-34.