



## Synthesis, Structural Study and Biological Activity Evaluation of Cr (III), Mn (II), Zn (II), Cd (II) and Hg (II) Complexes with New Schiff Base Ligand Derived from Isatin

Wurood Ali Jaafar

Department of chemistry /college of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq.

### Abstract

The New Schiff base [3E-3-((1,5-dimethyl-3-((4-nitrophenyl)imino)-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)indolin-2-one][L] was prepared by two steps, 4-aminoantipyrine was reacted with isatin in the first step to produce the precursor [A], then [A] was reacted with p-nitroaniline to give a new tridentate ligand [L]. this ligand[L] was reacted with some metal ions in Cr (III), Mn(II), Zn(II), Cd(II) and Hg(II) to give a series of new metal complexes of the general molecular formula  $[M(L)_2]Cl_n$ , where:  $M=Cr(III)$ ,  $n=3$ ;  $M=Mn(II), Zn(II), Cd(II)$  and  $Hg(II)$ ,  $n=2$ . All compounds were have been characterized by spectroscopic methods [ IR, UV-Vis, atomic absorption], elemental microanalysis, chloride content, magnetic susceptibility, conductivity measurements along with  $^1H, ^{13}C$ -NMR and mass spectroscopy for ligand [L] only. According to the results of the above techniques, the suggested geometrical structures for all prepared complexes were octahedral formula.

**Keywords:** Schiff base, Isatin, 4- amino antipyrine.

### Introduction

Schiff base compounds derivative from Isatin are among the most profoundly explored classes of organic reagent both from the theoretical and practical viewpoints [1]. Schiff base compounds are characterized by the presence of azomethine group (-CH=N-) as result of condensation between aldehydes or ketones with aromatic amines [2]. The presence of an azomethine linkage in aromatic compounds makes these reagents acts as a chromogenic in determined the trace amount of transition metals such as Ni in some natural food samples [3].

Also their tendency as ligands to coordinate with many metal ions was reported especially on these ligands having two or more donor atoms were concentrated in coordination chemistry, Coordination compounds are metal ions surrounded by ligands. Ligands are either anions or molecules That can donate electrons into the d-orbitals of the metal ion and form a bond in this chemistry of coordination the bio ligands have great attention because of their potential activities of transition metal complex [4].

Schiff bases played important role in different other area such as pharmacology as antifungal, antibacterial and anticancer [5]. In industry for the properties of their complexes as Thermal Initiation in Radical Polymerization [6]. In this work New Schiff base ligand and its complexes for Cr (III), Mn (II), Zn (II), Cd (II) and Hg (II) were prepared.

### Experimental

#### Materials and Physical Measurements

All chemicals used were of highest purity (BDH, Fluka, merck) and used without further purification. Elemental analysis was carried out by means of micro analytical unit of (EURO EA3000 Single) C.H.N element analyzer/Ibn sina company .Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in DMSO at room temperature.

Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of  $(4000-400) \text{ cm}^{-1}$  using KBr disc. A

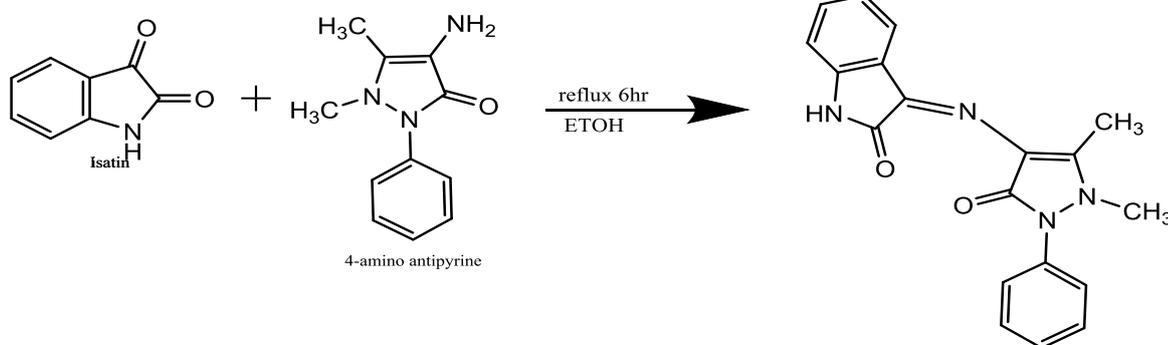
mass spectrum for the ligand was obtained by (+) electro spray technique using bruker instruments. Electrical molar conductivity measurements of the complexes were recorded at (25°C) for (10<sup>-3</sup>)M solutions of the samples in ethanol using a PW 9526 digital conductivity meter.<sup>1</sup>H,<sup>13</sup>C NMR spectra were recorded using DMSO-d<sub>6</sub> at Bruker 400MHz spectrometer.

The chloride content determined using potentiometric titration method on 686-Titro Processor-665 Dosim A-Metrohm/Swiss. The magnetic moments were measured with a magnetic susceptibility balance (Jonson Matty Catalytic system division). Melting points were obtained using an electro thermal apparatus Stuart, melting point and

metals were determined with a Shimadzu (A.A.) 680G atomic absorption spectrophotometer.

### Preparation of Derivative (3E)-3-[(1, 5-dimethyl-3-oxo-2-phenyl-2, 3-dihydro-1H-pyrazol-4-yl) imino]-1, 3-dihydro-2H-indol-2-one] [A]

In a round bottom flask, 4-aminoantipyrene (0.01 mol, 2.03 g) in (15 ml) ethanol and Isatin (0.01mol, 1.47 g) in (15 ml) ethanol added few drops of glacial acetic acid to solution the mixture was refluxed for (6 hr.) [7], the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous CaCl<sub>2</sub>. The preparation of Schiff base is showed in Scheme 1.



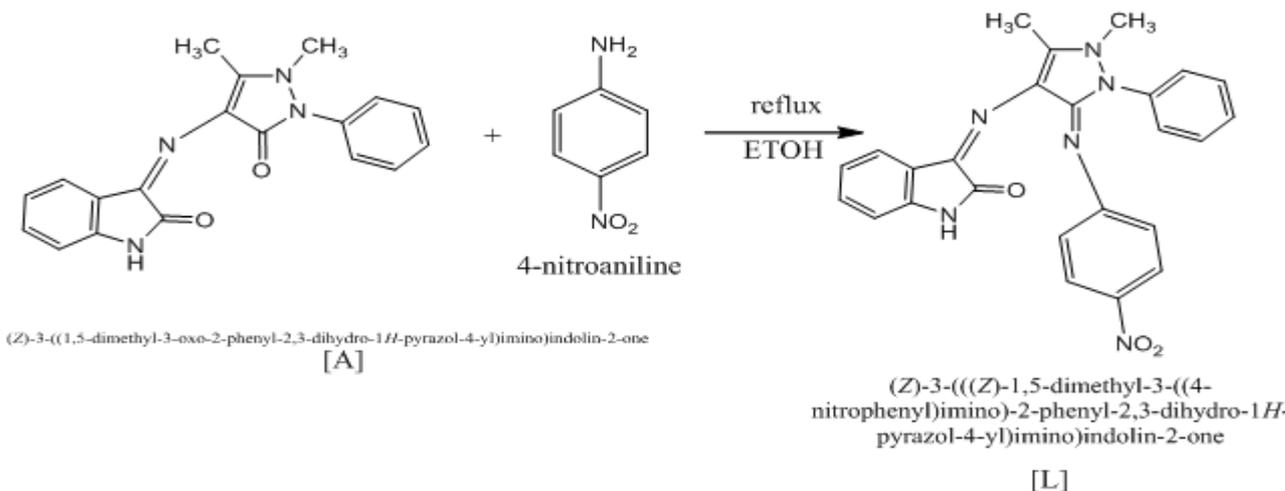
(Z)-3-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)indolin-2-one [A]

Scheme 1: Preparation of the precursor [A]

### Preparation of New Schiff base ligand[L]

The Schiff base ligand [L] was prepared by condensation of compound [A] (0.01 mol, 3.32 g) which was dissolved in (50 ml) ethanol and refluxed with (0.01 mol, 1.09 g) of p-nitroaniline for (12 hr.) [8]. Adding few drops from

glacial acetic acid, a clear colored solution was obtained. The Schiff base Ligand was isolated after the volume of mixture was reduction to half by evaporation and recrystallized by hot ethanol and dried over anhydrous CaCl<sub>2</sub> (Scheme 2).



Scheme 2: Preparation of the ligand [L]

## Preparation of Metal Complexes

The (1:2) chelate complexes of the metal and the ligand are prepared by dissolving (0.002 mol, 0.423 g) Schiff base [L] in (25 ml) of absolute ethanol. The corresponding hydrated metal chloride salts of ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{HgCl}_2$ ) of (0.001 mol) was dissolved in absolute ethanol

(25 mL) was mixed with hot ethanol solution of the ligand and refluxed for (1 hr.) on a water bath, on cooling the contents. The complexes separated out in each case. The product was filtered, washed with ethanol and dried under vacuum. Table.1 collects the physical properties and analytical data for those complexes.

**Table1: Physical properties and analytical data of the ligand and its complexes**

No.	Compound	Color	M wt.	M.P C°	Found (Calc.)%				
					C	H	N	M	Cl content
1	$\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3$	Reddish Brown	452.47	168-170	66.20 (66.25)	4.35 (4.42)	18.50 (18.58)	—	—
2	$[\text{Cr}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_3$	Brown	1102.4	250-252	54.40 (54.42)	3.60 (3.62)	15.20 (15.23)	4.70 (4.71)	9.63 (9.66)
3	$[\text{Mn}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	Brown	1029.9	228-230	58.21 (58.25)	3.85 (3.88)	16.30 (16.31)	5.30 (5.33)	6.85 (6.89)
4	$[\text{Zn}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	BrownLight	1040.3	202-204	57.63 (57.67)	3.83 (3.84)	16.11 (16.14)	6.25 (6.28)	6.80 (6.82)
5	$[\text{Cd}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	Light Brown	1087.4	230-232	55.14 (55.17)	3.65 (3.67)	15.40 (15.44)	10.22 (10.29)	6.50 (6.52)
6	$[\text{Hg}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	Light Brown	1175.4	232-234	51.00 (51.04)	3.38 (3.40)	12.40 (12.42)	17.00 17.10	6.00 (6.04)

## Results and Discussion

The metal complexes are insoluble in water and soluble in DMSO, DMF, and  $\text{CHCl}_3$ , acetone, methanol and ethanol.

### Infrared Spectra of ligand and Complexes

The IR spectral data of Schiff base ligand (Fig1) and their complexes are presented in Table 2. The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation.

**Table 2: Characteristic IR absorption bands of the ligand (L) and its complexes in  $\text{cm}^{-1}$**

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L= $\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3$	1718(s)	1616(s) 1663	---	---
$[\text{Cr}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_3$	1699(s)	1611(m) 1650	499(m)	415(w)
$[\text{Mn}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	1734(s)	1624(s) 1651	590(m)	420(w)
$[\text{Zn}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	1701(s)	1614(s) 1642	586(m)	418(m)
$[\text{Cd}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	1700(s)	1610(m) 1650	500(m)	450(m)
$[\text{Hg}(\text{C}_{25}\text{H}_{20}\text{N}_6\text{O}_3)_2]\text{Cl}_2$	1710(s)	1600(s) 1635	519(m)	425(m)

The band in IR spectrum of free ligand at  $1718 \text{ cm}^{-1}$ , assignable to stretching vibration  $\nu(\text{C}=\text{O})$  group of Isatin which was shifted to higher or lower frequency in the IR spectra of the complexes, suggesting the involvement of the carbonyl oxygen atom in coordination [9]. The appearance of a new non-ligand band around  $(450-415) \text{ cm}^{-1}$  in IR spectra of all complexes due to  $\nu(\text{M}-\text{O})$  substantiates [10]. The two bands at  $(1616 \text{ and } 1663) \text{ cm}^{-1}$  in IR

spectrum of free ligand can be attributed to the stretching vibration of two imine groups  $\nu(\text{C}=\text{N})$ , which were shifted to higher or lower frequency in the IR spectra of the complexes of Cr(III) (Fig 2) and Mn(II). These shifting indicated the coordination of the ligand with metal ion via nitrogen atoms of two imine groups [11,12] while the complexes of Zn(II), Cd(II) and Hg(II) shifting in to lower frequency indicated the coordination of

the ligand with metal ion via nitrogen atom of one imine group [13]. This is further substantiated by the presence of a new band around  $(590-499) \text{ cm}^{-1}$  assignable to  $\nu (\text{M-N})$  [10]. It is concluded that the ligand behaves

as a tridentate ligand coordinated to the metal ions via oxygen atom of carbonyl group of Isatin and nitrogen atoms of two imine groups for all the complexes.

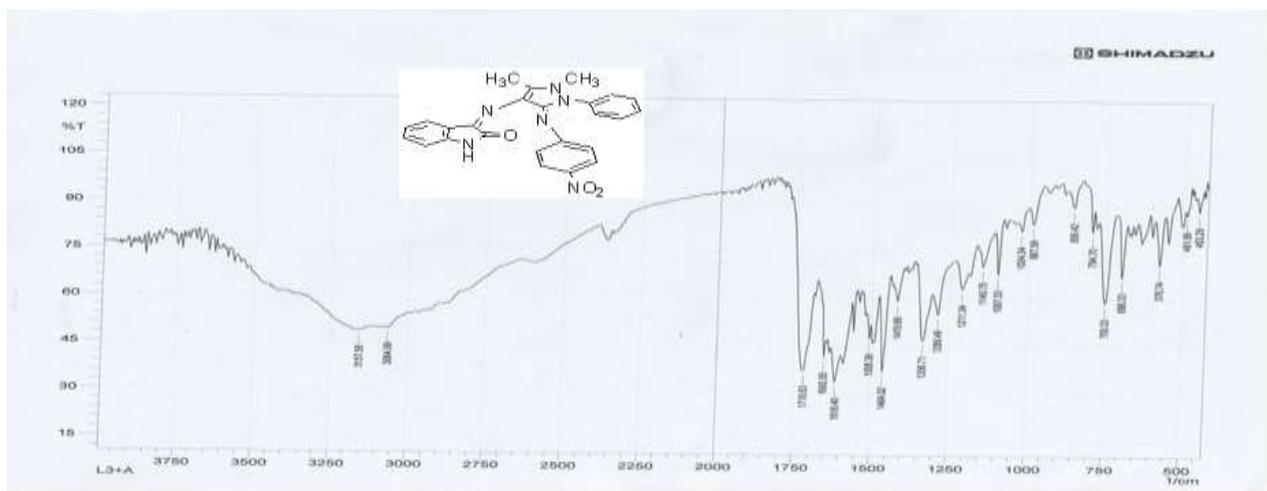


Fig.1: IR spectrum of the ligand

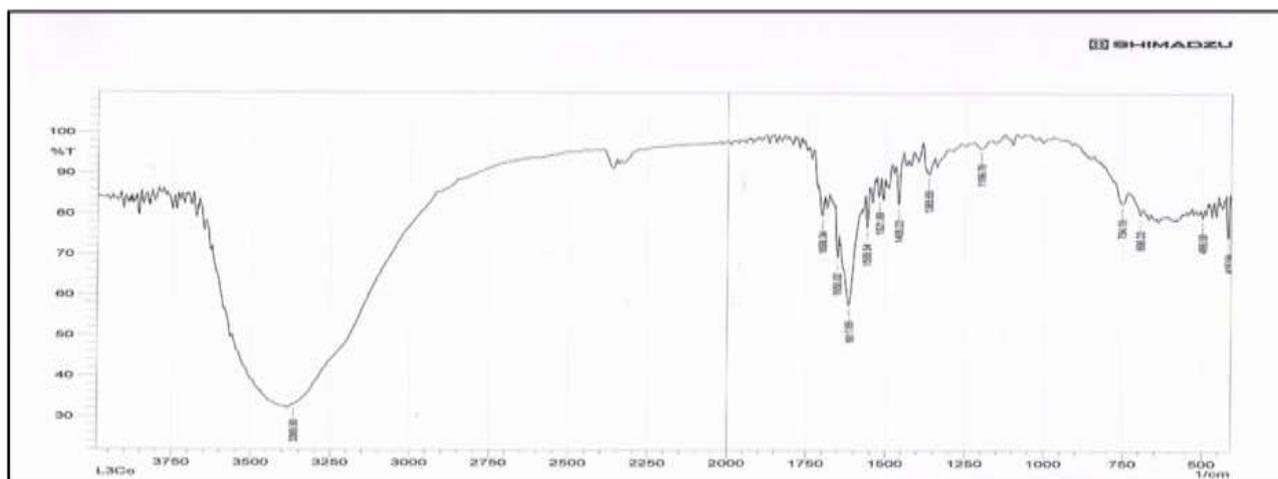


Fig.2: IR spectrum of ion complex of Cr (III) with the ligand

## Electronic Spectra

The Electronic spectra of ligand (Fig.3) and its Cr (III), Mn(II), Zn(II), Cd(II) and Hg(II) complexes were studied and the spectral data were listed in table (3). The UV-Vis spectrum of the Schiff base ligand was characterized mainly by two absorption peaks at (290) nm assigned to  $(\pi \rightarrow \pi^*)$  and at (458) nm assigned to  $(n \rightarrow \pi^*)$  [14]. These electronic transition were shifted towards higher or lower frequency in the electronic spectra of all prepared complexes, confirming the coordination of the ligand with metal ions.

The electronic spectrum of Cr(III) complex(Fig.4) displayed four new absorption peaks the two peaks at (281 and 443)nm may be assigned to intra - ligand and the other peaks at (635)nm and (780)nm were attributed to (d-d) electronic transition

type  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  respectively, suggesting octahedral geometry around Cr(III) ion[15]. The electronic spectrum of Mn (II) complex showed four new absorption peaks, the peaks at (280 and 441) nm may be assigned to intra - ligand. The other peak at (482) nm was attributed to (d-d) electronic transition type  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$  while the last peak at (640)  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ . These peaks were a good agreement of octahedral geometry for Mn(II) complex [16].

The electronic spectrum of Zn(II), Cd(II) and Hg(II) complexes showed absorption peaks at (243, 244 and 241) nm refers to  $(\pi \rightarrow \pi^*)$  while at (440, 442 and 439)nm may be attributed to  $(n \rightarrow \pi^*)$  respectively [13], the metal ion of these complexes belong to  $d^{10}$  system and these metals do not show (d-d) electronic transition[16].

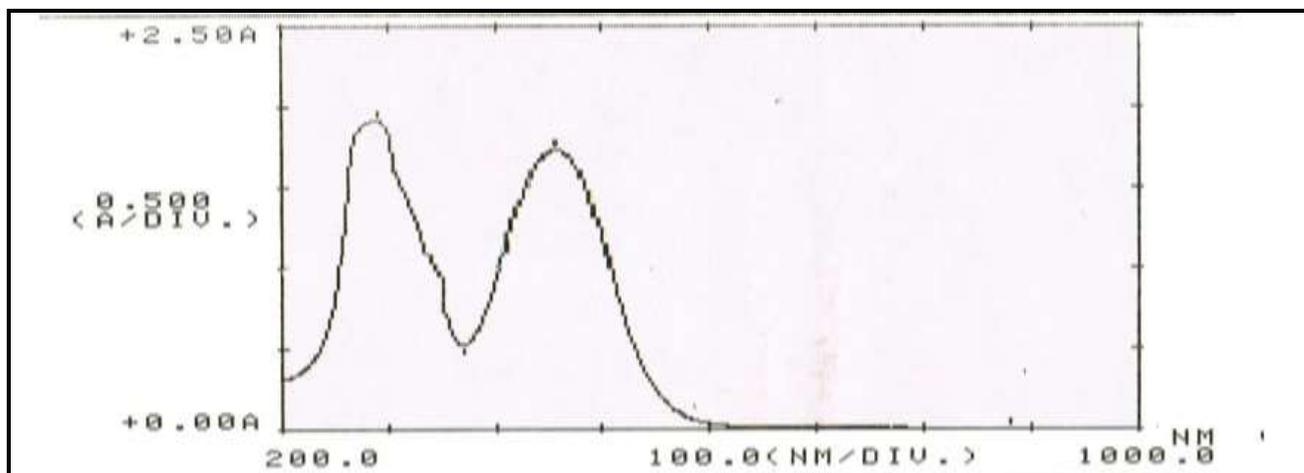


Fig. 3: Absorbance spectrum of ligand

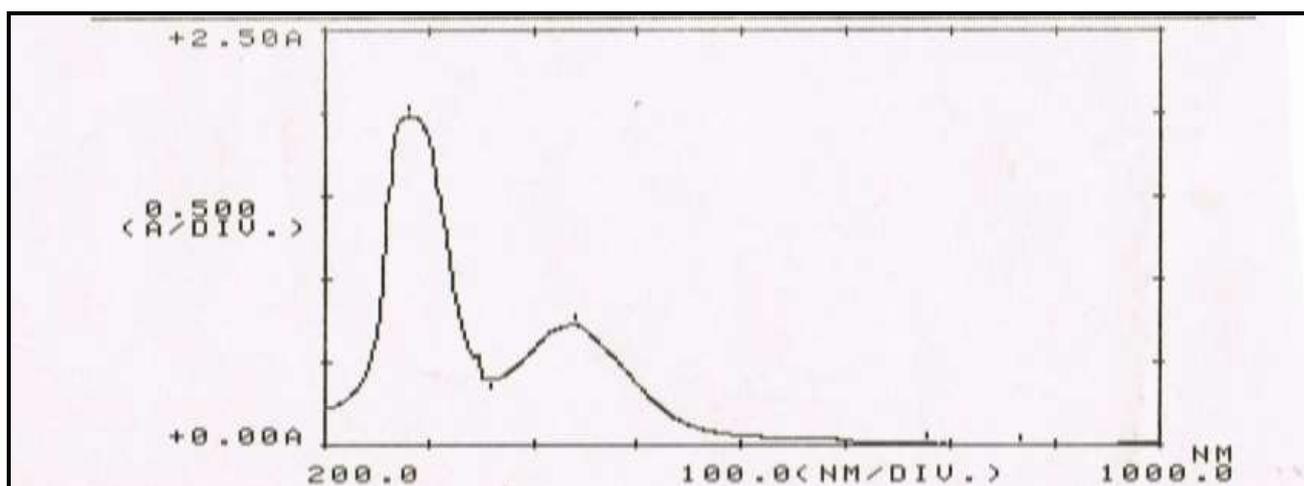


Fig.4: Absorbance spectrum of ligand with ion complex of Cr(III)

### Molar Conductivity

The molar conductance of Cr(III) complex in DMF lie in the  $(223.16) S \cdot cm^{-1} \cdot mole^{-1}$ , indicating it's 1:3 electrolyte behavior, while

the molar conductance of Mn(II), Zn(II), Cd(II) and Hg(II) complexes lie in  $(131.42-152.64) S \cdot cm^{-1} \cdot mole^{-1}$  range, indicating 1:2 electrolyte nature [17,18].

Table 3: The electronic spectra of the ligand and its chelate complexes

Compounds	$\lambda_{Max}$ . nm(cm <sup>1</sup> )	Transition	$\epsilon_{Max}$ .	$\square_m S \cdot cm^2 \cdot mole^{-1}$
$C_{25}H_{20}N_6O_3$	290 (3448)	$\pi^* \rightarrow \pi$	2317	-----
	458 (2183)	$\pi^* \rightarrow n$	2141	
[Cr ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]Cl <sub>3</sub>	281 (35587)	Intra - ligand	2107	223.16
	443 (22573)	Intra - ligand	729	
	635(15015)	${}^4T_{1g}(f) \rightarrow {}^4A_{2g}(f)$	475	
	780 (12820)	${}^4T_{2g}(f) \rightarrow {}^4A_{2g}(f)$	10	
[Mn ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]Cl <sub>2</sub>	280 (35714)	Intra - ligand	2115	131.42
	441 (22675)	Intra - ligand	834	
	482(20746)	${}^4T_{2g}(G) \rightarrow {}^6A_{1g}$	32	
	640 (15625)	${}^4T_{1g}(G) \rightarrow {}^6A_{1g}$	10	
[Zn( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]Cl <sub>2</sub>	243(41152)	Intra - ligand	720	142.53
	440(22727)	Intra - ligand	512	
[Cd ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]Cl <sub>2</sub>	244(40983)	Intra - ligand	579	148.62
	442(22624)	Intra - ligand	455	
[Hg( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]Cl <sub>2</sub>	241(41493)	Intra - ligand	703	152.64
	439(22779)	Intra - ligand	622	

### Magnetic Measurements

• Cr (III) complex shows magnetic moment  $\mu_{eff}$ . (3.82 B.M) corresponding to three unpaired electrons. This value suggests an octahedral environment around the Co (II) ion [19].

• Mn (II) complex shows magnetic moment  $\mu_{eff}$ . (5.51 B.M) at room temperature corresponding to two unpaired electrons. This value indicates an octahedral geometry around the Mn (II) ion [20].

- The magnetic moment value  $\mu_{\text{eff}}$ . Of the Zn (II), Cd(II) and Hg(II)[21] complex (0.00 B.M) because of diamagnetic in nature( $d^{10}$ ).

### Biological Screening: the Antibacterial Activity Test

In our study the synthesized compounds have been screened for their antibacterial activity against the *Staphylococcus aureus*(G+), *E-*

*coli*(G-), *Pseudomonase*(G-) and *Proteus*(G-) strains by the agar diffusion technique[22]. Each of the compounds was dissolved in DMF to give a final concentration of (0.001) mg/ml, and from the data shown in Table (4), all compounds exhibited a biological activity against the 4 kinds of bacteria.

Table 4: The biological activity of the synthesized compounds

compound	<i>Staphylococcus aureus</i> (G+)	<i>E-coli</i> (G-)	<i>Pseudomonas</i> (G-)	<i>Proteus</i> (G-)
$C_{25}H_{20}N_6O_3$	3	2	2	3
[Cr ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]	5	3	6	3
[Mn ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]	17	7	15	9
[Zn( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]	8	4	9	7
[Cd ( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]	5	4	2	3
[Hg( $C_{25}H_{20}N_6O_3$ ) <sub>2</sub> ]	7	3	6	6
Control	2	7	11	5

### (NMR) Spectra for ligand

The  $^1H$  and  $^{13}C$  correlated NMR analysis were used to characterize the ligand. The spectra were recorded in DMSO- $d_6$  solution.

#### $^1H$ NMR Spectrum for the Ligand

In solution, as in the solid state, this phenomenon has been confirmed by the IR and the NMR spectra.  $^1H$  NMR spectrum for ligand, Fig. (9) In DMSO- $d_6$  displayed signal at chemical shift ( $\delta_H = 2.37$  ppm) attributed

to the proton of the antipyrene group (N-CH<sub>3</sub>) [23], and at (3.39ppm) attributed to (=C-CH<sub>3</sub>). The resonances at chemical shift ( $\delta_H = 6.40-7.8ppm$ ), are assignable to protons of aromatic ring of isatin and antipyryn. The appearances of these protons as a multi are due to mutual coupling. The sharp singlet signal at ( $\delta_H = 8.9$  ppm) is attributed to the protons of amide group of isatin ring O=C-NH [24].

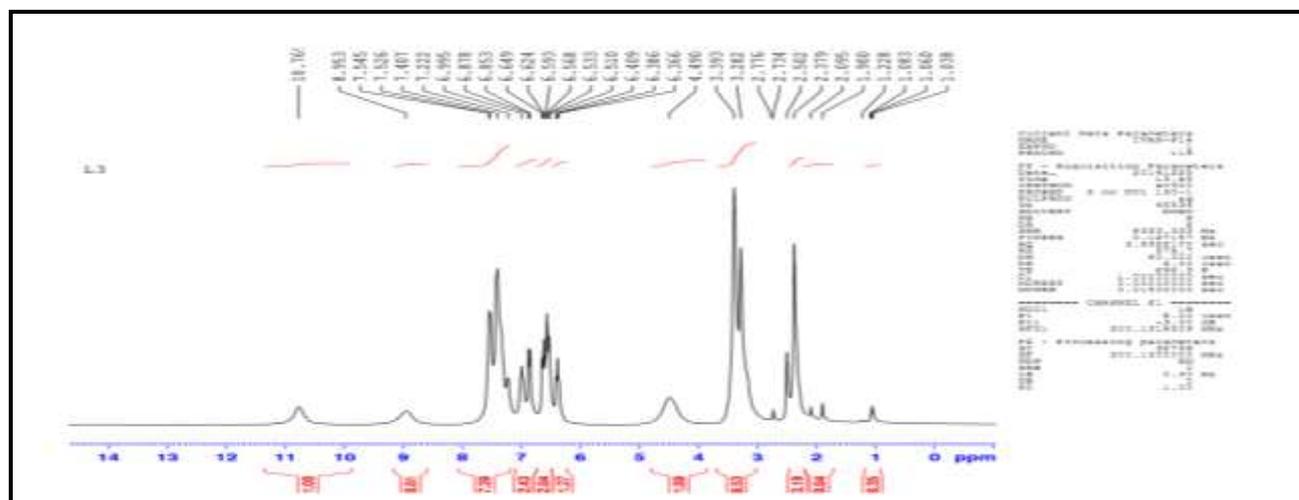


Fig.9:  $^1H$  NMR spectrum for the ligand in DMSO- $d_6$

#### $^{13}C$ NMR Spectrum for Ligand

The  $^{13}C$  NMR spectrum of ligand, Fig.(10) in DMSO- $d_6$  solvent shows chemical shifts at range ( $\delta = 132.17, 127.33, 129.20, 121.54, 129.19, 127.82$  ppm) assigned to aromatic carbon atoms of antipyryn. The chemical shift at ( $\delta = 10.81$  ppm) attributed to the (C-CH<sub>3</sub>) oh antipyryn, while the chemical shifts at ( $\delta = 39.73$  ppm) are assigned (N-CH<sub>3</sub>). The chemical shifts at

( $\delta = 158.93$  and  $155ppm$ ) assigned to azomethen groups. The chemical shifts at range ( $\delta = 119.44, 132.17, 125.26, 127.79, 116.36, 143.93ppm$ ) assigned to aromatic carbon atoms of isatin, while an amide group at (168 ppm), at last the chemical shifts ( $\delta = 136.58, 152.49, 114.38, 127.30, 114.32, 121.54$  ppm) refer to aromatic carbon atoms of aniline ring[25,26].

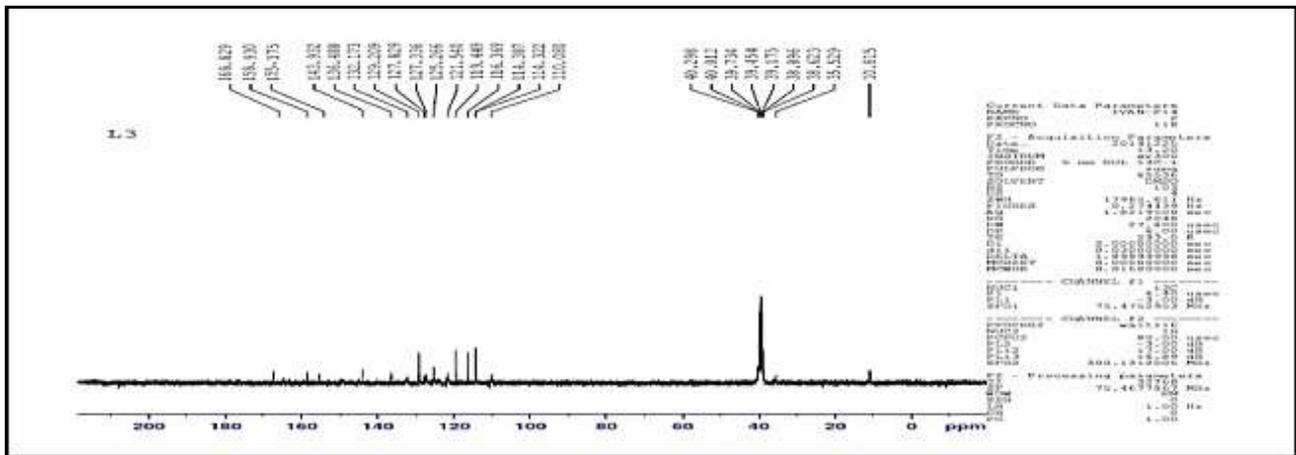


Fig.10: <sup>13</sup>C NMR spectrum of ligand in DMSO-d<sup>6</sup>

**Mass Spectrum of Ligand**

The electro spray mass spectrum of ligand Fig.(11) shows the parent ion peak at (M/Z)=(452), which corresponds to[M<sup>+</sup>], other

fragments and their relative abundance and fragmentation pattern is shown in Fig.(13).[27,28].

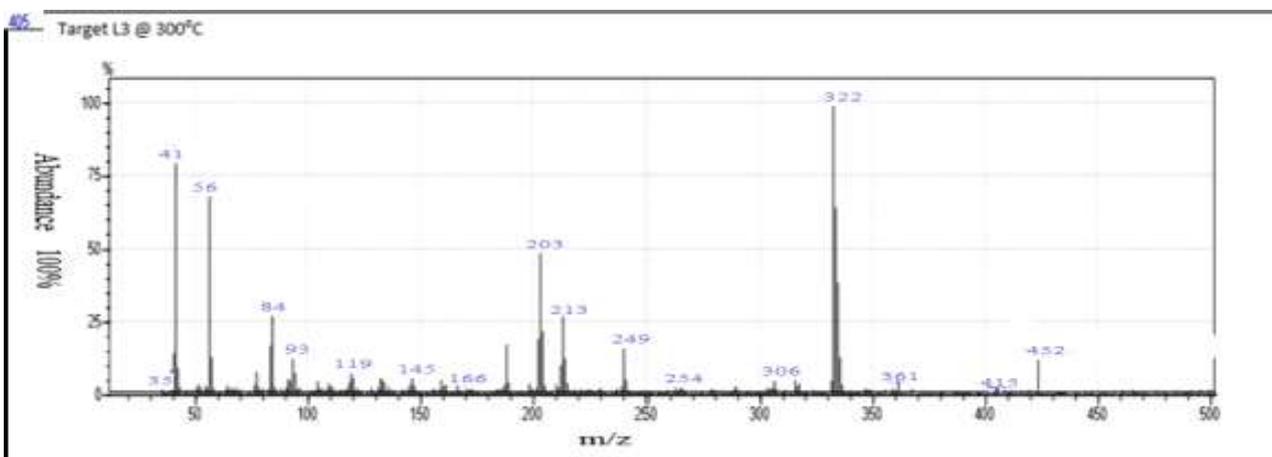
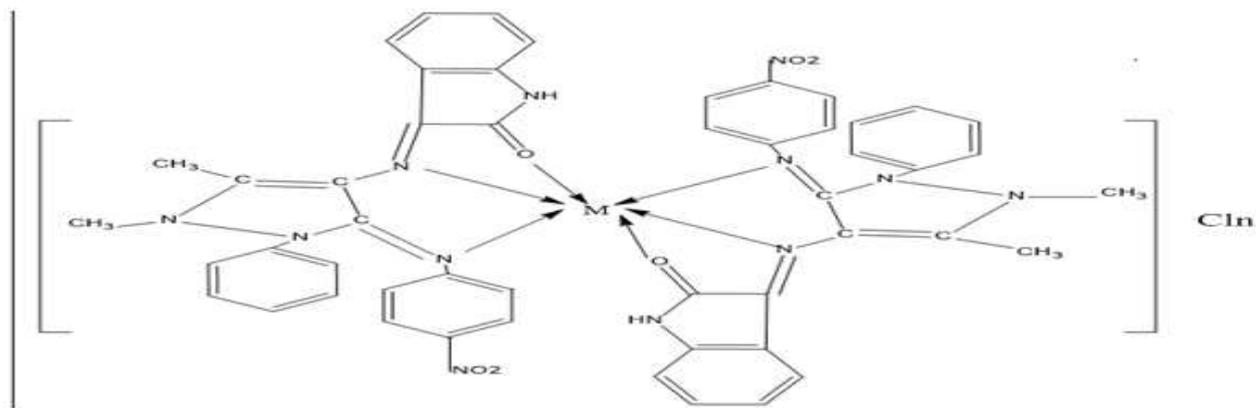


Fig.11: mass spectrum of ligand

**Suggested Structure**

On the basis of elemental microanalysis, magnetic moment and spectroscopic studies for the ligand [L] and Co(II), Ni(II) complexes, we suggest that the ligand behaves as tridentate on Complication with metal ions via the oxygen atom of carbonyl group of Isatin and nitrogen atoms of two

imine group While the ligand behaves as didentate on Complication with the Cu(II) via the oxygen atom of carbonyl group of Isatin and nitrogen atom of imine group. All we found that the ratio M: L was 1:2. According to these results, the complexes of Cr(III) , Mn(II), Zn(II), Cd(II) and Hg(II) have octahedral geometry(Fig 12).



M= Cr (III), n=3; Mn(II), Zn(II), Cd(II), Hg(II),n=2

Fig. 12: The suggested structural of complexes with Schiff base ligand [L]

## References

1. Abdullah MA, Salman Khan A (2010) *J. Molecules*. 15,6850-6858.
2. Shalin K, Durga ND, Sexena PN (2009) *Journal of Scientific & Industrial Research*, 68, 181-187.
3. Fakhari A, Khorrami Afshin R, Naeim H (2005) *Talanta*, 66, 813-817.
4. Kolat NA, Yildiz A, Temel H, Jihan S, Gul K (2012) *J.Dufeed*1(1): 15-22.
5. Lednicer D (1984) *The Organic Chemistry of Drug Synthesis, Vol-III*, Wiley Inter science Publication, New York 90, 283.
6. Ahlam SM (2009) *J. Eng. & Tech*, 27 (6): 1093.
7. Hadi MA (2013) *J. Pharm. Chim. Acta*. 3(2): 127-134.
8. Raman N, Kulandaisamy A, Jeyasubramanian K (2002) *Indian Journal of chemistry*, 41 A, 942-949.
9. Ahmad RH, Moagtoof Mahmood, S Abid, Allah MA (2012) *J. of Kufa for chemical science*, 4, 35-44.
10. G Socrates "Infrared Characteristic Group Frequencies" Wiley, (1980), New York.
11. M Tumer, C Celik, H Koksal, S Serin (1999) *Transition Met. Chem*. 24, 52.
12. Omer B, Ibrahim MA, Mohamed Moamen, S Refat (2014) *J. Canadian chemical Transactions*, 108-121.
13. El-Sonbati AZ, Diab MA, El-Bindary AA, Abou-Dobara MI, Seyam HA (2013) *J. Spectrochim. Acta Part A Mol. Biomol. Spectrosc*, 104,213–221.
14. ABP Lever "Inorganic Electronic Spectroscopy second edition" (1984) New York.
15. Singh DP, Malik V, Kumar R, Kumar K, Dhiman SS (2010) *J. Serb. Chem. Soc.*, 75(10): 1369.
16. AA El-Asmy, TY Al-Ansi, YM Shaiba (1989) *Trans. Meta. Chem.*, 14, 446.
17. WJ Geary (1971) *Coord. Rev.* 7, 81.
18. Ramasubramanian AS, Bhat BR, Dileep R, Rani S (2010) *J Sce Chem*. 2(12): 136.
19. Ali A (2004) Chemistry Department, College of Science, University of Babylon.
20. Carlin R Van A (1977) *a magnetic properties of Transition Metal Compounds*. Springer – Verlage, New York.
21. Mulay L (1963) *a magnetic Susceptibility*. John Wiley and sons, New York. 1 (4).
22. RC Shank, JP Duguid, BP Marmion, RA Swain (1975) "The practical of medical microbiology 12<sup>th</sup> ed.", 2.
23. MS Suresh, V Prakash (2011) *J. Chem*. 8 (3): 1408-1416.
24. MS Suresh, V Prakash (2011) *Inte. J. Cur. Res*. 3 (2): 068-075.
25. N Raman, A Kulandaisamy, C Thangaraja (2004) *Synth. React. Inorg. Met. Chem*. 34, 1191–1210.
26. A Kulandaisamy, T Kavitha, S Angaiarkanni, P Thillaiarasu (2013) *Chem. Sci. Trans*. 2, 147–152.
27. AP Mishra, R Mishra, R Jain, S Gupta (2012) *J. Mycobi.* ,40,1,20-26.
28. A Patel, S Bari, G Talele, J Patel M Sarangapani (2006) *J.IJPR* ,4, 249-254.

