



**RESEARCH ARTICLE**

## Employing the Physicochemical, Spectroscopy, Antimicrobial and Antifungal Efficacy Studies of P-Hydroxy Acetophenone Based Azo Schiff Base Complexes

**Wurood Ali Jaafar, Salah Mohammed Fezea, Rehab Kidhem Rahem Al-Shemary**

*Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham/ University of Baghdad, Adhamiyah, Baghdad, 10001, Iraq.*

### Abstract

The azo Schiff base [Reaction of 4-aminoanypyrrine and P-hydroxy acetophenone] and O-Phenylene diamine have been prepared. One azo Schiff base chelate of Co(II), Ni(II), Cu(II) and Zn(II)ion was also prepared. The chemical frameworks of the azo Schiff base and like elemental analyses (CHN), determinations of molar conductance,  $^1\text{H}$  &  $^{13}\text{C}$  NMR, IR mass and electronic spectroscopy .The elemental analyses exhibited the combination of [L: M] 1:1 ratio. Established on the values IR spectral, it is showed that the azo Schiff base compound acts as neutral hexadentate ligand bonded with the metal ion from two hydroxyl, two azomethine and two azo groups of the azo Schiff base compound in chelation was confirmed by IR ,  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectral outcomes. The UV-Vis spectral values appeared the existence of  $\pi \rightarrow \pi^*$  (phenyl ring),  $n \rightarrow \pi^*$  ( $\text{N}=\text{N}$ , -OH and  $\text{HC}=\text{N}$ ) and an octahedral structure was suggested for the coordinate. The mass spectral outcomes assured the purity of the ligand. Furthermore, the antimicrobial and antifungal efficacy results revealed that the metal complexes were found to be more active than the free ligand. In general the activity order of the synthesized compounds can be represented as  $\text{Fe (II)} > \text{Cu (II)} > \text{Ni (II)} > \text{Zn (II)} > \text{Co (II)} > \text{L}$ .

**Keywords:** Azo Schiff base, P-hydroxy acetophenone, antifungal efficacy, Spectroscopy.

### Introduction

The compounds like aromatic amines are closely applied chemicals. They may be used to preparation pharmaceuticals [1], explosives [2], rubber [3], epoxy [4], polyurethane [5], pesticides [6] and polymers [7], also to being intermediates for the preparation of azo colorants and antioxidants in elastomers [8]. Aromatic amines may be produced through the burning of organic compounds, containing in emissions of tobacco smolder[9]. They are may be originated surely in plants like beans, corn grains and tea [10].

The coordination compounds including azo ligands are of significant importance and play a pivotal role in industry, technology and life operations [11].Colorants that contain chromophores of dyes generally composing of  $\text{C}=\text{N}$ ,  $\text{N}=\text{N}$ ,  $\text{C}=\text{C}$ , heterocyclic and aromatic rings, including sulfur, nitrogen or oxygen, have been greatly applied in high technologies and several scopes, containing, paper, leather, biological staining, textiles, lasers, ink-jet printers liquid crystalline

displays, plastics and in specialized enforcements, like, cosmetic, food, photochemical, and drug productions [12]. One of the most important characteristics of azo moiety is depending of (lone pair of orbital) two electrons on atom of nitrogen, whether attached to an aromatic ring carrying a supplemental donor positions is well suitable for coordination and its complexes compose both azomethine and using cobaltite) as completing metal have variety of purposes in analytical [13], clinical [14], biological [15] and pharmamacological regions [16].

Our aim, in this research is to Employing the physicochemical, Spectroscopy, antimicrobial and antifungal efficacy studies of P-hydroxy acetophenone, 4-aminoanypyrrine, P-hydroxy acetophenone and O-Phenylene diamine Based Azo Schiff base and its chelate with Cu(II) ,Co(II), Fe(II), Zn(II) and Ni(II) ion.

### Instrumentation

Mass spectra were measured in Al-al-Bayt university-Jordan, on "Shimadzu – Gas

Chromatography Mass Spectrometer QP 5050A" in the range m/z (40 to 600) with an experiment of 1.65 Kv and vacuum pressure < 1 pa. An Applied Research-Laboratories model "3410 Minitorch Se quintal Inductively Coupled Plasma Spectrometer" (I.C.P) in Ibn-Sina State Company, was used for the atomic emission spectroscopy measurements. Molar conductivity was measured using "Pw-9526-Digital Conductivity meter". The IR Spectra were measured using "Shimadzu F.T.I.R 8400S Fourier.

Transform Infrared Spectrophotometer". Magnetic susceptibility of complexes was obtained at room temperature using Magnetic Susceptibility Balance Model-M.S.B. Auto Apparatus, in Al Nahrain University. C.H.N. Elemental analyses were performed in Al-al-Bayt University-Jorden on "Euro Vector- EA3000A C.H.N. Analyzer, Italy". Melting points were measured using "Stuart Melting Point Apparatus". The UV-Vis spectra were recorded using "Shimadzu UV-Vis Spectrophotometer".

## Materials

The following chemicals were used as received from suppliers; mercury chloride 98%, copper chloride dihydrate 98%, cobaltous chloride hexahydrate 98.8%, (Merck), nickel chloride hexahydrate 99.9%, 4-amino antipyrine and P-hydroxyl acetophenone (B. D. H). The pH of the medium (4-8) was adjusted with glacial acetic acid– ammonium acetate ammonia –buffer solution. Solutions were made of the ligand ( $1 \times 10^{-3}$ - $1 \times 10^{-5}$ M) in absolute ethanol and

same concentration range of metals salts in buffer solutions.

## Preparation of Azo Ligand

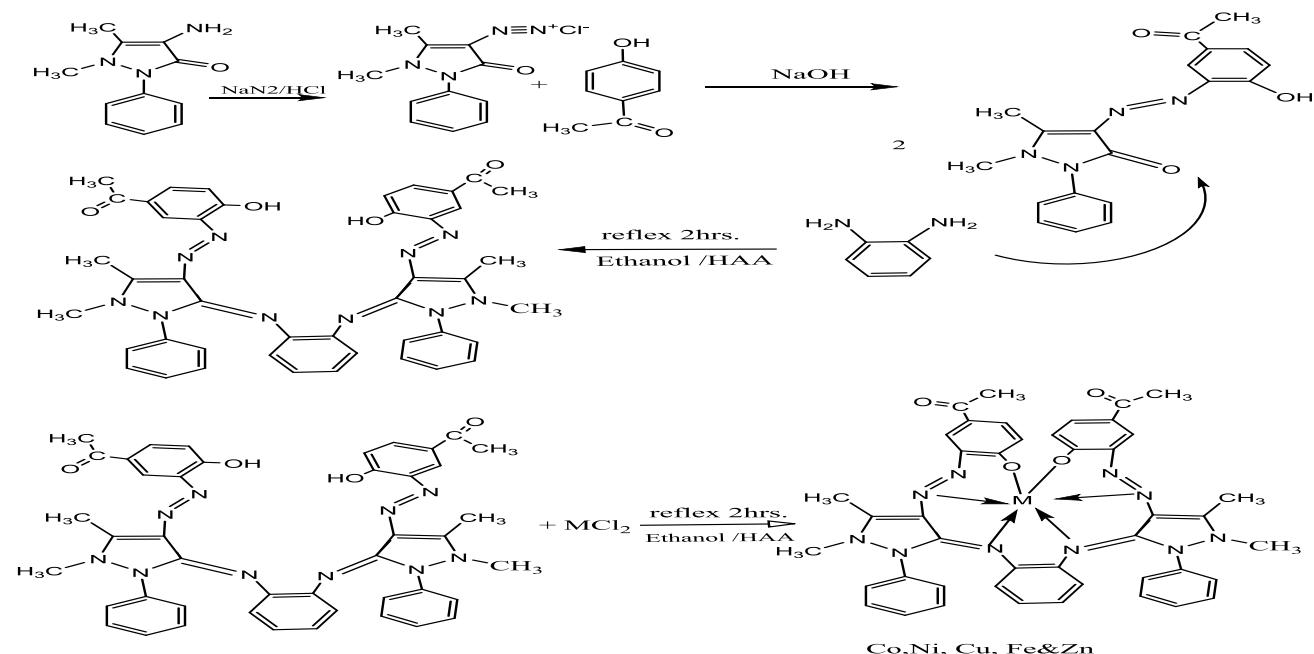
The azo Schiff base under investigation was synthesized by mixing (0.101g, 0.05mmole) of 4- amino antipyrine with 0.05 mole of 0.068g of P-hydroxy acetophenone in 50 mL of ethanol in presence of 10% NaOH solution, NaNO<sub>2</sub> solution and conc. HCl. The obtained azo ligand was acidified by dilute HCl until pH= 2-4. The isolated compound was filtrated, washed several times with distilled water until the filtrate becomes free from chloride ion by testing it with few drops of AgNO<sub>3</sub> solution dried and recrystallized from suitable solvent

## Preparation of Azo Schiff base

The Schiff base was prepared by dissolving (0.305g, 0.1mmole) of Azo ligand and (0.054g, 0.05mmole) of o-phenylene diamine in 50mL ethanol. The mixture was refluxed for two hours, and the obtained product was concentrated in vacuum to remove the solvent. The product was filtrated, dried and recrystallized from suitable solvent.

## Preparation of Azo Schiff Base Chelate

The reaction of the azo Schiff base (0.01mole) with 0.01mole of the salt of Cu ,Co, Fe, Zn and Ni chlorides in 20 mL ethanol was refluxed for two hours, next filtered and washed several times with hot ethanol until the filtrates become colorless. The resulted chelate was dried in desecrator over CaCl<sub>2</sub> for a night.



## Antimicrobial Study

The biological activities of prepared azo Schiff base and its metal complexes have been screened for the antifungal and antibacterial activities by well diffusion process, and (0.001mol) of the supply solution was synthesized by dissolving the components in DMSO, and the solutions were sequentially diluted to get the concentration data in lower inhibitory (MIC) ( $\mu\text{g mL}^{-1}$ ).

Fungal stains (Rhizoctonia bataticola, Candida albicans and Aspergillus niger) were incubated at 37°C for 48h and four bacterial stains (Bacillus subtilis, Escherichia coli Staphylococcus aureus and Pseudomonas aeruginosa) were incubated for 24h at 37°C. Standard antifungal drug NY statin and antibacterial Streptomycin were applied for rapprochement under analogous status.

## Dyeing Process

The dyeing characteristics of the prepared ligand and its complexes were examined on "Fine Textile State Company in Baghdad" unlit the Azoic Dyes (the icy dyeing method). Dyes were applied on Cotton fabric as shade 100 A laboratory model glycerin - bath high temperature beaker-dyeing instrument to be utilized.

The lastly powdered dye (2.5g) was nearly mixed with (0.1g) of Azotic dyes dispersing agent .The solution was next sparsed in an ultrasonic vibrator at room temperature for 30 mins .The pH of the solution was detected at (10) by adding of Na OH .The dyeing of the fabric was completed for 1 hour at 15-20 °C

## Results and Discussion

A Schiff base ligand is condensed from O-Phenylene diamine and 4-aminoanypyrrine then azo Schiff base ligand formed by coupling reaction of (E)-4- ((5-acetyl-2-hydroxyphenyl) diazenyl)-1, 5- dimethyl-2phenyl-1, 2-dihydro-3H-pyrazol-3-one with P-amino acetophenone. This azo Schiff base ligand is used for the synthesis of metal complexes [Cu (II), Co (II), Ni(II), Fe(II) and Zn(II)] was given in the Scheme 1 -3. The prepared compounds were then analyzed and the structure of the compounds was based by Elemental analyses molar conductance, UV-

Vis,  $^{13}\text{C}$  NMR  $^1\text{H}$  NMR mass, and IR spectrometry.

## Elemental Analysis and Molar Conductance

The mononuclear metal complexes were deduced Table (1) the electrolytic nature of their molar conductivities which were determined at  $10^3 \text{ M}$  in DMF. The data of all the complexes have been given in the range 13.4–25.2 ohm $^1 \text{ cm}^2 \text{ mol}^1$  indicating their non-electrolytic naturein [7].

**Infrared Spectra** The infrared spectral data of the azo Schiff and its Co (II), Ni(II), Cu(II), Fe(II) and Zn(II) chelate were studied in particular. The considerable vibrational assignments and their bands are specified in Table 4. The ligand spectrum presented band at  $1475 \text{ cm}^{-1}$  attributed to vibration of (N=N) azo moiety that wave is transferred in the chelate to lower values elucidating its participation in chelation through atom of nitrogen.

A band at  $1640 \text{ cm}^{-1}$  is characteristic of the (C=N) azomethine moiety in the ligand. This frequency is transferred to lower vibration with a change in shape in the spectra of the metal complexes proposing the coordination of nitrogen of (C=N) azomethine to the metal ion, the lowering of stretching vibration of azmethine may be assigned to lowering of v(C=N) frequency .

The new band found in range (453-453) cm order as an outcome of composition (M-N) frequency [8]. A broadband at  $3441 \text{ cm}^{-1}$  that is designated to the v(O-H) frequency in the ligand component unnoticed in the chelate composition displaying its sharing in coordination. The v(C-O) band is depressed about 27-20 cm $^{-1}$  elucidating coordination by the C-O group [9].

This group are changed of position in the spectrum of the chelate is confirmed the involvement of the oxygen atom of the hydroxyl group of the ligand by the present of new band in the range (547-571 cm $^{-1}$ ) that is not appearance in the azo Schiff base elucidating the existence of the vM-O vibrationselucidating the involvement of ligand compound in complication with the metal ion through azomethine nitrogen atom and this also shows the reduction of electron density in the azomethine ligand[10].

**Table 1: Conditions and properties of the preparation of ligand and its complexes**

Compounds	formula	Molecular Weight	Colour	Yield%	M.P.	%Elemental Analysis Found % (Calculated)			
						C	H	N	M
[H <sub>2</sub> AZSB]	C <sub>46</sub> H <sub>46</sub> N <sub>10</sub> O <sub>4</sub>	802.83	Light Brown	67	173	68.15 (68.81)	5.34 (5.77)	17.12 (17.44)	-
[Co(AZSB)]	C <sub>46</sub> H <sub>44</sub> CoN <sub>10</sub> O <sub>4</sub>	859.86	Dark Brown	78	236	63.82 (64.26)	5.03 (5.16)	15.94 (16.29)	6.18 (6.85)
[Ni(AZSB)]	C <sub>46</sub> H <sub>44</sub> N <sub>10</sub> NiO <sub>4</sub>	859.55	brown	85	212	57.08 (64.27)	5.07 (5.16)	16.12 (16.29)	6.70 (6.84)
[Cu(AZSB)]	C <sub>46</sub> H <sub>44</sub> CuN <sub>10</sub> O <sub>4</sub>	863.28	Redish brown	76	222	63.89 (63.91)	4.89 (5.13)	15.82 (16.20)	7.12 (7.35)
[Fe(AZSB)]	C <sub>46</sub> H <sub>44</sub> FeN <sub>10</sub> O <sub>4</sub>	854.22	brown	70	228	64.08 (64.49)	4.86 (5.18)	16.11 (16.35)	6.24 (6.52)
[Zn(AZSB)]	C <sub>460</sub> H <sub>44</sub> ZnN <sub>10</sub> O <sub>4</sub>	866.30	Dark Brown	81	631	63.12 (63.78)	4.77 (5.12)	15.84 (16.17)	7.26 (7.55)

**Table 2:<sup>1</sup>H-NMR Chemical shifts for ligand [H<sub>2</sub>AZSB] (ppm in DMSO)**

CH <sub>3</sub> -C=	DMSO	CH <sub>3</sub> -CO	CH <sub>3</sub> -N	CH=(aromatic)	C-OH
2.40	2.50	2.58	3.22	6.87-7.92	8.12

**Table 3:<sup>13</sup>C-NMR Chemical shifts for ligand [H<sub>2</sub>AZSB] (ppm in DMSO)**

CH <sub>3</sub> -C=	CH <sub>3</sub> -CO	CH <sub>3</sub> -N=	DMSO	C-N-	C-N=	CH=(aromatic)	=N-C	C=N	-C-OH
8.5	26.8	36.02	40.28	95.56	101.89	121.34-136.43	141.21	152.54	161.78

**Table 4: The main frequencies of the ligand [H<sub>2</sub>AZDP] and its complexes (cm<sup>-1</sup>)**

Compounds	v(OH)	v(C=N)	v(N=N)	v(C-O)	v(M-O) v(M-N)
[H <sub>2</sub> AZSB]	3441 br.	1640	1475	1269	-
[Co(AZSB)]	-	1621 s.	1443 sh.	1310 sh.	571 w. 447m.
[Ni(AZSB)]	-	1628 s.	1449 sh.	1307 s.	560w. 4378m.
[Cu(AZSB)]	-	1618 s.	1453 sh.	1304s.	547w. 448m.
[Fe(AZSB)]	-	1625sh.	1450sh.	1301 sh.	562w. 465m.
[Zn(AZSB)]	-	1619 s.	1457 sh.	1311s.	559 w. 469m.

s= strong, br=broad, w = weak, sh = sharp, m = medium

**Table 5: Conditions to the preparation in the comounds, UV-Vis, conductance and magnetic properties mensuration datum**

Compound	$\mu_{eff}$	$\text{Am S.Cm}^2\text{molar}^{-1}$	$\lambda_{max}$ (nm)	Wave number (cm <sup>-1</sup> )	Transition Assignment
[H <sub>2</sub> AZSB]	-	-	268 311 367	37313 32154 27247	$\Pi-\Pi^*$ $\Pi-\Pi^*$ $\Pi-\Pi^*$
[Co(AZSB)]	3.60	15.5	264 309 448 584 742 968	37878 32362 22321 17132 13477 10330	L.F L.F C.T $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$ $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$ $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$
[Ni(AZSB)]	2.77	18.7	270 318 474 767 875 984	37037 31446 21097 13262 11261 10204	L.F L.F C.T $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$ $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$ $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$
[Cu(AZSB)]	1.80	13.5	271 443 957	37900 22573 10449	L.F C.T $^2E_g \rightarrow ^2T_{2g}$
[Fe(AZSB)]	4.85	21.9	267 436 546	37453 22935 18315	L.F C.T $^5T_{2g} \rightarrow ^5E_{2g}$
[Zn(AZSB)]	Dia	25.4	273 340 443	36630 29411 22573	L.F C.T C.T

**Table 6: Biological activity of AZO compounds on Bacterial and antifungal isolates -Inhibition Zone in (mm)**

Bacteria	[H <sub>2</sub> AZSB]	Co complex	Ni complex	Cu complex	Fe complex	Zn complex
Rhizoctonia bataticola	9	14	25	27	30	17
Candida albicans	6	15	17	22	37	20
Aspergillus niger	4	18	22	27	40	22
Bacillus subtilis	7	9	18	19	21	15
Staphylococcus aureus	10	13	18	23	19	19
Pseudomonas aeruginosa	6	18	20	20	23	17

**Table 7: VM, VL and Absorption of ligand, VM = volume of metal in ml, VL= volume of ligand in ml**

[H <sub>2</sub> AZSB]-CoCl <sub>2</sub>			[H <sub>2</sub> AZSB]-CuCl <sub>2</sub>		[H <sub>2</sub> AZSB]-NiCl <sub>2</sub>		[H <sub>2</sub> AZSB]-FeCl <sub>2</sub>		[H <sub>2</sub> AZSB]-ZnCl <sub>2</sub>	
VM	VL	Abs	Abs	Abs	Abs	Abs	Abs	Abs	Abs	
1 ml	0.25	1.315	1.320	1.331	1.334	1.326				
1	0.50	1.310	1.354	1.342	1.358	1.349				
1	0.75	1.353	1.352	1.356	1.343	1.349				
1	1	1.381	1.374	1.365	1.386	1.357				
1	1.25	1.367	1.382	1.374	1.364	1.351				
1	1.50	1.348	1.375	1.358	1.376	1.382				
1	1.75	1.310	1.367	1.375	1.378	1.371				
1	2.0	1.387	1.406	1.377	1.375	1.364				
1	2.25	1.381	1.395	1.406	1.406	1.406				
1	2.50	1.367	1.404	1.395	1.381	1.383				
1	2.75	1.410	1.432	1.417	1.409	1.402				
1	3.0	1.400	1.437	1.458	1.408	1.415				
1	3.25	1.414	1.401	1.418	1.456	1.473				
1	3.50	1.431	1.384	1.442	1.412	1.401				
1	3.75	1.440	1.412	1.358	1.371	1.384				
1	4	1.408	1.354	1.447	1.414	1.422				

**Table 8: Absorbance at different pH and optimum concentration of [H<sub>2</sub>AZSB] - metal ion solution**

Metal Ion	$\lambda_{\text{max}}$ (nm)	Molar Conc. $\times 10^{-4}$	Absorbance at pH					
			4	5	6	7	8	9
Co(II)/[H <sub>2</sub> AZSB]	443	2	0.007	0.026	0.015	0.017	0.007	0.005
Cu(II)/[H <sub>2</sub> AZSB]	451	1.5	0.004	0.032	0.065	0.032	0.009	0.021
Ni(II)/[H <sub>2</sub> AZSB]	463	1.5	0.026	0.043	0.070	0.038	0.012	0.017
Fe(II)/[H <sub>2</sub> AZSB]	468	2	0.087	0.112	0.251	0.172	0.115	0.108
Zn(II)/[H <sub>2</sub> AZSB]	476	2.5	0.056	0.134	0.162	0.074	0.052	0.047

**Table 9: Absorbance at  $\lambda_{\text{max}}$  for Molar Concentration of Mixed Solution of Ligand**

Metal Ion	Co(II) /[H <sub>2</sub> AZSB]	Cu(II) /[H <sub>2</sub> AZSB]	Ni(II) /[H <sub>2</sub> AZSB]	Fe(II) /[H <sub>2</sub> AZSB]	Zn(II) /[H <sub>2</sub> AZSB]
Molar Conc. $\times 10^{-4}$	2	1.5	1.5	2	2.5
pH/ $\lambda_{\text{max}}$	7.0/443	7.0/451	7.0/463	7.0/468	7.0/476
Absorbance at ( $\lambda_{\text{max}}$ )					
1:0.25	0.062	0.043	0.131	0.032	0.050
1:0.50	0.078	0.055	0.177	0.064	0.070
1:0.75	0.103	0.073	0.210	0.096	0.090
1:1.00	0.119	0.095	0.271	0.124	0.111
1:1.25	0.131	0.114	0.300	0.158	0.122
1:1.50	0.145	0.128	0.348	0.182	0.140
1:1.75	0.172	0.147	0.398	0.206	0.165
1:2.00	0.188	0.173	0.451	0.227	0.183
1:2.25	0.180	0.173	0.461	0.225	0.186
1:2.50	0.178	0.175	0.461	0.218	0.182
1:2.75	0.180	0.172	0.450	0.223	0.180
1:3.00	0.184	0.173	0.460	0.230	0.188
1:3.25	0.189	0.173	0.460	0.225	0.181
1:3.50	0.185	0.172	0.448	0.228	0.185
1:3.75	0.178	0.170	0.450	0.219	0.178
1:4.00	0.185	0.169	0.451	0.221	0.185

**Table 9: UV-Vis spectral data at ( $\lambda_{\text{max}}$ ) for Job method of [H<sub>2</sub>AZSB]- complex solution at optimum concentration and pH**

Metal Ion	Co(II) /[H <sub>2</sub> AZSB]	Cu(II) /[H <sub>2</sub> AZSB]	Ni(II) /[H <sub>2</sub> AZSB]	Fe(II) /[H <sub>2</sub> AZSB]	Zn(II) /[H <sub>2</sub> AZSB]	Absorbance at ( $\lambda_{\text{max}}$ )
$\frac{V_m}{V_m + V_L}$						
0.1	0.058	0.067	0.140	0.095	0.058	
0.2	0.131	0.122	0.280	0.152	0.119	
0.3	0.168	0.177	0.462	0.218	0.171	

<b>0.4</b>	0.176	0.190	0.450	0.220	0.179
<b>0.5</b>	0.152	0.141	0.383	0.187	0.143
<b>0.6</b>	0.118	0.108	0.312	0.162	0.128
<b>0.7</b>	0.091	0.093	0.232	0.131	0.082
<b>0.8</b>	0.062	0.051	0.148	0.082	0.048
<b>0.9</b>	0.034	0.028	0.080	0.053	0.0205

**Table 10: Stability constant and  $\Delta G$  for the ligand complexes**

Compounds	As	Am	$\alpha$	K	Log K	1/K	$\Delta G$
Co(II)/[H <sub>2</sub> AZSB]	1.343	1.369	0.019	3×10 <sup>9</sup>	9.1	0.11	-52.8
Cu(II)/[H <sub>2</sub> AZSB]	1.383	1.392	0.0065	2×10 <sup>9</sup>	9.0	0.11	-52
Ni(II)/[H <sub>2</sub> AZSB]	2.178	2.398	0.0093	1×10 <sup>8</sup>	8	0.125	-45.6
Fe(II)/[H <sub>2</sub> AZSB]	1.990	2.357	0.17	3×10 <sup>9</sup>	9.5	0.13	-54.6
Zn(II)/[H <sub>2</sub> AZSB]	2.230	2.458	0.0943	10×10 <sup>8</sup>	9	0.12	-51.7

[Fe (AZSB)] > [Co (AZSB)] > [Cu(AZSB)] > [Zn(AZSB)] > [Ni(AZSB)]

### Electronic Spectra and Magnetic Moments of Metal Complexes

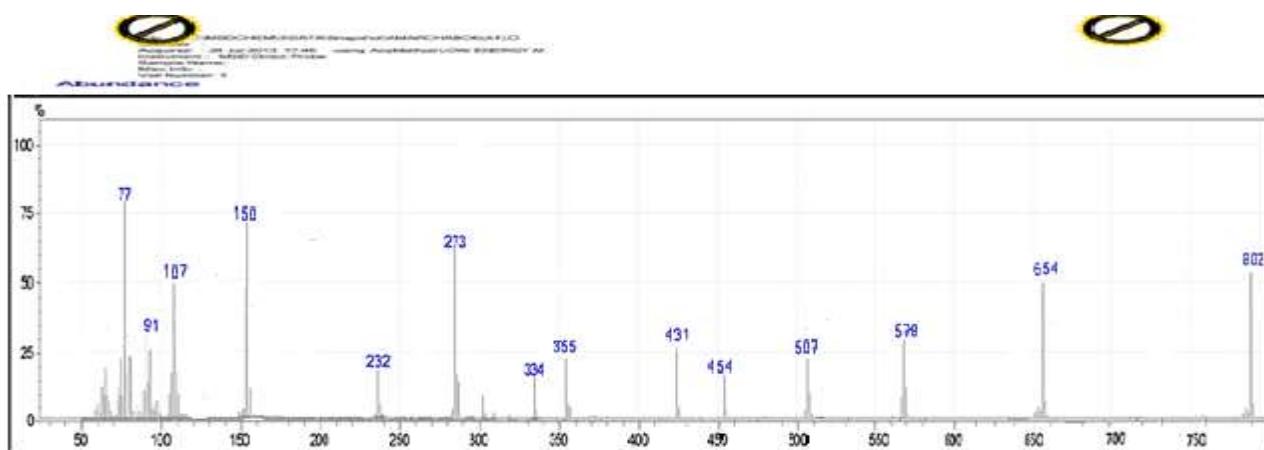
The free azo Schiff base ligand solution in ethanol exhibits three eminent peaks at 268 , 311 and 326 nm which are characterized of N=N-, C=N , C=O and other chromophore moieties(Table 5). The magnetic sensitivity data of Co (II) complex was 3.60 B.M proposed an octahedral structure. The prominent electronic spectral peaks were at 584, 742 and 968 nm attributed to 3A2g (F) →3T1g (P), 4A2g (F) →4T1g (F) and 4A2g (F) →4T2g (F) transferences respectively [11], which uncommonly offered supplemental backing to octahedral structure of the Co (II) complex.

The Ni(II) complex spectrum was characteristic of an octahedral structure with outstanding peaks at 767 , 875 and 984 nm are attributed to 3A2g(F)→ 3T1g(P) ,3A2g(F)→3T1g(F) and 3A2g(F)→ 3T2g(F) transferences. The magnetic sensitivity of 2.78 B.M. also proposed an octahedral structure. The Cu (II) complex was reddish brown in colour attributed to strong C.T band tailing off region in 957 nm are attributed to 2Eg → 2T2g transference [12]. The magnetic sensitivity value (1.80 B.M.) lies well within the expected range (1.7-2.2 B.M.). The brown solution of Fe (II) complex in DMF exhibited spectral peaks which were

interfered with CT peaks [13]. The peaks noticed at 546 nm could very well be attributed to 5T2g →5E2g transference. The magnetic sensitivity data of 4.85 B.M contented the octahedral structure [14]. The dark brown solution of Zn (II) complex was diamagnetic and the spectral peaks were all similar to those of the ligand as d-d transferences were lost .The dark brown solution of zinc(II) complex in DMF offered high intensity peaks at 273 ,340 and 443 nm attributed to electronic transferences of LMCT, N=N- chromophores , C=O and -C=C respectively.

### Mass Spectra

The mass spectrum of azo Schiff base [H<sub>2</sub>AZSB] confirmed the proposed composition of the ligand, suggestive a molecular ion [M+] peak at m/z at 802, rhythmic with the molecular weight of [H<sub>2</sub>AZSB] ligand Figure (1). The other peaks exposed at m/z = 654, 578, 507, 454, 431,355,232,150,107, 92 and 77 representing to [C<sub>38</sub>H<sub>40</sub>N<sub>9</sub>O<sub>2</sub>] +, [C<sub>32</sub>H<sub>36</sub>N<sub>10</sub>O<sub>2</sub>] +, [C<sub>30</sub>H<sub>36</sub>N<sub>8</sub>] +, [C<sub>26</sub>H<sub>26</sub>N<sub>6</sub>O<sub>2</sub>] +, [C<sub>24</sub>H<sub>31</sub>N<sub>8</sub>] +, [C<sub>24</sub>H<sub>31</sub>N<sub>8</sub>] +, [C<sub>18</sub>H<sub>27</sub>N<sub>8</sub>] +, [C<sub>12</sub>H<sub>17</sub>N<sub>5</sub>] + , [C<sub>12</sub>H<sub>17</sub>N<sub>5</sub>] +,[C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>] +, [C<sub>6</sub>H<sub>6</sub>N] + and [C<sub>6</sub>H<sub>5</sub>] + respectively [15].

**Figure 1: Mass for ligand (H<sub>2</sub>AZSB)**

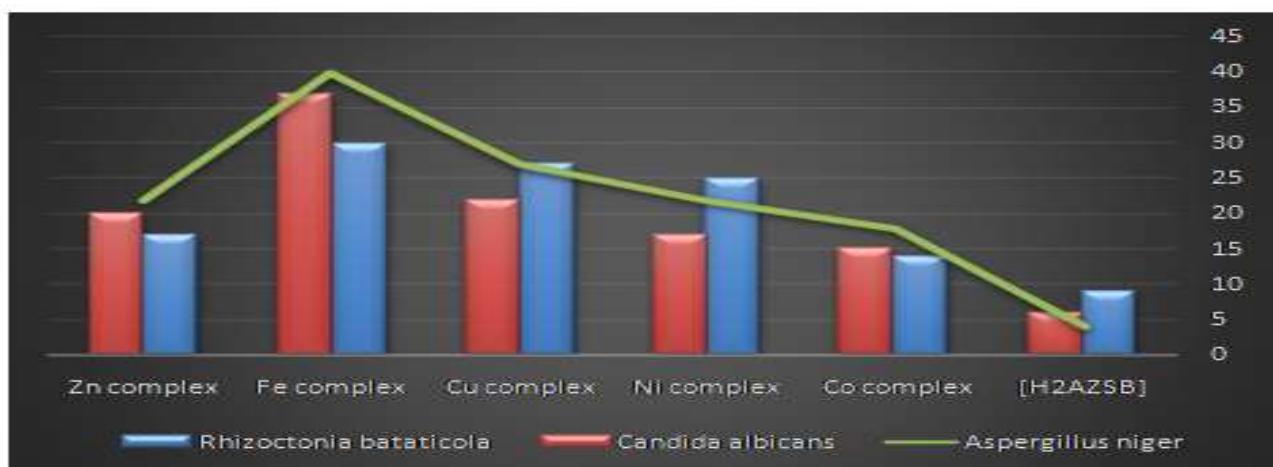


Figure 2: Difference between the antifungal efficacy of ligand and metal complexes

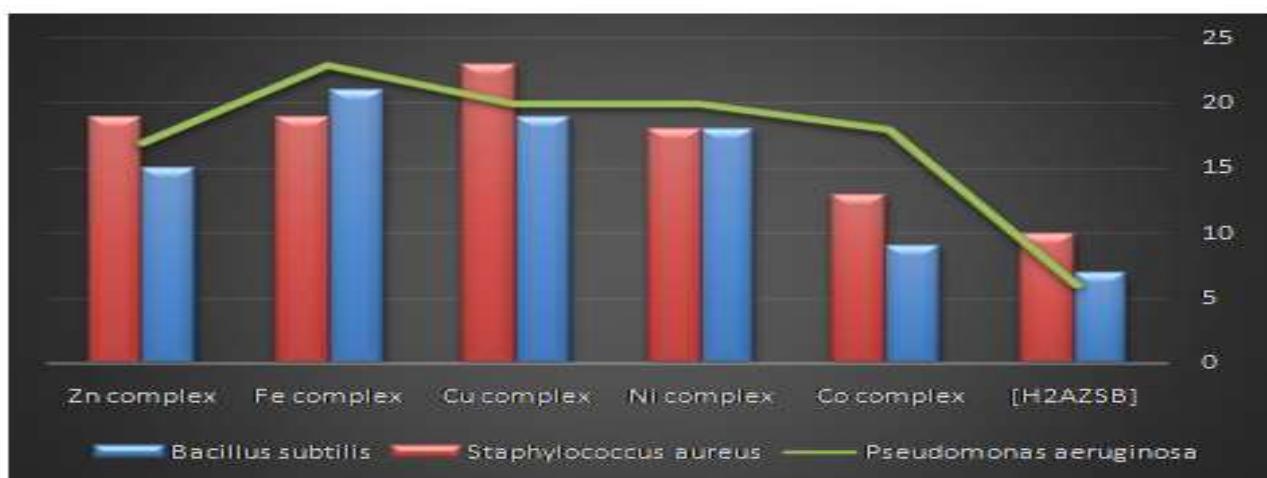


Figure 3: Difference between the antimicrobial efficacy of ligand and metal complexes

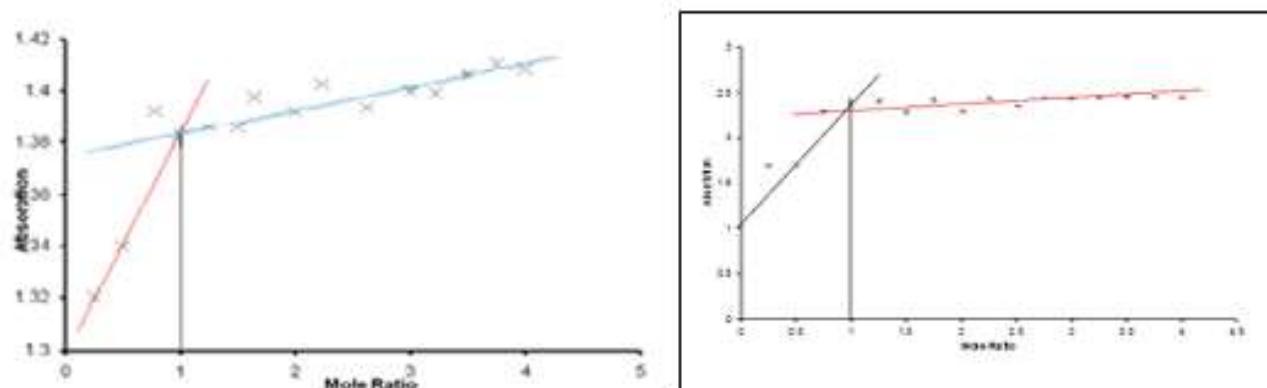
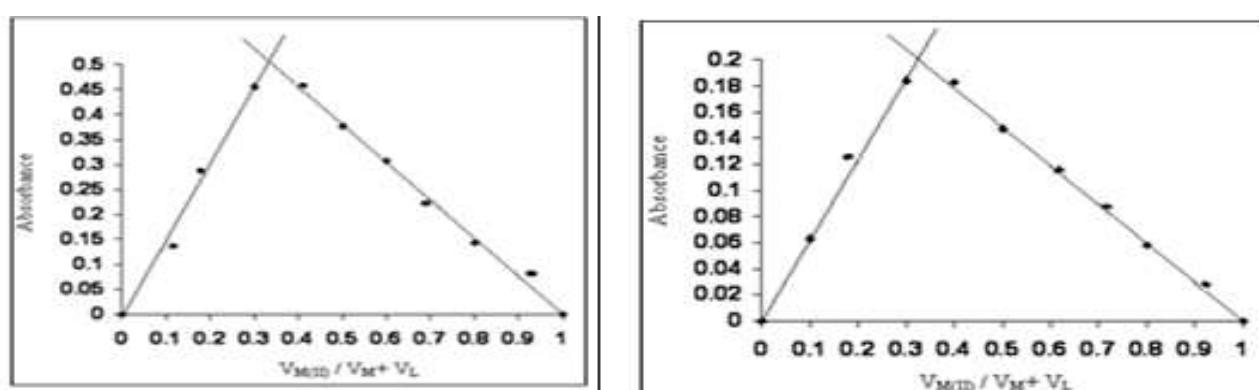
Figure 4: The mole ratio curve of complex /Cu (AZSB)/ in solution ( $1 \times 10^{-3}$  mole. l<sup>-1</sup>) at ( $\lambda=451$  nm )and complex /Ni(AZSB)/ in solution ( $1 \times 10^{-3}$  mole. l<sup>-1</sup>) at ( $\lambda=463$  nm )

Figure 5: Job Method Plot for Ligand Complex Solution



**Figure 6: Dyeing of Cotton by of ligand and [Cu (AZSB)] complex**

### Nuclear Magnetic Resonance Spectrum of Azo Schiff Base

The  $^1\text{H}$  NMR spectrum of the azo Schiff base compound was determined single in d6-DMSO solvent. The azo Schiff base spectral results show Table (1) singles at 6.12 ppm which is attributed to the presence of proton of the hydroxyl groups. The multiple single which appeared in range 6.87-7.92 ppm in the spectrum of the azo Schiff base compound is due to the existence of ring groups [16].

Meanwhile, the singles at 2.40, 2.58, 3.22 and 3.50 ppm assigned to the presence of methyl for  $\text{CH}_3\text{-C=}$ ,  $\text{CH}_3\text{-CO}$ ,  $\text{CH}_3\text{-N}$  and DMSO solvent groups in the ligand. The  $^{13}\text{C}$  NMR spectrum of ligand displays singles for carbons of azo ( $=\text{N}-\text{C}-$  and azmethine ( $-\text{N}=\text{C}-$ ) groups was observed between 141.21 and 152.54 ppm [16].

The signal observed at 161.78 ppm is assigned to ( $\text{C}-\text{O}$ ) phenolic carbon. Also, the spectrum showed peaks at 121.34–136.43 ppm corresponding to carbons of the ring of phenyl. And another data of the ligand shown in the Table (2) 3.6. Antimicrobial Study. The antimicrobial activity results (Table 6) expose which the Fe (II) and Cu (II) complex offers fairly good activity with all the tested bacterial strains, and in general the activity order of the synthesized compounds can be represented as  $\text{Fe (II)} > \text{Cu (II)} > \text{Ni (II)} > \text{Zn (II)} > \text{Co (II)} > \text{L}$ .

The higher activity of the metal complexes may be possessing to the influence of metal ions on the membrane of ordinary cell. Both the characteristics polar and nonpolar characteristics have been bear Metal complexes; this produces them suitable for permeation to cells and the tissues. In addition, chelation may suppress or enhance the biochemical potential of bioactive organic types. Moreover, lipophilicity, that holds the rate of entry of

molecules into the cell, is modified by coordination, so the metal complex can become more active than the free ligand. Therefore, the metal complexes show greater biological activities than the unlinked ligand and free metal ion that in truth is in congruence with the literature. These metal complexes have a priority in which the particular bioactivities of the unlinked ligand and metal ions are collective that could make them more powerful antimicrobial agents [16].

The complexes were made through direct reaction from the ligand ( $\text{L}$ ) alcoholic solution to the metal ions aqueous solution at a M:L ratio from 1: 1 in the perfect pH. Datum elemental analysis and metal contain for compounds were at good agreements for calculated values. Molar conductance for (10-3M) at DMMF solution for compounds described non-electrolytic type, datum are recorded at Magnetic estates of the produced complexes have been happened to a paramagnetic for all the complexes except Zn(II) complex was a diamagnetic that were accounted for octahedral structures in Table 7.

Then a calibration curve was plotted on absorbance against molar concentration in the range ( $1\times 10^{-4}$  to  $3.5\times 10^{-4}$  M) from a mixed ethanol -aqueous to metal ions and ligand, only rate concentration about ( $3\times 10^{-4}$  to 1M) followed Beer's law and appeared evident intense color[17]. The (Best-fit straight lines) have evidenced for factor of correlation  $R > 0.990$ . The optimum concentration was selected for complex solutions affording height absorbance to a constant in steady ( $\lambda_{\text{max}}$ ) at various pH. It is obvious that the concentrations  $1.5\times 10^{-4}$  molar and  $2\times 10^{-4}$  molar are subjected to be the optimum concentration.

Probation outcomes proof that absorbance from all produced compounds are extreme and steady at a buffer solution from  $\text{NH}_4\text{CH}_3\text{CO}_2$  at pH range (4-9). It has been found which all produced compounds had perfect pH = 7 as shown at Figure 4. Table (9) shows the absorbance and ( $\lambda_{max}$ ) of the complex solution at different pH and concentration. It is obvious that the concentrations  $3 \times 10^{-4}$  molar and  $2.5 \times 10^{-4}$  molar are subjected to be the optimum concentration [18].

To inquire into interaction between made metal ions and ligand beneath learning to the synthesis to the compounds, spectra from incorporating solutions for the metal ions and ligand into obtain at condensation and best pH = 7, as well as firm wave length ( $\lambda_{max}$ ) have been studies at first. Thereafter mole ratio metal into ligand (M:L) (1:1) has been defined to equip the

$$K = \frac{A_m}{A_s} = \frac{a^m}{a^s} = K^{1/m}$$

Where  $a$  = degree of dissociation,  $c$  = the concentration in mole/ L of the complex solution,  $A_m$ = the absorption of solution containing the same deal of excess of azo Schiff base and metal and  $A_s$  = the absorption of solution containing a stoichiometric deal of

compounds. Ideal condensation has been chosen to compound solution based that solution gives highest absorbance in steady ( $\lambda_{max}$ ) in various pH. Probation outcomes proof that absorbance from all produced compounds are extreme and steady at a buffer solution from  $\text{NH}_4\text{CH}_3\text{CO}_2$  at pH range (4-9).

It has been found which all produced compounds had perfect pH = 7. Stoichiometry of Complexes reorder by job and mole ratio process writing of the complexes made in solutions has been permanent. In two positions outcomes disclose 1:1 ligand into ratio. The (K) is constant of successive stability of the (1:1) ligand: metal complex may be determined from the equation:

$$K = \frac{A_m}{A_s} = \frac{a^m}{a^s} = K^{1/m}$$

metal ion and azo Schiff base and The (K) data of refers to high stability of synthesized complexes. The thermodynamic parameters of ( $\Delta G$ ) Gibbs free energy were also researching. The  $\Delta G$  value has been determined from the equation.

$$\Delta G = -RT \ln K$$

Where; T= absolute temperature (Kelvin) and R = gas constant (8.3 J.mol<sup>-1</sup>.K). All products were contained in Table 10. The negative value of ( $\Delta G$ ) signalizes that the reaction between (L) and metal ions under study are spontaneous.

The matters which absorb the visible wavelength of light in range 400-700nm called are coloring agents, therefore they show colored to our eyes. These can be either inorganic or organic in nature. Colorants from Azo type are the extreme substantial class of

## Conclusion

The coordination ability of the newly synthesized azo Schiff base has been proved in complication reaction with Fe (II), Co (II), Ni (II), Cu (II), and Zn (II) ions. From the physicochemical analysis values , UV-vis ,IR mass ,(<sup>1</sup> H &<sup>13</sup> C nmr only ligand ) spectra, and magnetic measurements

pigments and synthetic dyes symbolizing representing 60-80% of all organic colorants. They are applied closely, as colorants for cosmetics, fibers, hair, waxes, plastics, food, papers, mineral oils, leather, stuffs and textile [19]. Dye [H<sub>2</sub>AZDP] and its complexes were utilized on fabric of cotton. The dyeing of the fabric was done assigning to the experimental method. These dyes provided colors in the range of brown varying between dark brown and light brown with depth and good brightness on the fabric [20].

of the ligand and its metal complexes confirmed the suggested coordination of the ligand through nitrogen of the azo group, oxygen of OH group, and nitrogen of the azomethine group as hexadentate. The process of coordination commonly impacts the biological efficacy of the complexes which are potent versus pathogens.

## References

1. Anu Kajal, Suman Bala, Sunil Kamboj, Neha Sharma, Vipin Saini (2013) Review Article, Schiff Bases: A Versatile Pharmacophore Article ID 893512, 14.
2. Maria DMC, Ribeiro D, Jorge MG, Ana LRS, Paula CFC, Bernd S (2004) J. Mol. Catal. A: Chem., 224: 207-212.
3. Robert J, AL-Massy, Chereryl A Janson, Chen-Chenkan, Zuzana Hostomska (1992) Structures of apo and complexes Escherichiacoliglycinamideribonucleotidet ransformylase, Proc. Natl. Acad. Sci USA 6114-6118 89.
4. Ali Mohammed Yimer (2014) Chemical Synthesis, Spectral Characterization and Antimicrobial Studies on complexes of Ni(II), Cu(II) and Zn(II) with N, N-di(o-hydroxybenzenoylmethylene)ethylenediamine, American Journal of Bio Science 2(6-1): 22-34
5. F Albert, Cotton Geoffrey, Wilkinson Carlos, A Murillo, Manfred Bochmann (1999) Advanced Inorganic Chemistry, 6<sup>th</sup> Edition; John Wiley and Sons USA, 37-50.
6. Gilles Gasser, Ingo Ott, Nils Metzler-Nolte (2011) Organometallic Anticancer Compounds, J. Med. Chem., 54: 3–25.
7. Kirshener Wei SYK, Francis D, Bergman JH (1966) Anticancer and potential antiviral activity of complex inorganic compounds, J. Med. Chem., 9: 369-372.
8. Shayma AS, Alazawi Abbas, AS Alhamadani (2007) Synthesis and characterization of mixed ligand complexes of 8- hydroxyquinoline and Schiff base with some metal ions, Um-Salama Science Journal, 4(1).
9. Shatha MHO, Al Naimi Synthesis, Characterization and Antibacterial Activities of Mixed Ligand Complexes of Symmetrical Schiff Base and 8-Hydroxyquinoline with Zn(II), Cd(II) and Hg(II), Saudi Journal of Pathology and Microbiology.
10. Joana C, Carolina M, Sofia S, Pedro VB, Alexandra RF (2015) Ann. Med. Chem. Res. 1(2): 1010, 1-5.
11. Chandra S, Sangeetika J (2004) EPR and electronic spectrum studies on copper (II) complexes of some N-O donor ligands, J. Indian Chem. Soc, 81: 203-206.
12. Ferreira EI, Tavares LC (2002) “Potential tuber culostatic agents. Topliss application on benzoic acid [(5-Nitro-thiophen-2-yl)-methylene]-hydrazide series” Bio org. Med. Chem., 10, 557-560.
13. Lever ABP (1984) Inorganic electronic spectroscopy. Amsterdam, the Netherlands, Elsevier, New York.
14. Omid Taheri, Mahdi Behzad, Abolfazl Ghaffari ,Maciej Kubicki, Grzegorz Dutkiewicz, Abolfazl Bezaatpour, Hossein Nazari, Ali Khaleghian, Abolfazl Mohammadi Mehdi Salehi (2014) Synthesis, crystal structures and antibacterial studies of oxidovanadium(IV) complexes of salen-type Schiff base ligands derived from meso-1,2-diphenyl-1,2-ethylenediamine ,Transition Metal Chemistry, 39 (2): 253–259
15. Kojima M, Taguchi H, Tsuchimoto M, Nakajima K (2003) Co. ord. Chem. Rev., 237, 183-196.
16. Long NJ (1995) Chem. Int. Edition 34, 21.
17. Cusumano M, Messina MA, Nicolo F, Pietro MLD, Rotondo A, Rotondo E (2004) ture Eur. J. In. org. Chem., 4710-4717.
18. Avaji PG, Kumar CHV, Patil SA, Shivananda KN, Nagaraju C (2009) Eur. J. Med. chem.
19. Anant Prakash, Devjani Adhikari (2011) Application of Schiff bases and their metal complexes-A Review, International Journal of Chem. Tech. Research, 34, 1891-1896.
20. VR Rajewar, MK Dharmale , SR Pingalkar (2014) Synthesis and Spectral Characterization of Lanthanide Complexes Derived from 2-[(4-Bromo-2,6-Dichloro-Phenylimino)-Methyl]-4,6DiiodoPhenol,An International Open Free Access, Peer Reviewed Research Journal , 30, (4): 2049-2058.

