



**SOME TRANSITION METAL COMPLEXES WITH NEW SCHIFF BASE  
LIGAND HEXADENTATE  
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**ABSTRACT**

A new hexadentate Schiff base ligand derived from condensation of 4-aminoantipyrine with aromatic diketone and thiosemicarbazide, and its metal complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility measurement and spectral (electronic, IR, Uv-Vis, <sup>1</sup>H NMR) studies. It has been originated that the Schiff base ligand with Co (II), Ni (II), Cu (II) and Zn (II) ions from mononuclear complexes on 1 : 1 (metal : ligand) stoichiometry. The conductivity data confirm the electrolytic nature of the complexes. The Co (II), Ni (II), and Zn (II) complexes show an octahedral configuration. Electronic absorption spectra of the Cu (II) complex suggest a square- planar geometry around the central metal ion. The IR spectral data suggest the involvement of sulphur and azomethine nitrogen in coordination to the central metal ion.

**Key words:** Hexadentate, Schiff base ligand, 4-aminoantipyrine, Bis thiosemicarbazone.

**INTRODUCTION**

There has been a significant exploitation in recent years towards the formulation of new materials containing poly functional units (ligands) able to coordinate with metallic ions. Schiff base ligand are considered “privileged ligands”, because they are easily prepared by the condensation between aromatic amines and aromatic aldehydes or ketones have a wide variety of applications in many fields. Interest in multidentate acyclic, macrocyclic compounds<sup>1-4</sup> is continually increasing because of their unique properties and use in the synthesis of poly nuclear metal complexes<sup>5-8</sup>.

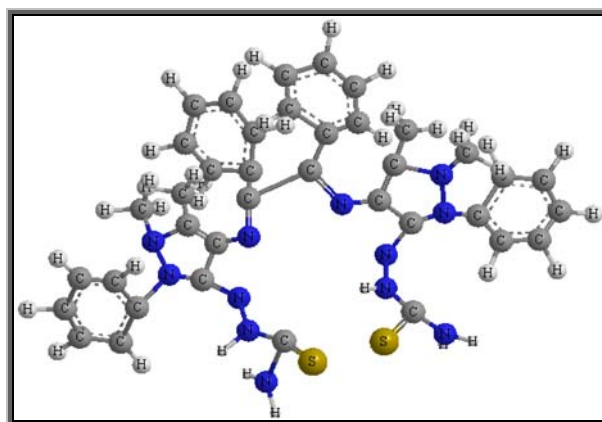
Metal complexes of the Schiff base ligands have a variety applications including clinical<sup>9</sup>, analytical<sup>10</sup>, industrial<sup>11</sup> and biological<sup>12-16</sup>, in addition to their important roles in catalysis and organic synthesis<sup>17</sup>. Some research groups found that the Schiff base metal complexes derived from 4-aminoantipyrine can specially cleave the DNA<sup>18-20</sup> and have a variety of application in analytical and biological areas<sup>21,22</sup>. The aim of the present study was to synthesize and characterize Co (II), Ni (II), Cu (II) and Zn (II) metal complexes with newly synthesized Schiff base ligand derived from 4-aminoantipyrine, benzil and thiosemicarbazide.

**EXPERIMENTAL**

**Materials and measurements**

All chemical are of highest purity and used as supplied. The electro thermal melting point model

9300 was used to measure the melting points of the ligand and its complexes. Elemental analyses of (C.H.N) were estimated by measurement of Microanalytical unit of 1108 C.H.N Elemental analyzer.



**Fig. 1: Molecular structure of ligand (2Z, 2'Z)-(1E, 1'E)-1,2-diphenylethane-1,2-diyldene)bis(azan-1-yl-1-ylidene)bis(1,5-dimethyl-2-phenyl-1H-pyrazole-4(2H)-yl-3 (2H)-ylidene) bis(hydrazinecarbothioamide)**

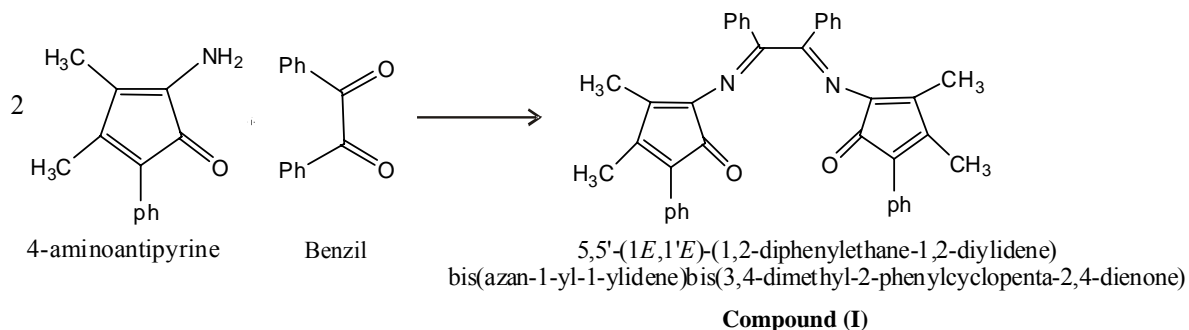
FTIR Spectra were recorded using KBr discs in range 4000-400  $\text{cm}^{-1}$  of FTIR Shimadzu Spectrophotometer Model 8400-Uv-Vis spectra were recorded in ethanol on Shimadzu spectrophotometer double beam Model 1700-Uv-Vis spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained in DMSO solution using (Burker, Ultra Shield 3000 MKZ, Switzer and spectrophotometer). Magnetic Susceptibilities were measured as powder samples using Faraday method, a balance Magnetic MSB-MKI was employed for this purpose. The diamagnetic corrections were made by Pascals constants<sup>23</sup>. Molar conductance measurements were determined in (DMF) by using an Alpha Digital conductivity meter Model 800 physical characterization of the ligand and its metal chelate complexes was listed in Table 1.

### Preparation of new Schiff base ligand (DEAPH)

The method of preparation was as follows -

### Preparation of compound (I) (DEPD)

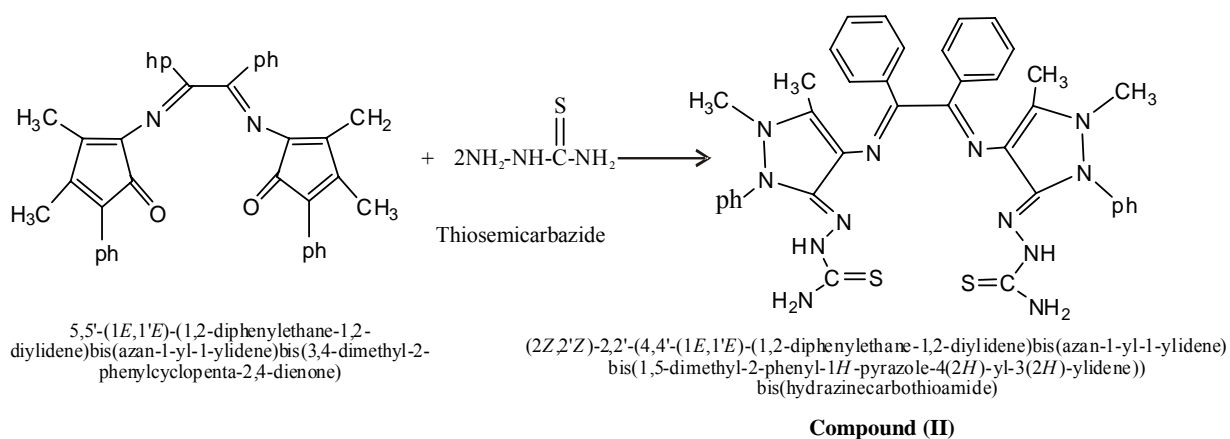
The compound (I) was prepared using the following method by condensation of 4-amino antipyrine (2.03 g, 10 mmol) dissolved in ethanol 30 mL was added to ethanolic solution of benzil ( 2.1 g, 5 mmol) (2 : 1) mole ratio, and few drops of glacial acetic acid were added to reaction mixture with continuous stirring and refluxing at 75°C for (20 hr), the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous  $\text{CaCl}_2$ . m.p (143-146°C) **Scheme 1**.



**Scheme 1**

### Preparation of compound (II) (DEAPH)

The new Schiff base ligand (DEAPH) was prepared by condensation of compound (I) (5.8g, 10 mmol) was dissolved in 50 mL ethanol and refluxed with (1.82 g, 20 mol) of thiosemicarbazide for (15 hr) adding three drops from glacial acetic acid. A clear colored solution was obtained. The Schiff base ligand was isolated after the volume of mixture was reduced to half by evaporation and recrystallized by hot ethanol and dried over anhydrous  $\text{CaCl}_2$ . m.p (118-120°C).



**Scheme 2: Preparation of the ligand (DEAPH)**

### Preparation of metal complexes

The metal complexes were prepared by the mixing of (30 mL) ethanolic solution of the metal salt (1 mmol) namely ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$ ). With (0.72 g, 1 mmol) of the ligand dissolved in (30 mL) methanolic solution (1 : 1) (metal : ligand) ration. The resulting mixture was refluxed for (1 hr) with constant stirring. A colored product appeared on standing and cooling the above solution. The precipitated solid complexes were filtered, washed with (5 mL) of hot ethanol to remove any traces of the unreacted starting materials. Finally, the complexes were dried under vacuum.

**Table 1: Physical data and analysis of ligand and its complexes**

Compound	Colour	M.P. (°C)	Yield %	Formula	Calc. (Found)%			
					C	H	N	M
L=(DEAPH)	Yellow	118-120	72	$\text{C}_{38}\text{H}_{38}\text{N}_{12}\text{S}_2$	62.80 (62.72)	5.23 (5.30)	23.14 (23.26)	-----
$[\text{Co(L)}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Dark green	138-140	67	$[\text{Co}(\text{C}_{38}\text{H}_{38}\text{N}_{12}\text{S}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}]$	52.21 (52.14)	4.58 (4.73)	19.23 (19.37)	6.67 (6.81)
$[\text{Ni(L)}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Brown	202 d	69	$[\text{Ni}(\text{C}_{38}\text{H}_{38}\text{N}_{12}\text{S}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}]$	52.18 (52.44)	4.57 (4.82)	19.22 (19.42)	6.72 (6.48)
$[\text{Cu(L)}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Red	146-148	80	$[\text{Cu}(\text{C}_{38}\text{H}_{38}\text{N}_{12}\text{S}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}]$	51.90 (51.87)	4.55 (4.73)	19.12 (19.33)	7.22 (7.31)
$[\text{Zn(L)}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Dark yellow	150-152	78	$[\text{Zn}(\text{C}_{38}\text{H}_{38}\text{N}_{12}\text{S}_2)\text{Cl}_2 \cdot \text{H}_2\text{O}]$	51.81 (51.67)	4.54 (4.36)	19.09 (19.21)	7.38 (7.19)

L = ligand, d = Complex metal with decomposition

## RESULTS AND DISCUSSION

The ligand was yellow powder, but the prepared complexes of this ligand vary in color depending of metal ion. The experimental results of the elemental analyses of the ligand and its metal complexes are good agreement with theoretical expectation. The elemental analyses of the complexes indicate that the (metal : ligand) ratios were (1 : 1) in the  $[ML]Cl_2$  where  $M = Co(II), Ni(II), Cu(II)$  and  $Zn(II)$ . The complexes were found to be stable in air and moisture at room temperature and insoluble in water, but its soluble in common organic solvents. The observed molar conductance value of the complexes in DMF at room temperature is consistent with electrolytic nature of the complexes. Physical and analytical data of the ligand and its complexes are listed in Table 1.

### Microanalysis

The elemental analysis data the complexes as shown in Table 1 exhibit the formation 1 : 1 [M : L] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base ligand were listed by TLC technique and C, H and N elemental analyses.

### Infrared spectral studies of the ligand and its complexes

The data of the IR spectra of Schiff base ligand and its complexes were compared with the IR spectra of the free ligand in order to determine the involvement of coordination sites in chelation and to detect the changes that might have taken place. The obtained data are summarized in Table 2 with some assignments of the important characteristic bands.

**Table 2: Some IR frequencies in ( $cm^{-1}$ ) of the ligand and its metal complexes**

Ligand/complexes	$\nu$ (OH) water	$\nu$ (C=N)	$\nu$ (NH-C=S)	$\nu$ (C=S)	$\nu$ (M-N)	$\nu$ (M-S)
L=(DEAPH)	----	1645	1180	804	---	---
[Co(L)]Cl <sub>2</sub> .H <sub>2</sub> O	3400	1630	1161	765	534	503
[Ni(L)]Cl <sub>2</sub> .H <sub>2</sub> O	3405	1625	1164	761	530	495
[Cu(L)]Cl <sub>2</sub> .H <sub>2</sub> O	3408	1628	1178	805	537	498
[Zn(L)]Cl <sub>2</sub> .H <sub>2</sub> O	3400	1635	1160	760	530	502

In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamido  $-NH-C=S$  functional group. The  $\nu$  (S-H) band at  $2560\text{ cm}^{-1}$  is absent in the IR spectrum of ligand but  $\nu$  (N-H) band at  $3261\text{ cm}^{-1}$  and  $3170\text{ cm}^{-1}$  are present, indicating that in the solid state, the ligand remains as the thione tautomer<sup>24,25</sup>. The infrared spectrum of the ligand indicated the presence of primary amine  $\nu$  ( $NH_2$ ) group due to appearance of absorption of frequency<sup>26</sup> at  $3371\text{ cm}^{-1}$ . A strong absorption band at  $1645\text{ cm}^{-1}$  due to  $\nu$  (C=N) present in the free ligand has shifted to lower side by  $15-25\text{ cm}^{-1}$  in all four complexes, this indicates the involvement of (C=N) azomethine group in coordination<sup>27</sup>. The appearance of broad band around  $3400\text{ cm}^{-1}$  in the spectra of complexes may be due to  $\nu$  (OH) water molecules<sup>28,29</sup>. The bands near ( $1180, 804$ )  $cm^{-1}$  in the free Schiff base ligand may be assigned to  $\nu$  (NH-C=S) and  $\nu$  (C=S). This has shifted to lower wave number in complexes indicates that sulphur is coordinating to the metal ion<sup>30</sup> excepted the copper complex appearance do not changes of these groups. The far IR spectra of the metal chelates show some new bands at  $534 \pm 10\text{ cm}^{-1}$  and  $503 \pm 10\text{ cm}^{-1}$  have been assigned to  $\nu$  (M-N) and  $\nu$  (M-S) modes respectively<sup>31-33</sup>. Representative example for there is given in Fig. 2.

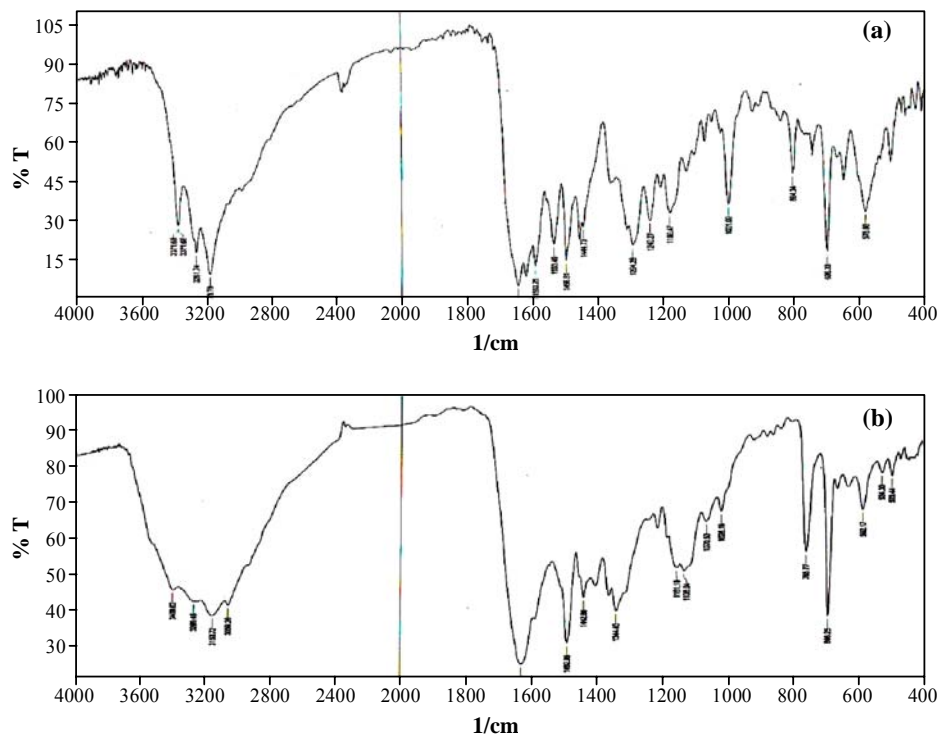


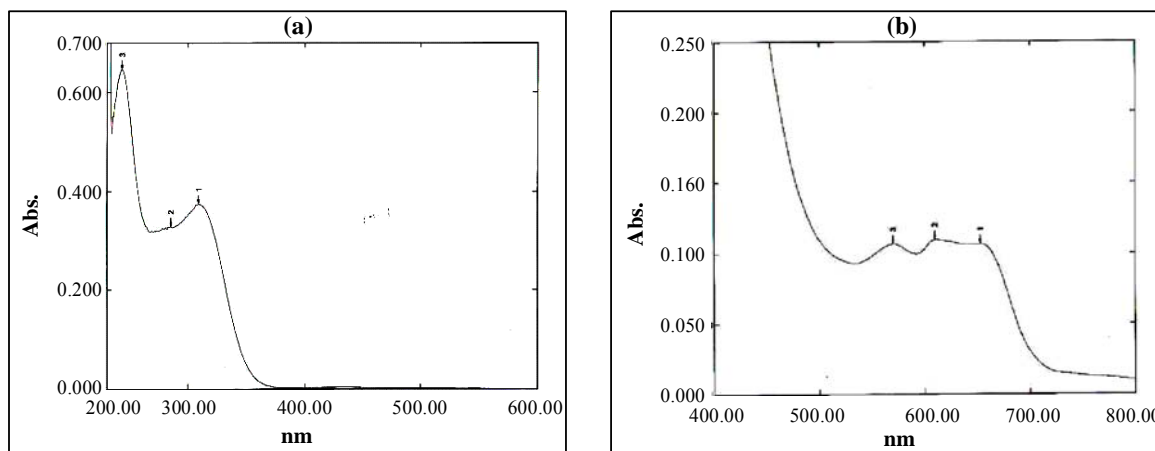
Fig. 2: IR spectra of (a) the ligand (DEAPH) & (b)  $[\text{Co}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$

### Electronic spectral and magnetic moments

The spectral data and the magnetic moment of prepared complexes are listed in Table 3. Fig. 3 Shows the spectra of the ligand and  $[\text{Co}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$ . The electronic spectrum of the Schiff base ligand exhibits intense absorption at 242 nm ( $41322\text{ cm}^{-1}$ ), 285 nm ( $35087\text{ cm}^{-1}$ ) and 309 nm ( $32362\text{ cm}^{-1}$ ), which are attributed to  $\pi\text{-}\pi^*$  and  $\pi\text{-}\pi^*$ , respectively.

Table 3: Electronic spectra, conductivity and magnetic moment of complexes

Complexes	Abs. nm ( $\text{cm}^{-1}$ )	Transition	Conductivity $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$	$\mu_{\text{eff}}$ (B.M)
L=(DEAPH)	242 (41322)	$\pi\rightarrow\pi^*$	---	---
	285 (35087)	$n\rightarrow\pi^*$		
	309 (32362)			
$[\text{Co}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$	653 (15313)	${}^4\text{T}_{1g}\rightarrow{}^4\text{T}_{1g}(\text{F})$	145	5.47
	610 (16393)	${}^4\text{T}_{1g}\rightarrow{}^4\text{A}_{2g}(\text{F})$		
	570 (17543)	${}^4\text{T}_{1g}\rightarrow{}^4\text{T}_{1g}(\text{P})$		
$[\text{Ni}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$	670 (14925)	${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$	138	3.21
	468 (21367)	${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$		
$[\text{Cu}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$	541 (18484)	${}^2\text{B}_{1g}\rightarrow{}^2\text{A}_{1g}$	156	1.75
	350 (28571)	INCT		
	301 (3322)	INCT		
$[\text{Zn}(\text{L})]\text{Cl}_2\cdot\text{H}_2\text{O}$	-----	INCT	148	Dia



**Fig. 3: Electronic spectrum of : (a) the ligand (DEAPH) & (b) [Co(L)]Cl<sub>2</sub>.H<sub>2</sub>O**

### Cobalt complex (II)

The electronic spectrum of Co (II) complex showed three broad peaks at 653 nm (15313 cm<sup>-1</sup>), 610 nm (16393 cm<sup>-1</sup>) and 570 nm (17543 cm<sup>-1</sup>) assigned to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>2g</sub> (F), <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>A<sub>2g</sub>(F) and <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>1g</sub>(P), respectively<sup>34</sup>. The magnetic moment value of the Co (II) (d<sup>7</sup>) complex is (5.47 B.M)<sup>35</sup>. The spectrum resemble those reported for octahedral complex<sup>36</sup>.

### Nickel (II) complex (II)

The magnetic moment for the complex of Ni (II) (d<sup>8</sup>) was found to be (3.21 B.M), which with the range of octahedral Ni (II) complex<sup>37</sup>. The electronic spectrum of this complex show band at 670 nm (14925 cm<sup>-1</sup>) and 468 nm (21367 cm<sup>-1</sup>) which can be assigned to <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (F) and <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (P), respectively<sup>38</sup>.

### Copper (II) complex (II)

The magnetic moment value of Cu (II) (d<sup>9</sup>) complex (1.75 B.M), this value indicate within the expected for one electron, and d-d spectrum of this complex show band at 541nm (18484 cm<sup>-1</sup>), 350 nm (28571 cm<sup>-1</sup>) and 301 nm (3322 cm<sup>-1</sup>) which may assigned to <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub> transition and two intra-ligand charge transfer bands, these data suggest square-planar geometry around Cu (II)<sup>39,40</sup>.

### Zinc (II) complex

Metal complex is diamagnetic consistent with the (d<sup>10</sup>) configuration and the electronic spectra of these complex exhibit high intense charge transfer transition which are assigned to (INCT).

### <sup>1</sup>H NMR spectrum studies

The newly synthesized ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of <sup>1</sup>H NMR chemical shift. <sup>1</sup>H NMR spectra were determined in solution of DMSO with tetra methyl silane as an internal reference. The <sup>1</sup>H NMR spectrum of the ligand showed clear signals involved singlet at δ (2.5) ppm belong to the proton of solvent (DMSO) and multiples signals at δ (7.2-7.8) ppm which were assigned to aromatic protons of phenyl ring of benzil and antipyrine respectively. Multiple signals at δ (8.3-8.5) ppm which belong to amine groups. Singlet at δ (3.3) ppm belong to the proton of methyl. Singlet at δ (4.4) ppm belong to the proton of -C-NH, as shown in Fig. 4.

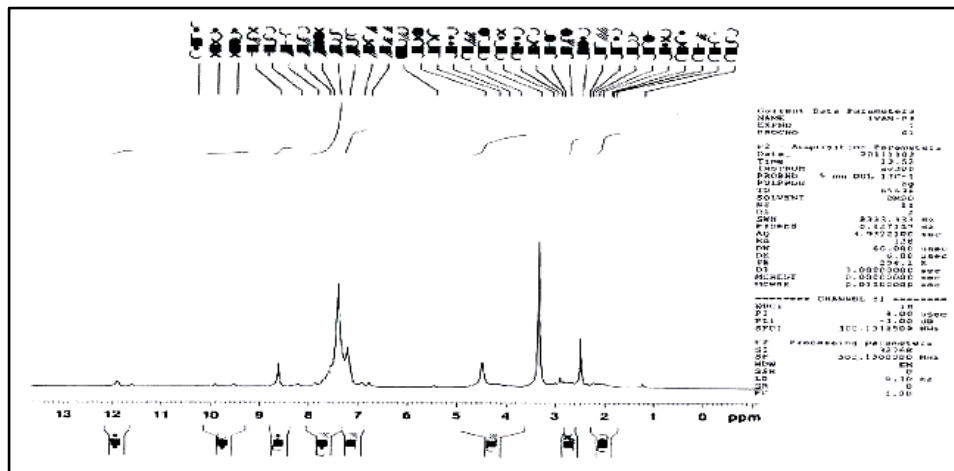


Fig. 4:  $^1\text{H}$  NMR Spectrum of ligand (DEAPH)

### Molar conductance

The molar conductance of the synthesized ligand complexes were measured using  $10^{-3}$  M DMF solvent at room temperature. All the complexes are 1 : 2 electrolytes in nature and may be formulated  $[\text{ML}]\text{Cl}_2$ , implying the non-coordination of chloride anion to the central metal ion.

The conductivity values of the chelate complexes are in the range (138-156)  $\text{S. mol}^{-1}.\text{cm}^2$ . These values indicated high conductivity of the complexes<sup>41</sup>.

### CONCLUSION

This paper report the preparation and identification of new hexadentate Schiff base and its complexes with Co (II), Ni (II), Cu (II) and Zn (II) metal ions. The isolated products were characterization by available techniques. All the proposed geometry of the complexes are octahedral expected the copper complex is a square-planar. According to these results the structural formulas of these complexes may be proposed in Fig. 5.

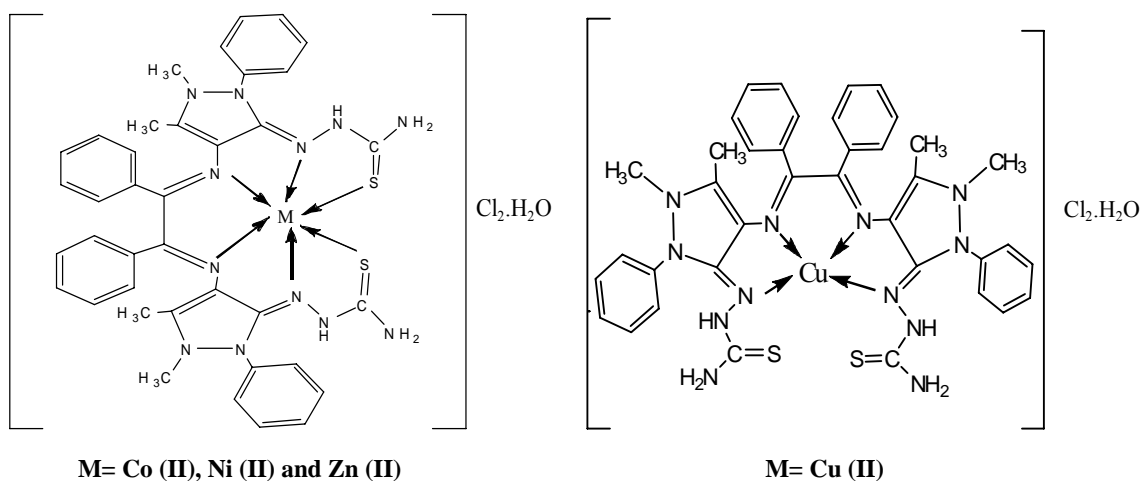


Fig. 5: The proposed structural formula of the metal chelate complexes

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