

Preparation of New Macrocyclic ligand and Characterization complexes of Some Transition metals

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Abstract

The chelate complexes of Ni (II),Cu(II) and Zn(II) with new Schiff base derived from 4-aminoantipyrine,4-dimethylaminobanzaldehyde,p-hydroxybanzaldehyde and ethylene diamine are prepared and characterized through elemental analyses,IR,electronic spectra, magnetic moment, and molar conductance measurement . The molar conductance data reveal that all the metal chelates of the ligand with Ni (II) , Cu (II) and Zn (II) are electrolytes . The coordinating ligand act as neutral tetra dentate manner , with N₄ doner sites of azo methine (C=N). The central metal ion displays the coordination number 4 in these complexes .

Key words : Schiff base ,Anti pyrine , Metal chalet complexes, Characterization.

الخلاصة

تضمن البحث تحضير معقدات كلايية لكل من ايونات النيكل(II) والنحاس(II) والارصين (II) مع عضيده قاعدة شف الجديدة المشتقة من 4-امينو انتيبيرين ،4-ثنائي مثيل امينو بنزليهايد ، بارا- هيدروكسي بنزليهايد واثلين ثنائي الامين . شخصت العضيده المحضرة ومعقداتها بوساطة التحليل الدقيق للعناصر والأشعة تحت الحمراء والأطياف الالكترونية والحساسية المغناطيسية وقياسات التوصيلية المولارية.أظهرت النتائج ان العضيده رباعية المخلب (N₄) ويتمتع المعقد بصفات ايونيه.

Introduction

Schiff base compounds are widely studied and used , attracting much attention in both organic synthesis and metal ion complexation⁽¹⁻⁴⁾. They have been synthysized from avariety of compounds,such as amino acid ,aromatic aldehydes and antipyrine⁽⁵⁻⁷⁾.Schiff bases of 4- amino antipyrine is very important in preparation new complexes ,these cpmpound present agreat variety of biological activity , clinical ,analytical and pharmacological areas^(8,9). Studies of a new kind of chemotherapeutic Schiff basees are now attracting the attention of biochemists⁽⁴⁾.Earlier work reported that some drugs showed increased activity , when administered as metal complexes rather than as organic compounds^(10,11). The coordinating properties of 4-amino antipyrine have been modified to give aflexible ligand system ,formed by condensation with a variety of reagents like aldehyde ,ketones ,thiosemicarbazides and carbazides⁽¹²⁻¹⁵⁾.

The present paper aims to prepare and characterize of new Schiff base derived from 4- amino antipyrine,4-dimethylaminobanzaldehyde and ethylenediamine and its complexes with Ni(II), Cu(II) and Zn(II) metal ions by available techniques .

Experimental

Materials and measurements

All chemicals used in this work were of highest purity and used as supplied by the manufactures. The melting points of ligand and its metal complexes were determined by Electro thermal melting point apparatus. Elemental analysis was performed by Micro analytical unit of EA 300 A C.H.N Elemental analyzer , Al -Albat university Jordan . FTIR spectra were recorded using (KBr pellets) 4000-400 cm⁻¹ on FTIR Testscan Shimadzu 8000 series.

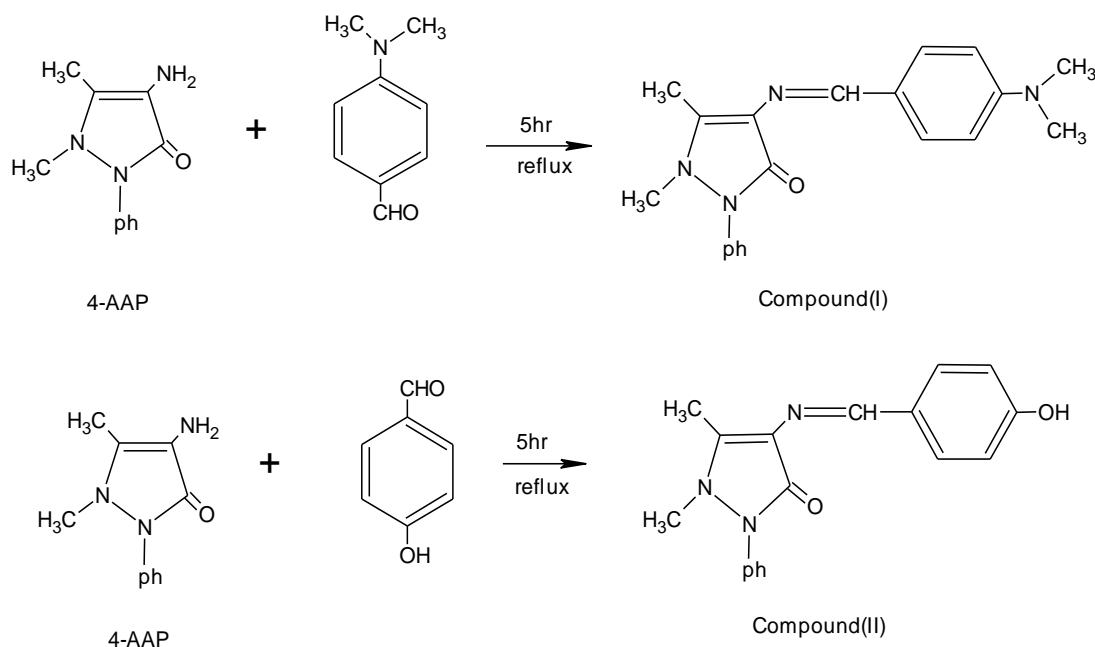
Electronic spectra were recorded in ethanol using Shimadzu Uv-Vis 1700 spectrophotometer. Electrical conductivity was measured by Digital Conductivity Meter Alpha-800 with solute concentration (10^{-3} M) in DMSO. The magnetic susceptibility were measured on powder samples using Faraday method for this purpose, Balance Magnetic (MSB-MKI) had been employed. The diamagnetic corrections were made by Pascal's constant⁽¹³⁾ .

Preparation of ligand

The method of preparation was as follows :

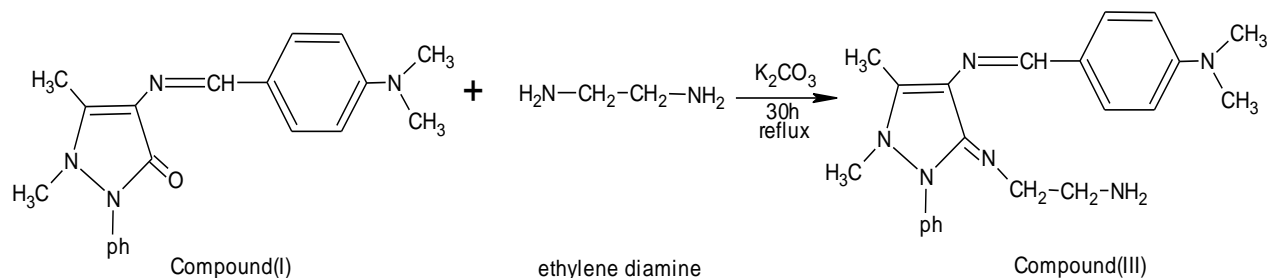
The new Schiff base was prepared by adding (50 ml) of 1- phenyl-2,3-dimethyl -4- amino pyrazol-5-one(4-amino antipyrine) (4-AAP) (2.03g ,0.01 mol) to the same volume of ethanolic solution of 4- dimethyl amino benzaldehyde⁽¹⁶⁾ (1.49g ,0.01 mol) and the same weight of 4- amino antipyrine dissolved in ethanolic solution (50ml) added to (1.22 g ,0.01mol) from p- hydroxy benzaldehyde dissolved in the same volume . The mixtures were refluxed with stirring for 5 h .

A yellow colored solid of (I), and (II) were collected by filtration recrystallized from hot ethanol and dried over anhydrous CaCl_2 . Scheme 1.



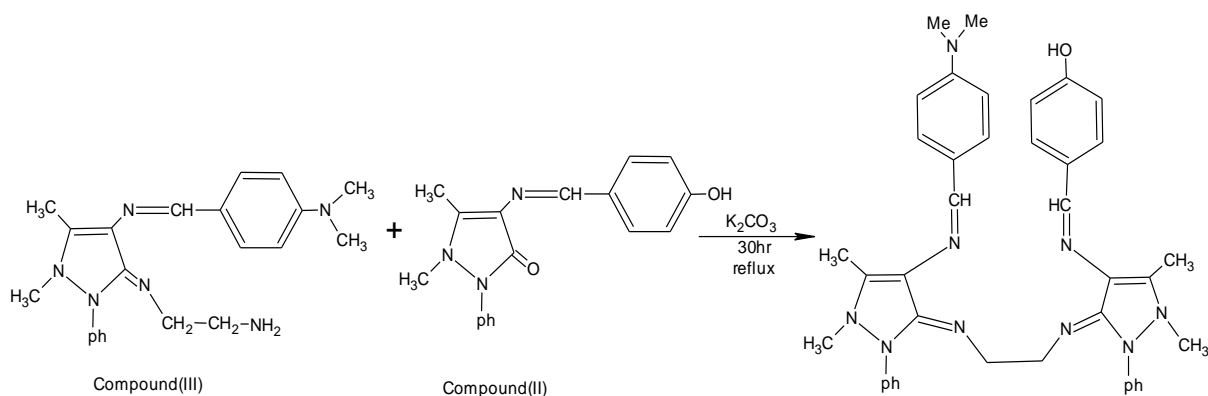
Scheme. 1.

Compound (I) (3.1g ,0.01mol) was added to an ethanolic solution (50 ml) of ethylene diamine (0.6g , 0.01 mol) . The mixture was refluxed for 30 h after addition of anhydrous potassium carbonate. The solid product compound (III) was collected by filtration ,recrytallized from hot ethanol and dried over anhydrous CaCl_2 . Scheme .2.



Scheme .2.

Compound (III) (3.76g, 0.01 mol) was dissolved in ethanol(50 ml) was mixed with compound (II) (3.07g ,0.01mol) dissolved in ethanol (50 ml). To this solution was added anhydrous potassium carbonate and the mixture was refluxed for 30 h. A dark yellow solid product was isolate after the volume of the mixture was reduction to half by evaporation and recrystilized by hot ethanol . The crystalline product was dried over anhydrous CaCl₂. Scheme. 3.



Scheme. 3.

Synthesis of complexes

All complexes were prepared by the same methods by adding (0.01 mol) of ligand dissolved in ethanol absolut (30 ml) to a solution of metal chloride (0.01 mol) for Ni(II),Cu(II) and Zn(II) dissolved in the same solvent (30 ml). After the mixture was refluxed for3 hrs. On cooling to room temperature,the colored complexes precipitated was collected by filtration and recrystallized form hot ethanol and dried over anhydrous CaCl₂.

Results and Discusion

The ligand is a dark yellow crystal which is soluble in common organic solvents. The reaction of the ligand with metal ions mentioned above gives vary in color depeding of metal ion . All complexes are quiet air-stable , in soluble in water , but its soluble in most organic solvents . Some physical and chemical properties for ligand and its complexes are listed in table.1. The elemental analysis and metal contents data are show in table.1.In all cases (1:1) (metal : ligand)solid complexes are isolated , that is agreement with the stoichiometric ratio found using molar ratio methods .

The higher conductivity values of the chelates complexes support the electrolytic nature of the metal complexes .Attempts to suggest the structure of the isolated complexes come from full investigation using the following studied .

Infrared Spectra

The IR spectra provide valuable information regarding the nature of the functional group attached to the metal ion . The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligand to the central metal ions are given in table.2.The spectrum of free ligand shows weak bands at 3130 cm^{-1} and 2999 cm^{-1} which due to $\nu(\text{C-H})$ aromatic and aliphatic respectively. The absorption band in free ligand observed at 3336 cm^{-1} attributed to the $\nu(\text{OH})$ of hydroxyl group⁽¹⁶⁾. The spectrum of the ligand shows two different bands absorption at $(1647 -1595)\text{ cm}^{-1}$ due to $\nu(\text{C=N})$ of azomethine group which is shifted to lower frequency in the spectra of all complexes ($1635-1581$) cm^{-1} with little change in shape in the spectra of the chelate complexes indicating the involvement of the(C=N) nitrogen in the coordination to the metal ions ^(17,18). All complexes show bands in $(1176-1072)\text{ cm}^{-1}$ and $(700-750)\text{ cm}^{-1}$ regions and can be assigned to phenyl ring vibrations ⁽¹⁹⁾.New bands are attributed to $\nu(\text{M-N})$ vibrations appearance in all complexes at $(475-400)\text{ cm}^{-1}$ respectively ^(19,20) .

Thus the above IR spectra data lead to suggest that ligand behaves as a tetra dentate chelating agent ,bonded to the metal ion via the four sites nitrogen atoms of azomethine group to give five-membered chelating ring . Representative example for their spectra is given in Fig .1.

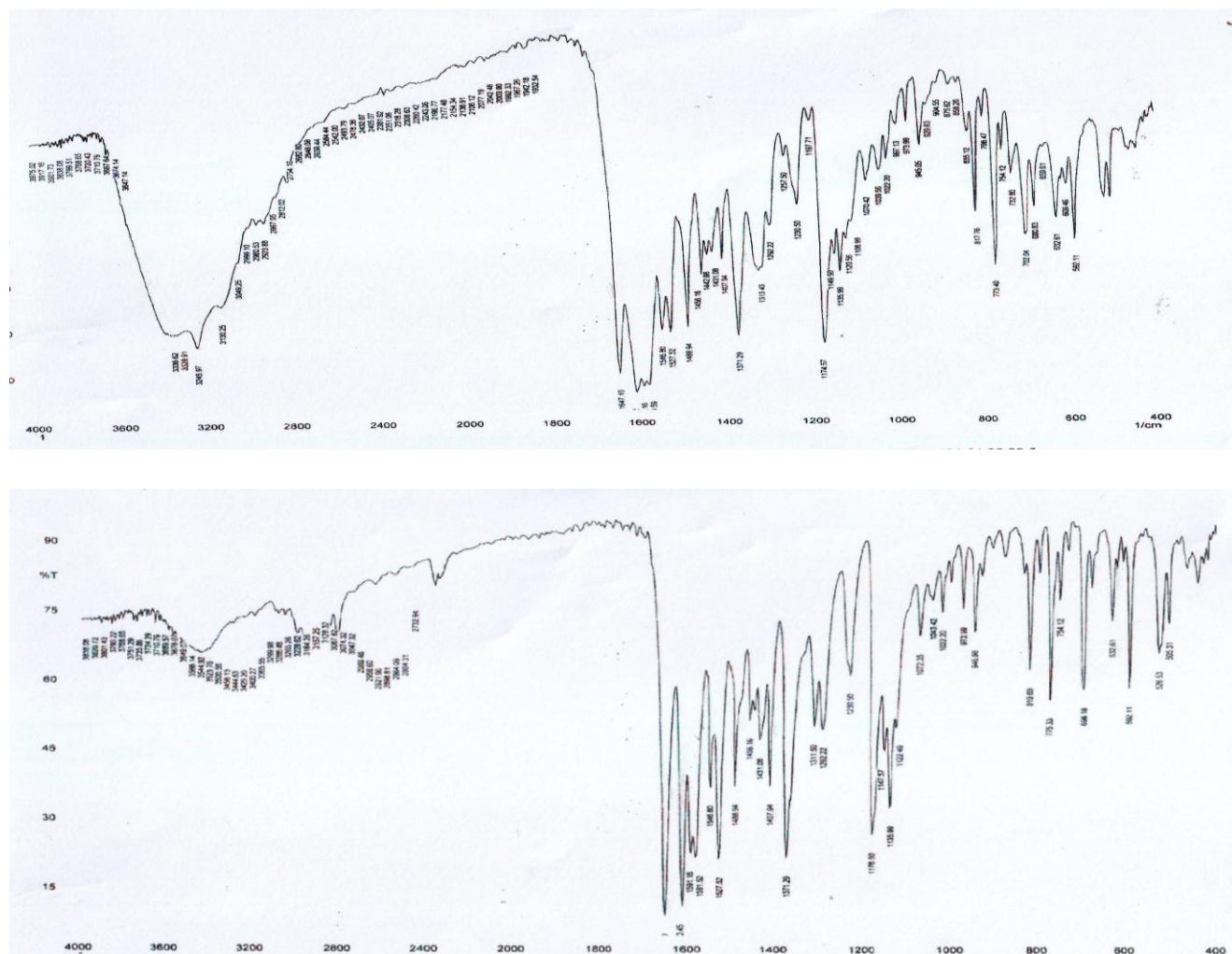


Fig .(1): IR spectra of : (a) the ligand & (b) [NiL] Cl₂

Magnetic measurement and electronic spectra

The data obtained from the measurements of electronic spectra and magnetic susceptibility are given in table 3.

The electronic spectrum of Ni(II) complex exhibit bands at 15820 cm^{-1} , 19610 cm^{-1} assignment to ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively^(21,22) Fig.(2) . The observed zero magnetic moment confirms the square-planar complexes for the Ni(II) complex in conformity with the fact that all known square- planar complexes of nickel (II) are diamagnetic .The magnetic moment value of the copper (II) complex (1.76 B.M) which may suggest an square – planar structure⁽²¹⁾ .The electronic absorptionband to the copper (II) shows a band central at 23752 cm^{-1} which may assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition in square – planar environment⁽²³⁾ . No transitions were observed in the visible region for Zn(II) complex consistent with the d^{10} configuration of the Zn(II) ion and the electronic spectra of this complex do not show any d-d transition band , its diamagnetic moment⁽²⁴⁾ .

According to these results the following structure formula of these chelate complexes may be proposed in Fig 3.

Conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between $(80-100)\text{ S.mol}^{-1}.\text{cm}^2$, in DMSO at room temperature these values indicating that high conductivity of the complexes⁽²¹⁾ . According to these results the structural formulas of these complexes may be proposed in Fig .3.

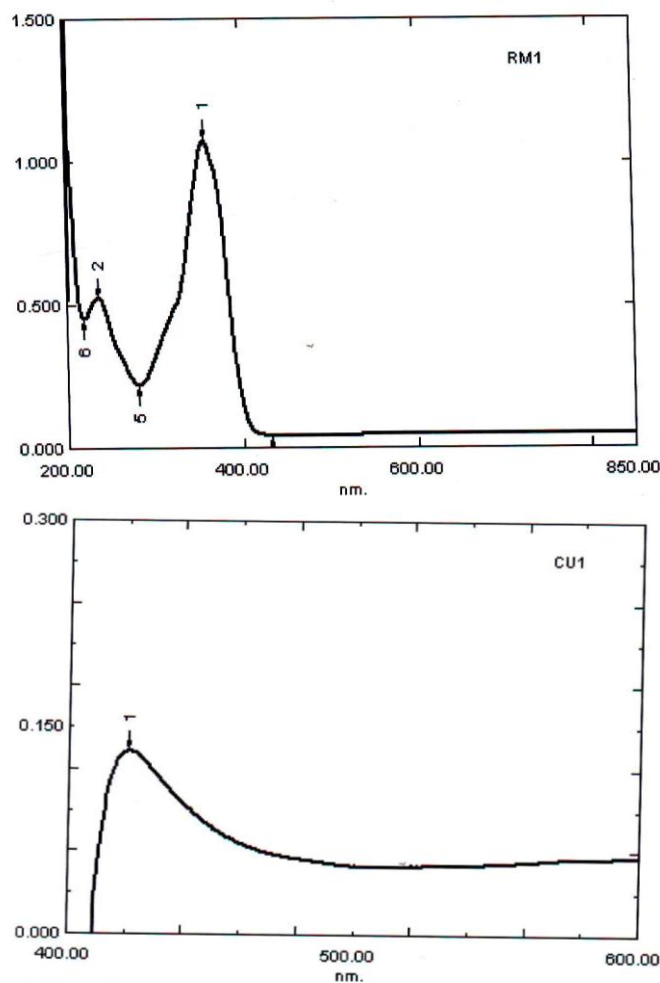


Fig . (2): U.V Spectrem of : (a) ligand & (b) $[\text{CuL}]\text{Cl}_2$

Table. 1: Physical properties and analytical data of the ligand (L) and its complexes.

No.	Compound	Colour	M.P °C	Formula	(Cacl)found%			
					C	H	N	M
1	HL	Dark Yellow	200	[C ₄₀ H ₄₃ N ₉ O]	(72.34) 72.15	(6.29) 6.50	(18.65) 18.93	(----)
2	[NiL] Cl ₂	Green	188	[C ₄₀ H ₄₃ N ₉ ONi] Cl ₂	(60.48) 60.39	(5.35) 5.44	(16.22) 15.84	(7.22) 7.37
3	[CuL] Cl ₂	Black	215	[C ₄₀ H ₄₃ N ₉ OCu]Cl ₂	(60.77) 60.02	(5.23) 5.41	(15.88) 15.75	(7.76) 7.94
4	[ZnL] Cl ₂	Yellow	175	[C ₄₀ H ₄₃ N ₉ OZn]Cl ₂	(59.67) 59.89	(5.46) 5.39	(15.42) 15.71	(8.33) 8.15

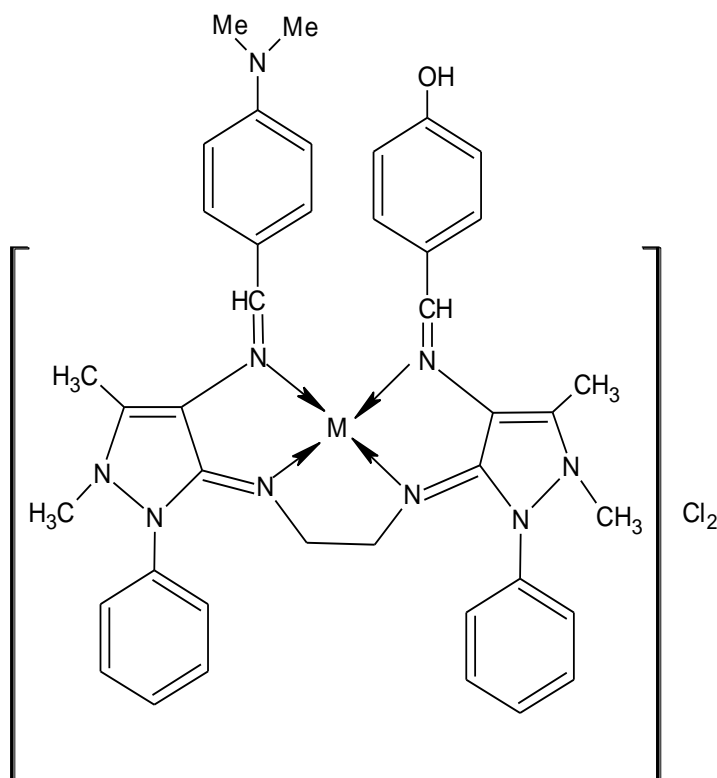
Table. 2: Characteristic IR absorption bands of the ligand and its complexes in cm⁻¹ units.

Compound	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=N})$	$\nu(\text{M-N})$
HL	3130 w	2999 w	1647 sh	----
[NiL] Cl ₂	3125 w	2989 w	1635.s	412 w
[CuL] Cl ₂	3130 w	2998 w	1620 m	425 w
[ZnL] Cl ₂	3120 w	2990 w	1630 s	445 w

HL = Ligand , s = strong , sh =shoulder , m= medium , w= weak

Table. 3: Electronic spectra and magnetic moment data of the complexes

Complex	Absorption bands (cm ⁻¹)	Transition	μ_{eff} (B.M)
[NiL] Cl ₂	15820 19610	¹ A _{1g} → ¹ A _{2g} ¹ A _{1g} → ¹ B _{1g}	Dia
[CuL] Cl ₂	23752	² B _{1g} → ² A _{1g}	1.76
[ZnL] Cl ₂	----	----	Dia



**Fig. 3: The proposed structural formula of prepared chelate complexes
M =Ni (II), Cu(II), and Zn(II)**

Conclusion

This paper reports the preparation and identification of new tetradentate Schiff base and its complexes with Ni(II), Cu(II) and Zn(II) metal ions. The isolated products were characterized by available techniques. All the complexes are stable and ionic in nature and the geometry is proposed for complexes showing square planar stereochemistry.

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