

Synthesis and Characterization of Some Transition Metal Complexes with New Schiff Base Ligand Derivative from Isatin.

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الخلاصة

تم تحضير قاعدة شيف جديدة (E)-3-[(Z)-3-(2-Hydroxy phenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino]indolin-2-one] شخضت هذه الليكاند بواسطة درجة الانصهار ,اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية -المرئية وحضرت معقداتها مع الايونات الفلزية الكوبلت والنيكل والنحاس (ثنائية التكافؤ) وتم التحقق من النسبة المولية بالاعتماد التحليل الدقيق (C.H.N) . وكانت النسبة المولية (M:L) (1:2) لجميع المعقدات . تم تشخيص المعقدات المحضرة باستعمال اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية المرئية والتوصيلية المولارية والحساسية المغناطيسية وقياسات درجة الانصهار . ونسبة وجود العناصر في المعقدات تم تقديرها باستعمال جهاز مطيافية الامتصاص الذري اللهي . واطهرت نتائج التحليل الدقيق للعناصر توافق كبير بين القيم النظرية والعملية . كانت المعقدات مستقرة جدا يمكن تركها لشهور دون اي تغييرات ملحوظة . وبالاعتماد على تحاليل الاجهزة والتحليل الطيفية فقد تم اقتراح الشكل الثماني السطوح لمعقدات ايونات كل من الكوبلت (II) والنيكل (II) وشكل المربع المستوي لمعقد النحاس (II) .

Abstract

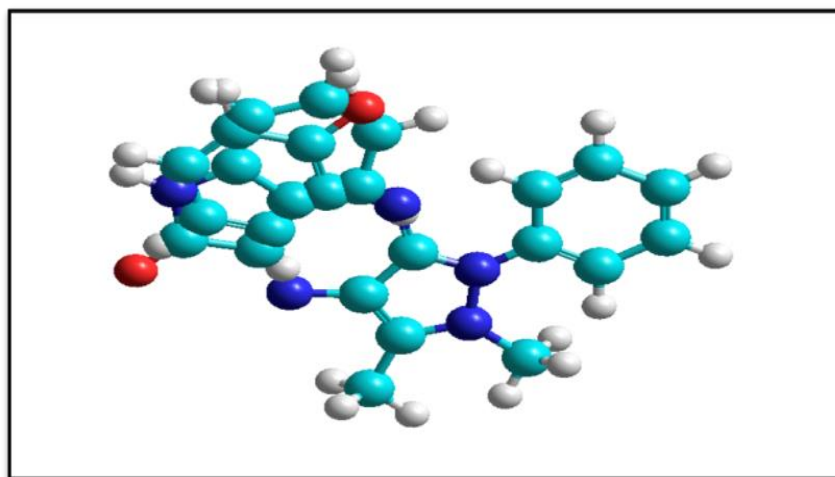
The New Schiff base ligand [(E)-3-[(Z)-3-(2-Hydroxy phenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino]indolin-2-one](2HDMIA) was prepared. The prepared ligand was characterized by melting point, IR and UV-Vis spectra. All preparation of complexes of the ions Co (II), Ni(II)and Cu(II) were deduced according to the molar ratio depending on the Micro elemental Analysis (C.H.N.). However ,the ratio were 1:2 (M: L)for all ions. The prepared complexes were characterized using IR, UV-Vis spectra, molar conductivity magnetic susceptibility and melting points measurements. The percentages of the metals in the complexes were measured by flame atomic absorption technique. Micro elemental Analysis (C.H.N.) were also found, the results are in agreement with the Calculated values. All the complexes are quite stable and could be Stored for months without any appreciable change. According to the results obtained by elemental and spectral analysis, an octahedral structure suggested for the prepared complexes of the ions Co (II)and Ni(II) and square planer of the Cu(II) complex.

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 bioligands 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 was prepared. This Polydentate ligand contains nitrogen and oxygen donor atoms having the following structure:



The structure of the ligand (2-HADMIA)

Experimental

Materials and physical measurements

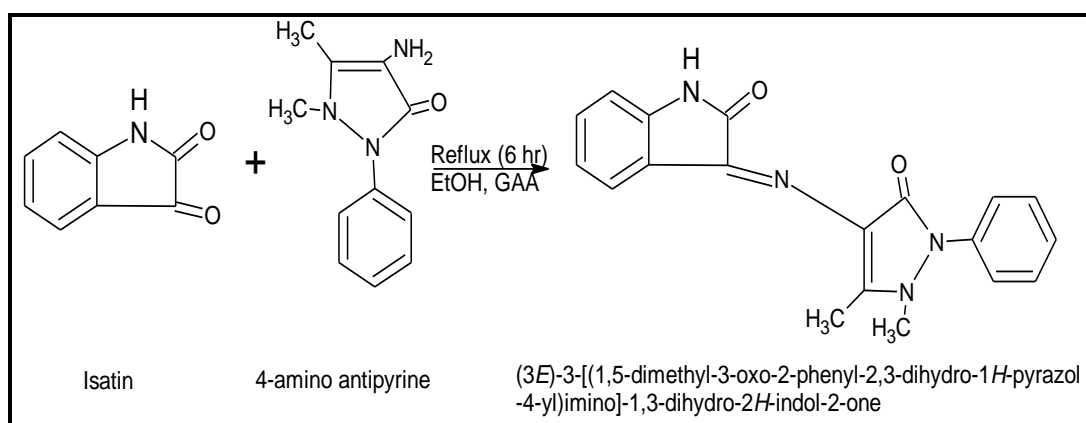
All chemicals used were of highest purity (BDH , Fluka , merck) and used without further purification.

Elemental analysis was carried out by means of micro analytical unit of (EURO EA3000 Single) C.H.N element analyzer/Babylon University .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) cm^{-1} using KBr disc. Auto .Electrical conductivity measured by Digital conductivity meter WTW,720 with solute concentration of 10^{-3}M in DMSO at room

temperature ,the metal percentages were determined using atomic absorption technique by Atomic Absorption spectrophotometer -5000 , perkin - Elmer .

1-Preparation of Schiff base (3E)-3-[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino]-1,3-dihydro-2H-indol-2-one(4-DMIA).

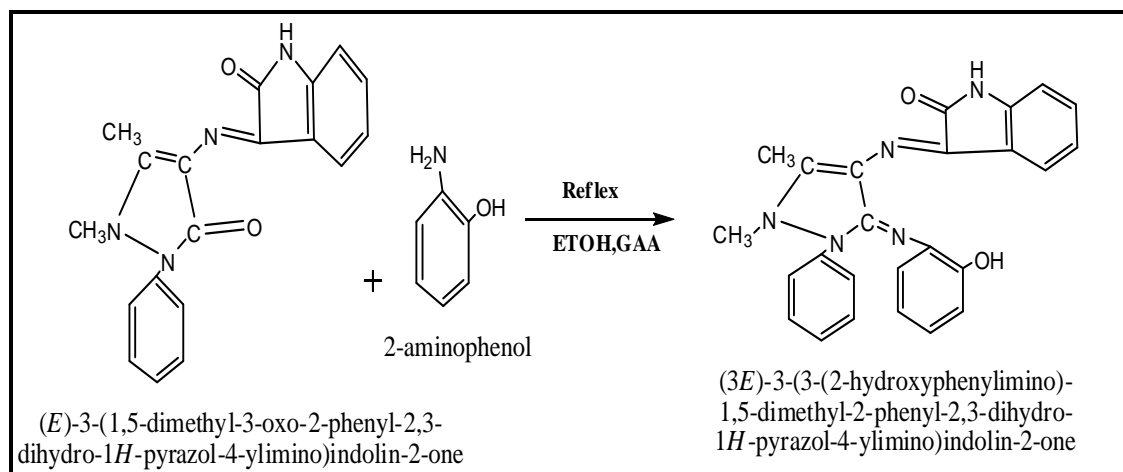
In a round bottom flask, 4-aminoantipyrine (0.01 mol, 2.03 g) in (15 mL) ethanol and Isatin (0.01mol, 1.47 g) in (15 mL) ethanol added few drops of glacial acetic acid to solution the mixture was refluxed for (6 hr.) ^[7], the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous CaCl₂. The preparation of schiff base is showed in **Scheme 1**.



Scheme 1: Preparation of the Ligand (4-DMIA)

2-Preparation of new Schiff base ligand (2-HDMIA)

The Schiff base ligand (2-HDMIA) was prepared by condensation of compound (4-DMIA) (0.01 mol, 3.32 g) which was dissolved in (50 mL) ethanol and refluxed with (0.01 mol, 1.09 g) of 2-amino phenol 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 CaCl₂ **Scheme 2**.



Scheme 2: Preparation of the ligand (2-HDMIA)

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 (2HDMIA) in (25 ml) of hot ethanol. The corresponding hydrated metal chloride salts of ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) of (0.001 mol) was dissolved in hot 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.

Table 1: Physical properties and analytical data of the ligand (2-HDMIA) and its complexes.

No.	Compound	Color	M wt.	M.P C°	Found (Calc.)%			
					C	H	N	M
1	$\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2$	Reddish Brown	423.474	168	70.91 (70.68)	5.00 (5.25)	16.54 (16.62)	—
2	$[\text{Co}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Brown	994.79	250	60.74 (60.37)	4.60 (4.46)	14.28 (14.08)	5.48 (5.92)
3	$[\text{Ni}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Brown	994.55	228	60.76 (60.38)	4.63 (4.46)	14.32 (14.08)	5.51 (5.90)
4	$[\text{Cu}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	Dark Brown	999.40	202	60.37 (60.09)	4.51 (4.44)	14.21 (14.02)	6.55 (6.36)

Results and discussion

The metal complexes are insoluble in water and soluble in DMSO, DMF, CHCl_3 , acetone, methanol and ethanol.

Infrared spectra of ligand and complexes

The IR spectral data of Schiff base ligand **Figure 1** 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 (2-HDMIA) and its complexes in cm^{-1} units.

<i>Compound</i>	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
$\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2$	1718(s)	1616(s) 1663	---	---
$[\text{Co}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$	1699(s)	1611(m) 1650	499(m)	416(w)
$[\text{Ni}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$	1734(s)	1624(s) 1651	590(m)	420(w)
$[\text{Cu}(\text{C}_{25}\text{H}_{21}\text{N}_5\text{O}_2)_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$	1701(s)	1614(s) 1663	586(m)	418(m)

The band in IR spectrum of free ligand at 1718 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 $(420-416) \text{ cm}^{-1}$ 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 Co(II) and Ni(II). **Figure 2 and Figure 3** These shifting indicated the coordination of the ligand with metal ion via nitrogen atoms of two imine groups^[11,12] while the complex of Cu(II) **Figure 4** showed 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 $\nu(\text{M}-\text{N})$ ^[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 the complexes of Co(II) and Ni(II) ions and the ligand behaves as a di dentate ligand coordinated to the Cu(II) ion via oxygen atom of carbonyl group of Isatin and nitrogen atom of one imine group.

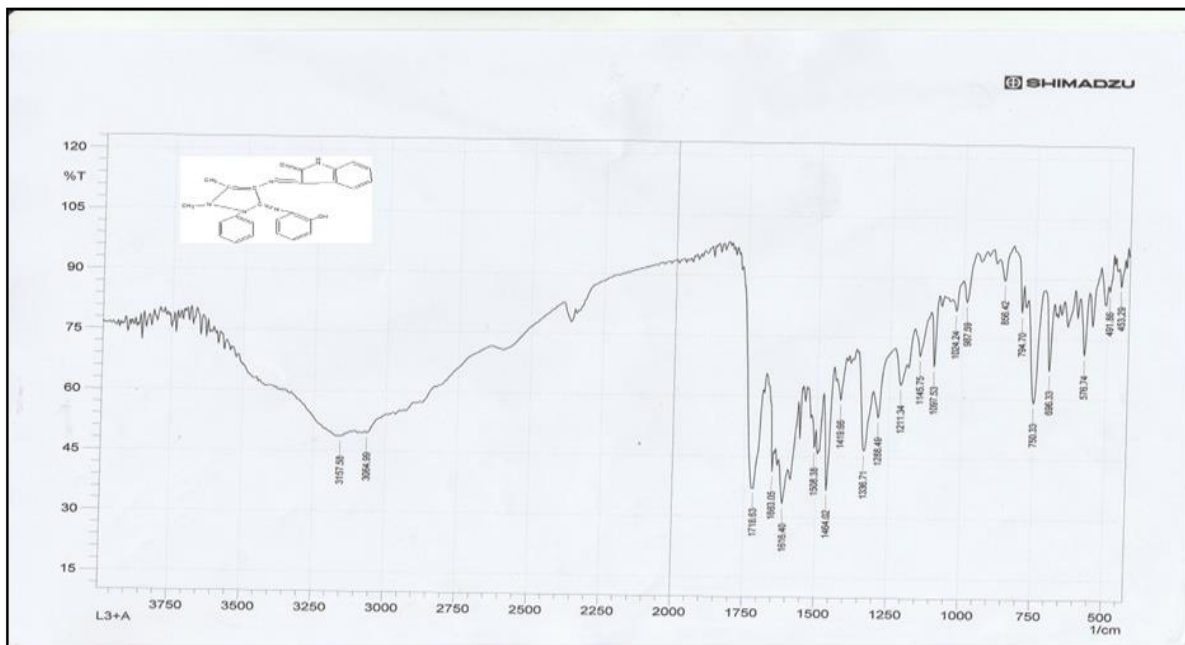


Fig. 1: IR spectrum of the ligand (2-HDMIA)

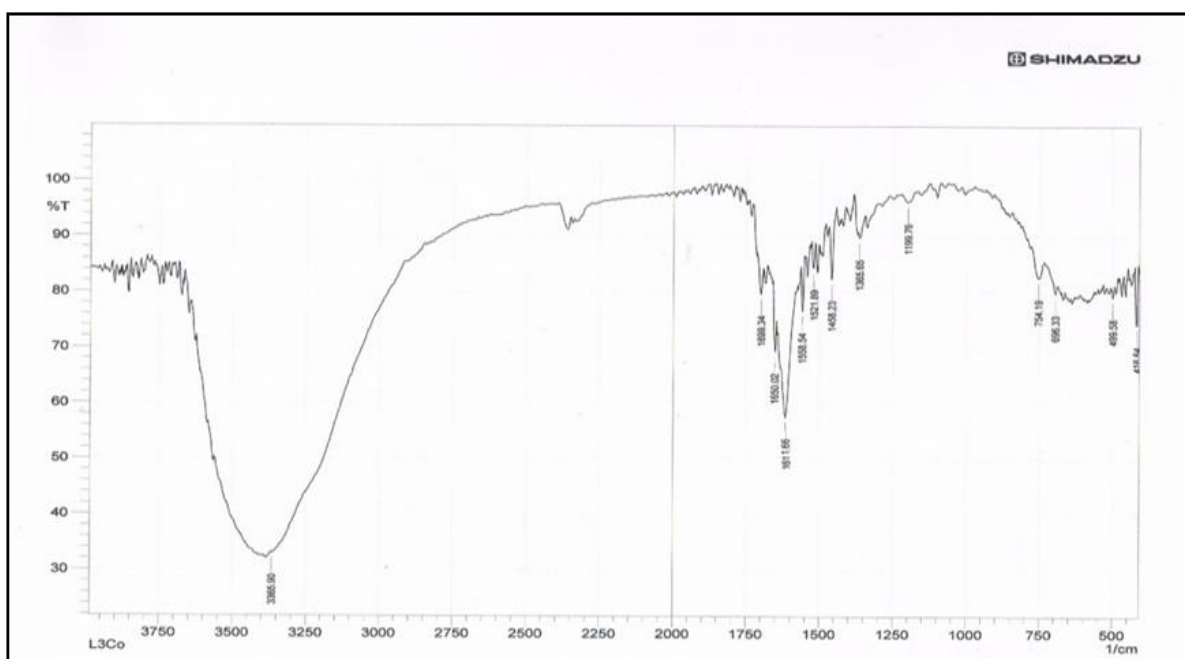


Fig. 2: IR spectrum of ion complex of Co(II) with the ligand (2-HDMIA)

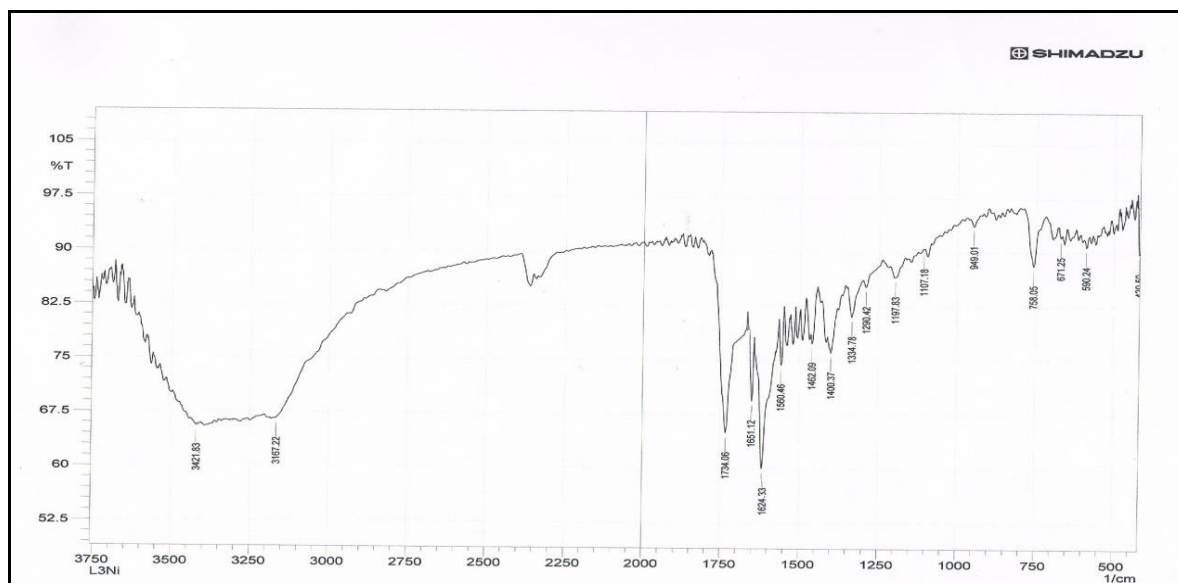


Fig. 3: IR spectrum of ion complex of Ni(II) with the ligand (2-HDMIA)

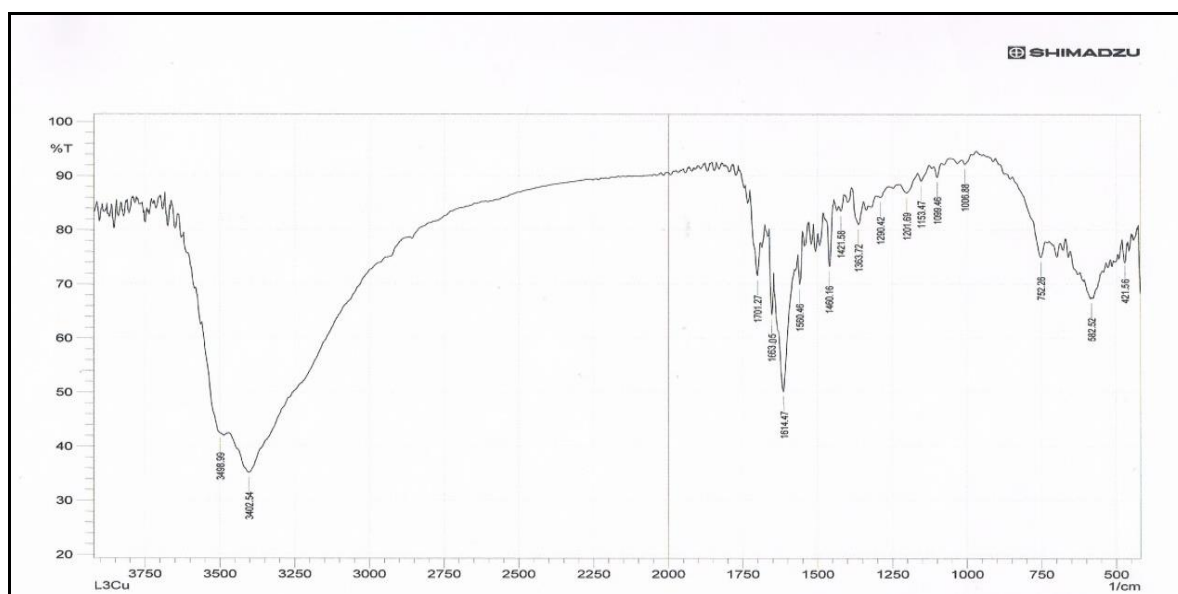


Fig. 4: IR spectrum of ion complex of Cu(II) with the ligand (2-HDMIA)

Electronic spectra

The Electronic spectra of ligand (2-HDMIA) **Figure 5** and its Co(II), Ni(II) and Cu(II) complexes were studied and the spectral data were listed in **Table 3**. The UV-Vis spectrum of the Schiff base ligand (2-HDMIA) was characterized mainly by two absorption peaks at (291) nm assigned to ($\pi \rightarrow \pi^*$) and at (460) 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 Co(II) complex **Figure 6** displayed four new absorption peaks the first peak at (280) nm may be assigned to intra - ligand, the second peak at (440) nm may be

assigned to charge transfer spectrum and the other peaks at (779 and 867)nm was attributed to (d-d) electronic transition type ${}^4T_{1g}(F)$ respectively. Suggesting octahedral $\rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ geometry around Co(II) ion^[15].

The electronic spectrum of Ni (II) complex **Figure 7** showed four new absorption peaks, the first peak at (279)nm may be assigned to intra – ligand. The second peak at(440)nm may be assigned to charge transfer spectrum which shielded (d-d) electronic transition type ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and the other peak at (642)nm was attributed to (d-d) electronic transition type ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ while the last peak at (977) ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$. These peaks were a good agreement of octahedral geometry for Ni(II) complex ^[16].

The electronic spectrum of Cu(II) complex **Figure 8** showed three new absorption peaks the first peak at (416) nm refers to charge transfer spectrum while the second and the third peaks appeared at (663 and 834)nm may be attributed to (d-d) electronic transition type ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{2g}$ respectively ,suggesting square planer geometry around Cu(II) ion ^[13].

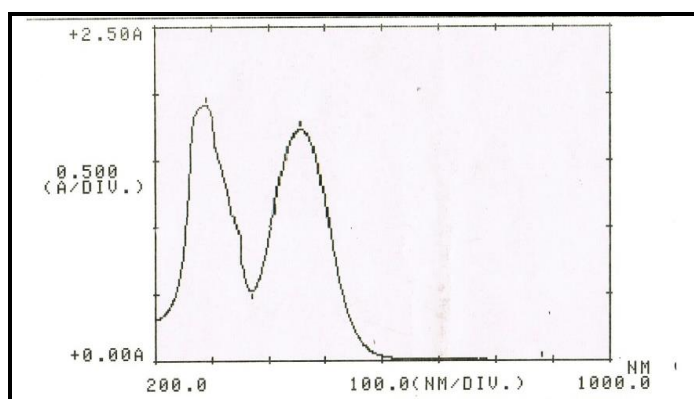


Fig. 5: Absorbance spectrum of ligand(2-HDMIA)

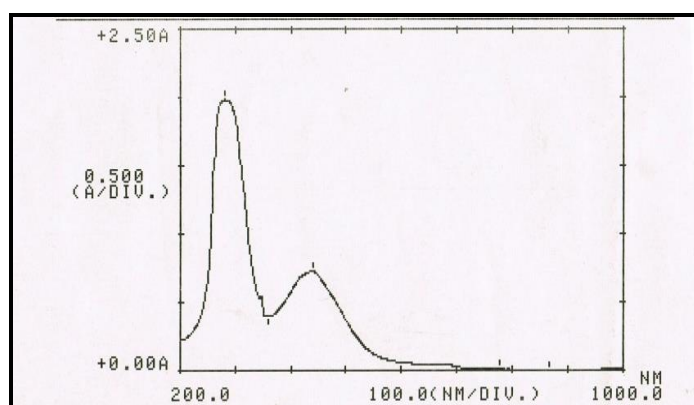


Fig. 6: Absorbance spectrum of ligand (2-HDMIA) with ion complex of Co(II)

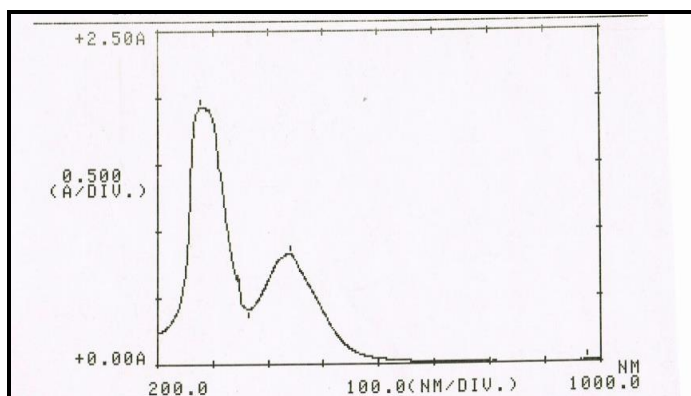


Fig. 7: Absorbance spectrum of ligand (2-HDMIA) with ion complex of Ni(II)

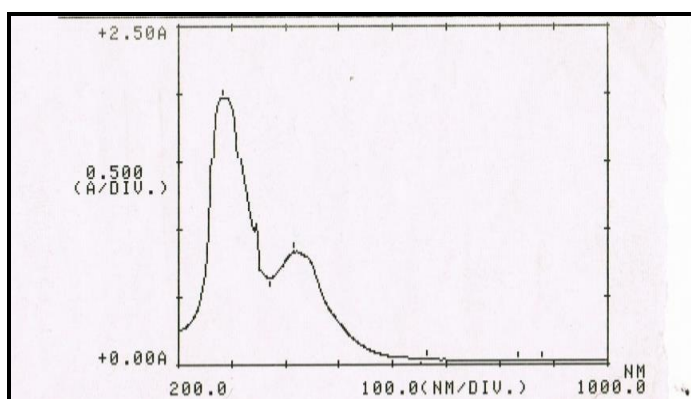


Fig. 8: Absorbance spectrum of ligand (2-HDMIA) with ion complex of Cu(II).

Table 3: The electronic spectra of the ligand (2-HDMIA) and its chelate complexes

Compounds	λ_{Max} nm(cm^{-1})	Transition	ϵ_{Max}
$C_{25}H_{21}N_5O_2$	291 (3436)	$\pi \rightarrow \pi^*$	2317
	460 (21739)	$n \rightarrow \pi^*$	2141
$[Co(C_{25}H_{21}N_5O_2)_2]Cl_2 \cdot H_2O$	280 (35714)	Intra - ligand	2107
	440 (22727)	C.T	729
	779 (12837)	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	10
	867 (11534)	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	7
$[Ni(C_{25}H_{21}N_5O_2)_2]Cl_2 \cdot H_2O$	279 (35842)	Intra - ligand	2115
	440 (22727)	C.T	834
	642 (15576)	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	32
	977 (10235)	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	10
$[Cu(C_{25}H_{21}N_5O_2)_2]Cl_2 \cdot H_2O$	280(35714)	Intra - ligand	2132
	416(24038)	C.T	839
	663(15083)	${}^2B_{1g} \rightarrow {}^2E_g$	43
	834(11990)	${}^2B_{1g} \rightarrow {}^2A_{2g}$	31

Magnetic measurements

- (i) Co (II) complex shows magnetic moment μ_{eff} . (4.92 B.M) corresponding to three unpaired electrons. This value suggests an octahedral environment around the Co (II) ion ^[17].
- (ii) Ni (II) complex shows magnetic moment μ_{eff} . (3.46 B.M) at room temperature corresponding to two unpaired electrons. This value indicates an octahedral geometry around the Ni (II) ion ^[18].
- (iii) The magnetic moment value μ_{eff} . of the copper (II)^[19] complex (1.79 B.M) which may suggest square planer geometry.

The magnetic moment μ_{eff} . were showed in **Table 4**.

Conductivity measurements

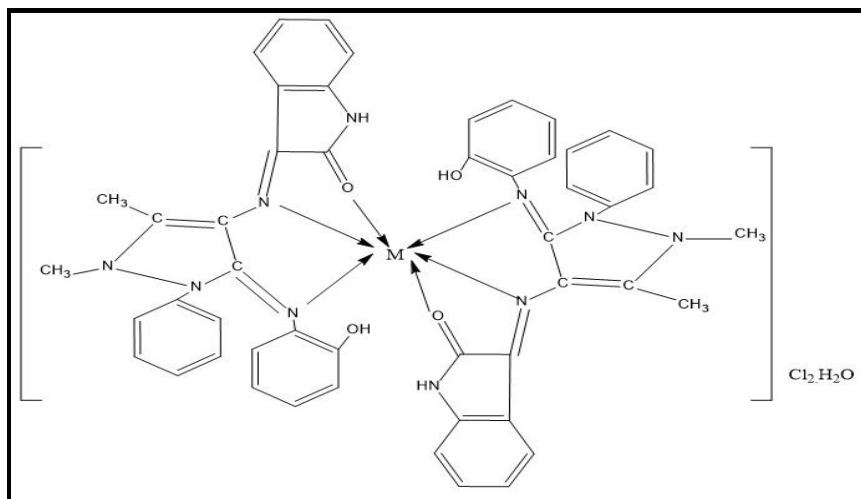
All soluble complexes showed molar conductivity values at range (70.11 – 75.98) S.cm². mol⁻¹ in DMSO solvent in 10⁻³M at room temperature, these values indicate high conductivity .and ionic structure (1:2) of these complexes ^[7].The conductivity values were listed in **Table 4**.

Table 4: Molar Conductivity and Magnetic moment μ_{eff} . of complexes

<i>Complexes</i>	<i>Molar Conductivity S.cm².mol⁻¹</i>	μ_{eff} . B.M
[Co (C ₂₅ H ₂₁ N ₅ O ₂) ₂] Cl ₂ .H ₂ O	75.31	4.92
[Ni (C ₂₅ H ₂₁ N ₅ O ₂) ₂] Cl ₂ .H ₂ O	77.56	3.46
[Cu (C ₂₅ H ₂₁ N ₅ O ₂) ₂] Cl ₂ .H ₂ O	72.24	1.79

Suggested Structure

On the basis of elemental microanalysis, molar Conductivity, magnetic moment and spectroscopic studies for the ligand (2-HDMIA) and Co(II), Ni(II) complexes, we suggest that the ligand behaves as tridentate on Complexation 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 Complexation 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 Co(II) and Ni(II) have octahedral geometry **Figure 9** while the complex of Cu(II) ion was square planer **Figure 10**.



M= Co (II), Ni(II)

Fig. 9: The suggested structural of Co (II), Ni(II) with Schiff base ligand (2-HDMIA)

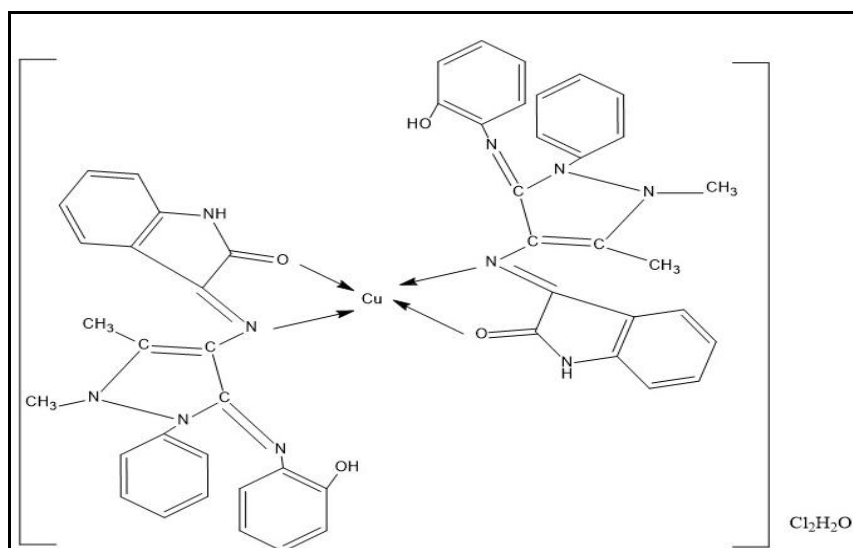


Fig. 10: The suggested structural of Cu (II) with Schiff base ligand (2-HDMIA)

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