

Study of Preparation and Identification of some Metals Complexes of New Tridentate Schiff base Ligand Type (NNO) Derived from Isatine

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Abstract: The New Schiff base ligand [(E)-3-[(Z)-3-(2-amino ethylimino)-1, 5-dimethyl-2-phenyl-2, 3-dihydro-1H-pyrazol-4-ylimino] indolin-2-one] (2DMIAP) was prepared. Three chelate complexes Have also been prepared by reacting this ligand with the metal ions Co(II), Ni(II) and Cu(II). (UV-Vis) electronic spectra of complexes showed bathchromic shift, as compared with that of free ligand. The infrared spectra of the chelating complexes have been studied, this may indicate that coordination between the metal ions and the prepared ligand takes place. The conductivity and magnetic measurements, Elemental micro analysis and the percentage of metal ions were determined. Depending on these results, the suggested geometrical structures of the prepared complexes of Co(II), Ni(II) and Cu(II) ions are octahedral.

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

Introduction

A great deal of work has been reported on the synthesis, spectral determination, physical properties and elemental analysis of different types of Schiff base ligands and their complexes with transition and non - transition elements, the transition metal complexes synthesis containing Schiff base ligands have important area of study in inorganic chemistry and industrial chemistry [1] for many years a great interest of Schiff base ligands derived from Isatin as chelating ligands and their metal complexes in coordination chemistry because of the widely studied of these ligands and their metal complexes in biological, clinical and spectral analytical applications [2] and many other industrial applications, such as the manufacturing of medicines [3,4]. 4-Aminoantipyrine (4-AAP) is also an important derivative of the 5 - pyrazolone class and is used for the detection and determination of number of compounds. However, literature on the use of 4-aminoantipyrine is very scanty as an electrophilic coupling reagent in analytical chemistry [5]. Some research groups found that the schiff base metal complexes derived from 4-Aminoantipyrine (4-AAP) can specially cleave the DNA [6-8] also have wide variety

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applications in different areas [9]. the aim of the present study was to Preparation and Identification of Co(II), Ni(II) and Cu(II) Complexes with the Newly synthesized Schiff base Ligand derived from 4-Aminoantipyrine, Isatin and 2-aminoethylamine.

Experimental

Materials and Physical Measurements

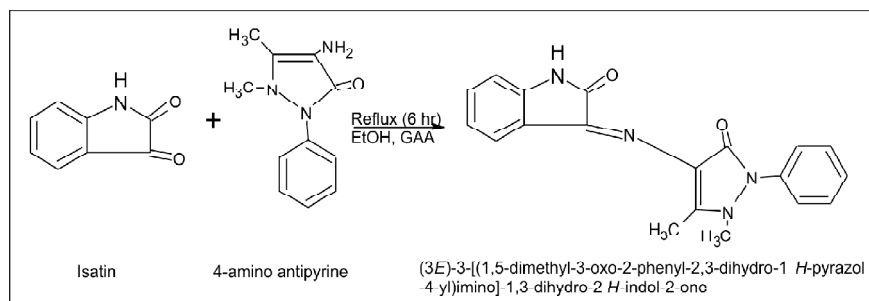
All chemicals used were of highest purity (BDH, Fluke or Merck) and used with out further purification. Elemental analysis was carried out by means of micro analytical unit of (EURO EA3000 Single) C.H.N element analyzer .Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol 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.

Preparation of New Schiff base ligand (2-DMIAP)

The preparation of the ligand (E)-3-[(Z)-3-(2-amino ethylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino]indolin-2-one include two steps the first one is preparation of the 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.which was resulted from condensation of 4-Aminoantipyrine and Isatin. The second step was preparation of the new schiff base ligand by acid catalyzed condensation of the product of step one with 2-aminoethylamine in absolute ethanol.

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).

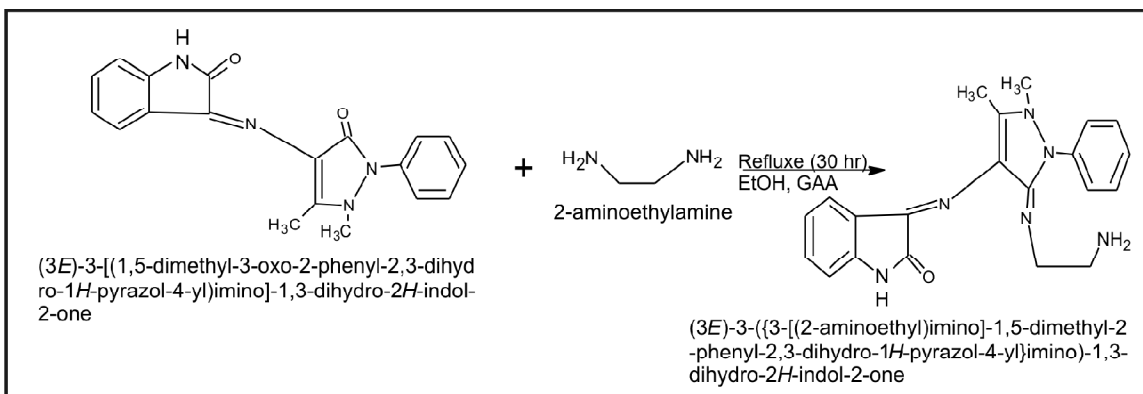
In a round bottom flask, 4-aminoantipyrine (0.01 mol, 2.03 g) in (15 mL) ethanol and isatin (0.01mol, 1.47 g) in (15 mL) ethanol added few drops of glacial acetic acid to solution the mixture was refluxed for (6 hr), the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous CaCl_2 . The preparation of schiff base is showed in Scheme 1. [10].



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

2-Preparation of new schiff base ligand (2-DMIAP)

The Schiff base ligand (2-DMIAP) 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, 0.601 g) of 2-aminoethylamine for (30 hr)[10]. 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 reduction to half by evaporation and recrystallized by hot ethanol and dried over anhydrous CaCl₂ (Scheme 2).



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

Preparation of metal complexes

The (1:2) chelate complexes of the metal and the ligand are prepared by dissolving (0.002 mol, 0.374 g) Schiff base (2-DMIAP) in (25 ml) of hot ethanol. The corresponding hydrated metal chloride salts of (CoCl₂·6H₂O, NiCl₂·6H₂O and CuCl₂·2H₂O) 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-DMIAP) and its Complexes

No.	Compound	Color	M.P C°	Found (Calc.)%			
				C	H	N	M
1	C ₂₁ H ₂₂ N ₆ O	Brown	160	67.12 (67.36)	5.32 (5.92)	22.68 (22.44)	—
2	[Co(C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂ ·H ₂ O	Reddish Brown	122	56.36 (56.25)	5.57 (5.17)	18.09 (18.74)	6.80 (6.57)
3	[Ni(C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂ ·H ₂ O	Reddish Brown	133	56.51 (56.27)	5.28 (5.17)	18.41 (18.75)	6.34 (6.55)
4	[Cu (C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂ ·H ₂ O	Olive	119	55.20 (55.97)	5.31 (5.14)	18.28 (18.65)	7.45 (7.07)

Results and Discussion

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

Infrared spectra of ligand and complexes

The IR spectral data of Schiff base ligand (Fig. 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. The spectrum of free ligand shows two weak bands 3066 cm^{-1} and 2985 cm^{-1} which due to ν (C-H) aromatic and aliphatic respectively, these bands are in stable in positions in both ligand and their complexes. The spectrum of the free ligand show band at 3419 cm^{-1} , which can be attributed to NH stretching vibration of Isatin [11].

Table 2
Characteristic IR absorption bands of the ligand (2-DMIAP) and its complexes in cm^{-1} units

No.	Compound	$\nu(\text{NH}_2)$	$\nu(\text{CP}\% \text{N})$ Amidic	$\nu(\text{CP}\% \text{O})$	$\nu(\text{M}\% \text{N})$	$\nu(\text{M}\% \text{O})$
1	$\text{C}_{21}\text{H}_{22}\text{N}_6\text{O}$	3389(asy.) 3359(sy.)	1612 1653	1722	.	---
2	$[\text{Co}(\text{C}_{21}\text{H}_{22}\text{N}_6\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3414(asy.) 3379(sy.)	1622 1658	1714	580	430
3	$[\text{Ni}(\text{C}_{21}\text{H}_{22}\text{N}_6\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3416(asy.) 3377(sy.)	1620 1664	1712	557	464
4	$[\text{Cu}(\text{C}_{21}\text{H}_{22}\text{N}_6\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3410(asy.) 3379(sy.)	1622 1668	1711	549	428

The Band in IR spectrum of free ligand at 1722 cm^{-1} , assignable to stretching vibration ν (C=O) group of Isatin which was shifted to lower frequency in the IR spectra of all complex, suggesting the involvement of the carbonyl oxygen atom in coordination[12,13]. The appearance of a new non-ligand band around $(464-428)\text{ cm}^{-1}$ in IR spectra of all complexes due to δ (M-O) substantiates [14]. The two bands at $(1612\text{ and }1653)\text{ cm}^{-1}$ in IR spectrum of free ligand can be attributed to the stretching vibration of two imine groups ν (C=N), which were shifted to higher frequency in the IR spectra of all complexes (Fig. 2 for Co(II) complex) These shifting indicated the coordination of the ligand with metal ion via nitrogen atoms of two imine groups [15,16]. This is further substantiated by the presence of a new band around $(580-549)\text{ cm}^{-1}$ assignable to $\nu(\text{M-N})$ [14]. 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.

Electronic Spectra

The Electronic spectra of ligand (2-DMIAP) (Fig. 3) 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

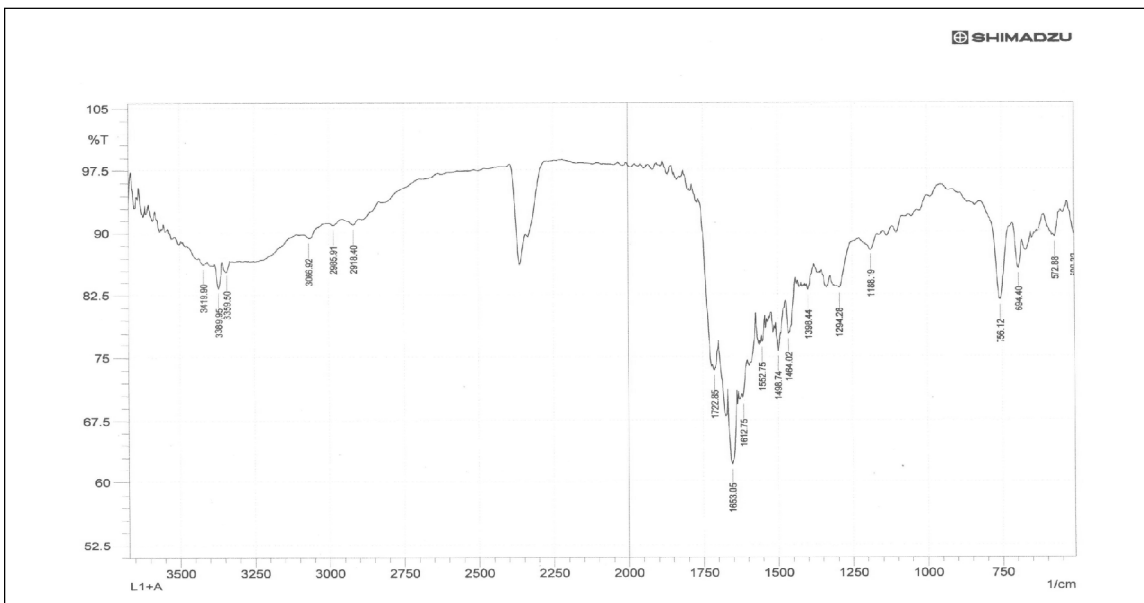


Figure 1: IR spectrum of the ligand (2-DMIAP)

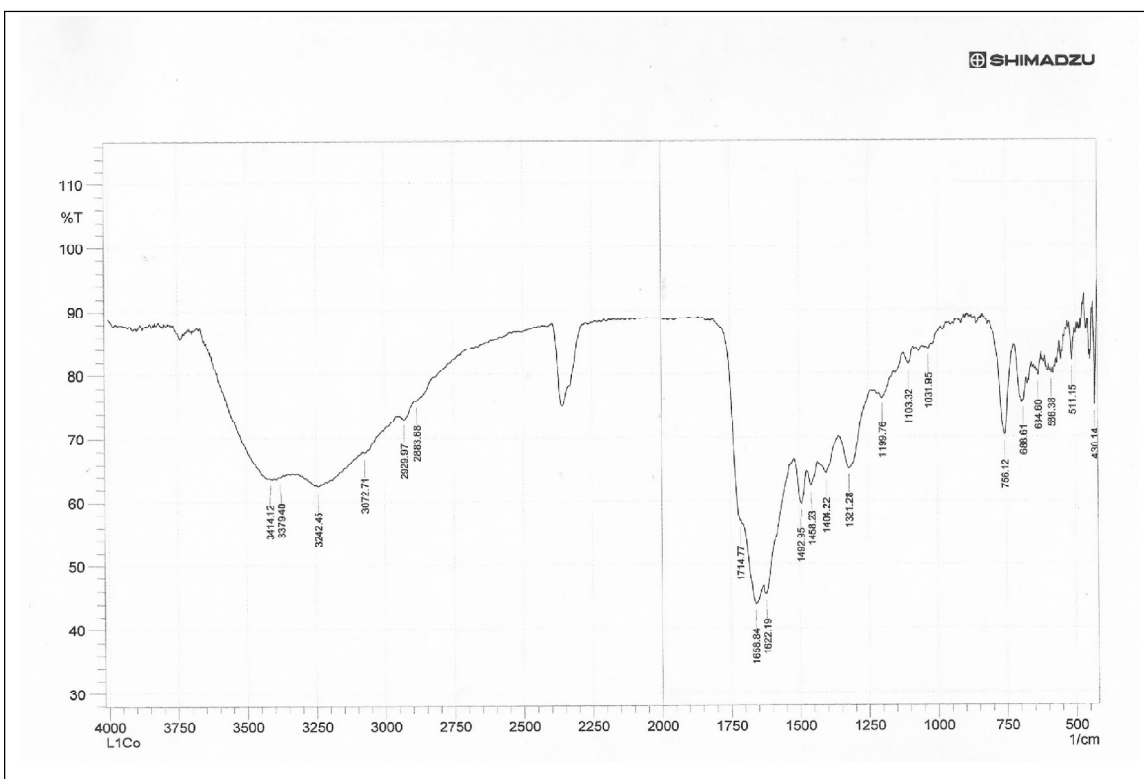


Figure 2: IR spectrum of ion complex of Co(II) with the ligand (2-DMIAP)

of the Schiff base ligand was characterized mainly by five absorption peaks at (279 and 346) nm assigned to ($\pi \rightarrow \pi^*$) and at (362,416 and 446)nm assigned to ($n \rightarrow \pi^*$) 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 (Fig. 4) displayed three new absorption peaks (464, 623and 869)nm which may be attributed to (d-d) electronic transition type ${}^4T_1g(F) \rightarrow {}^4T_1g(P)$, ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$ and ${}^4T_1g(F) \rightarrow {}^4T_2g(F)$ respectively, suggesting octahedral geometry around Co(II) ion [17]. The electronic spectrum of Ni (II) complex (Fig.5) showed two new absorption peaks , the first peak at (454)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 (707)nm was attributed to (d-d) electronic transition type ${}^3A_2g(F) \rightarrow {}^3T_1g(F)$. These two peaks were a good agreement of octahedral geometry for Ni(II) complex [18].The electronic spectrum of Cu(II) complex (Fig 6) showed three new absorption peaks the first peak at (442) nm refers to charge transfer spectrum while the second and the third peaks appeared at (543 and 842)nm may be attributed to (d-d) electronic transition type ${}^2B_1g^2 \rightarrow E_g$ and ${}^2B_1g \rightarrow {}^2A_2g$ respectively, suggesting distorted octahedral geometry around Cu(II) ion [19].

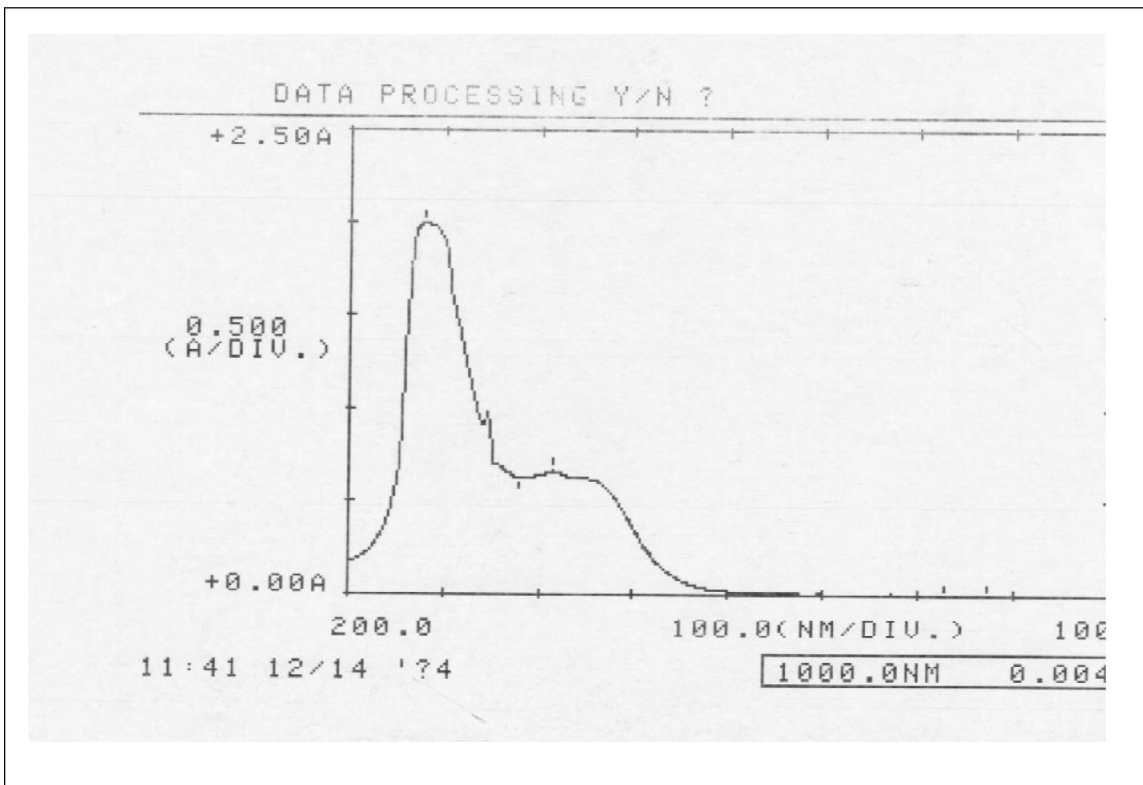


Figure 3: Absorbance spectrum of ligand (2-DMIAP)

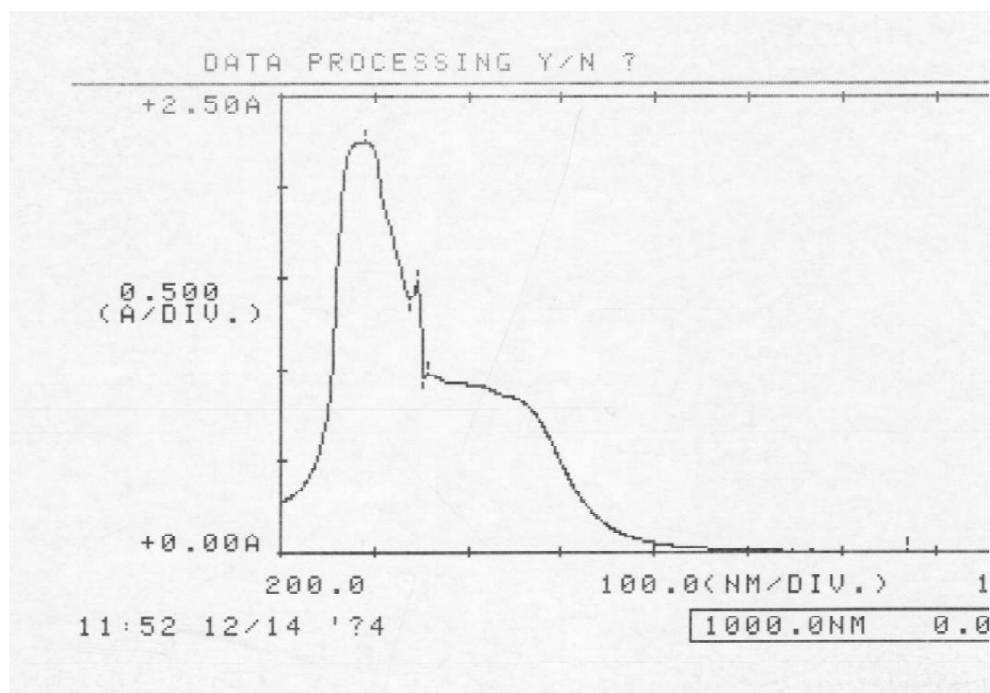


Figure 4: Absorbance spectrum of ligand (2-DMIAP) with ion complex of Co(II)

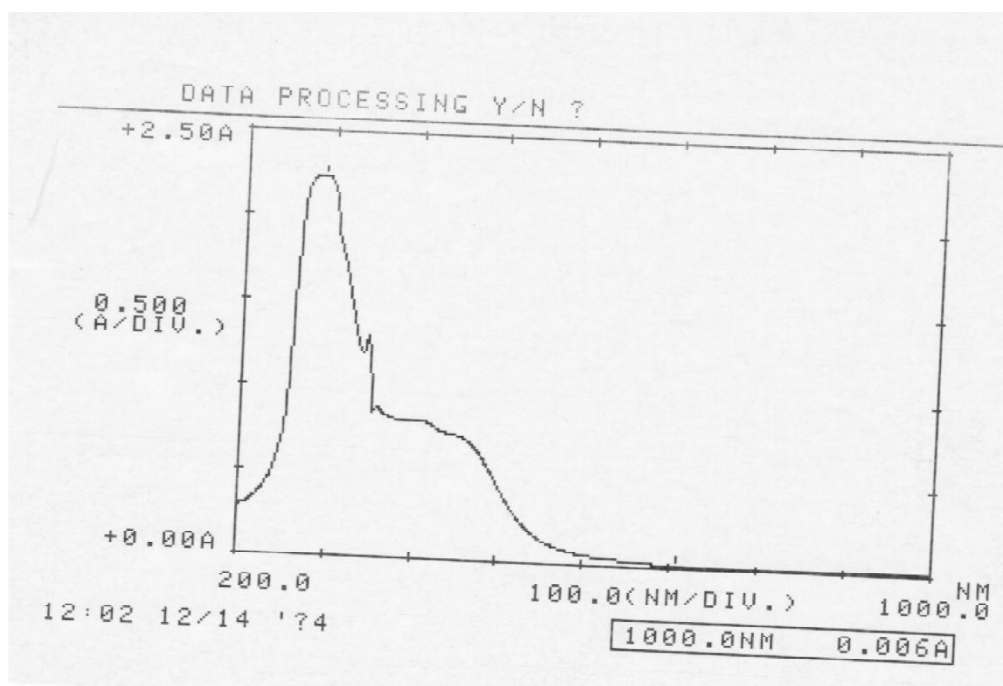


Figure 5: Absorbance spectrum of ligand (2-DMIAP) with ion complex of Ni(II)

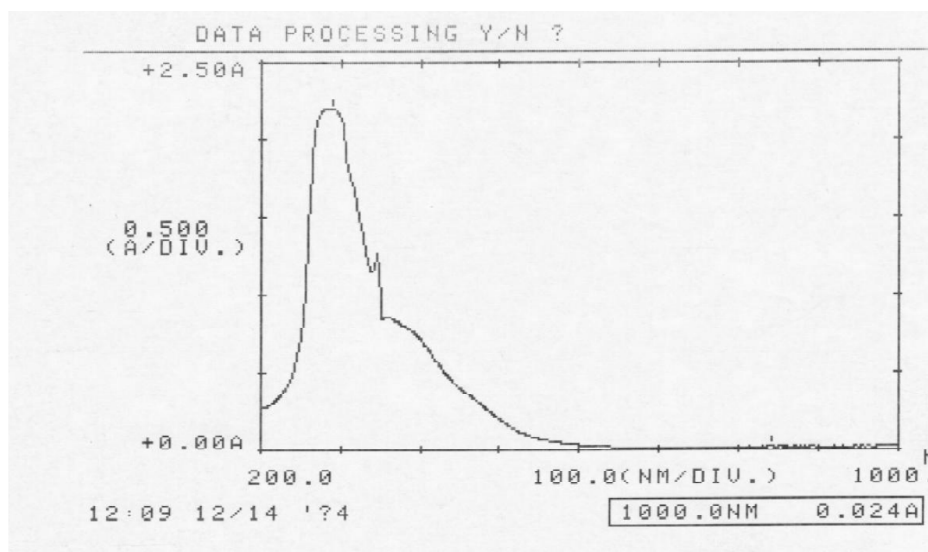


Figure 6: Absorbance spectrum of ligand (2-DMIAP) with ion complex of Cu (II)

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

Compounds	λ_{Max} nm(cm^{-1})	Transition	ϵ_{Max}
$C_{21}H_{22}N_6O$	279(35842)	$\pi \rightarrow \pi^*$	2004
	346(28902)	$\pi \rightarrow \pi^*$	980
	362(27624)	$\pi \rightarrow \pi^*$	704
	416(24038)	$\pi \rightarrow \pi^*$	665
	446(22422)	$n \rightarrow \pi^*$	615
$[Co(C_{21}H_{22}N_6O)_2]Cl_2 \cdot H_2O$	289(34602)	Intra - ligand	2252
	345(28986)	Intra - ligand	1488
	357(28011)	Intra - ligand	979
	409(24450)	Intra - ligand	923
	464(21552)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	327
	623(16051)	${}^4T_{1g}(F) \rightarrow {}^4A_{1g}$	49
869(11507)	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	7	
$[Ni(C_{21}H_{22}N_6O)_2]Cl_2 \cdot H_2O$	290(34483)	Intra - ligand	2234
	246 (28902)	Intra - ligand	1276
	362(27624)	Intra - ligand	882
	400(25000)	Intra - ligand	807
	454(22026)	$C.T, {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	730
	707(14144)	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	19
$[Cu(C_{21}H_{22}N_6O)_2]Cl_2 \cdot H_2O$	289(34602)	Intra - ligand	
	346(28902)	Intra - ligand	1250
	363 (27548)	Intra - ligand	854
	442(22624)	C.T	423
	543(18416)	${}^2B_{1g} \rightarrow {}^2E_g$	76
	842(11876)	${}^2B_{1g} \rightarrow {}^2A_{2g}$	22

Magnetic Measurements

- (i) Co (II) complex shows magnetic moment μ_{eff} . (4.01 B.M) corresponding to three unpaired electrons. This value suggests an octahedral environment around the Co (II) ion [20].
- (ii) Ni (II) complex shows magnetic moment μ_{eff} . (3.18 B.M) at room temperature corresponding to two unpaired electrons. This value indicates an octahedral geometry around the Ni (II) ion [21].
- (iii) The magnetic moment value μ_{eff} . of the copper (II)[22] complex (1.73 B.M) which may suggest an octahedral geometry.

The magnetic moment μ_{eff} . were showed in table (4)

Conductivity Measurements

All soluble complexes showed molar conductivity values at range (70.11 – 73.98) 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 [10]. The conductivity values were listed in table 4.

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

Complexes	Molar Conductivity S.cm ² .mol ⁻¹	μ_{eff} . B.M
[Co(C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂	70.11	4.01
[Ni(C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂	75.98	3.18
[Cu (C ₂₁ H ₂₂ N ₆ O) ₂]Cl ₂	73.14	1.73

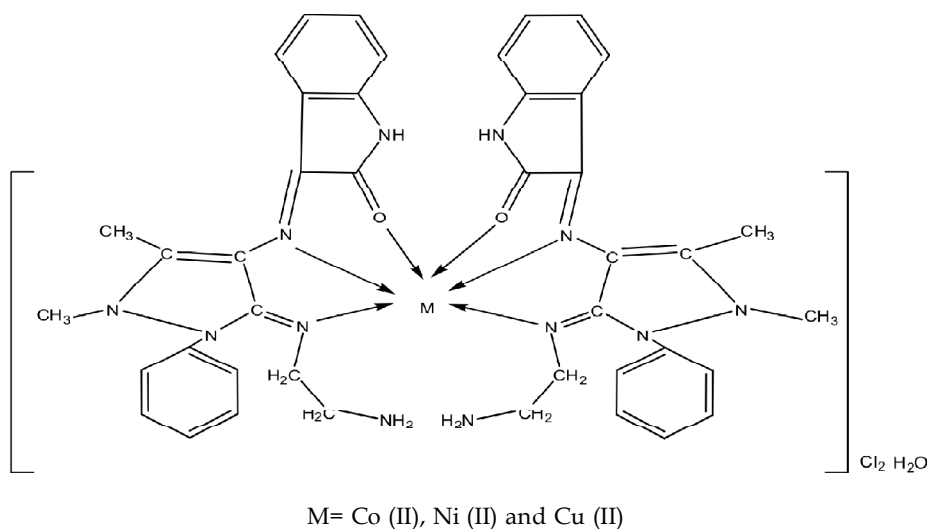


Figure 7: The suggested structural of Co (II), Ni (II) and Cu (II) with Schiff base ligand (2-DMIAP).

Suggested Structure

On the basis of elemental microanalysis, molar Conductivity, magnetic moment and spectroscopic studies for the ligand (L1) and Co(II), Ni(II) and Cu(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. All we found that the ratio M: L was 1:2. According to these results, all complexes have octahedral geometry around metal ion.

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