

Preparation and characterization of some transition metal mixed ligand complexes (Part 1)

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Abstract

New mixed ligand complexes have been prepared by reaction of chloride salts of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 2-((E)-4-((E)-phenyl-diazenyl) phenylimino) methyl) phenol [(PDIMP) = (HL₁)] and (Z)-2-((p-Tolylimino)methyl) phenol [(TIMP) = (HL₂)]. The resulting complexes were characterized by available techniques such as elemental analysis, determination of metal content M% , molar conductances, magnetic moment measurements, UV-Vis and IR spectral studies. The Schiff bases acts as a monobasic bidentate ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. From the analytical and spectral data the stoichiometry of these complexes have been found to be [M(L₁)(L₂)(H₂O)₂] {where M = Mn(II), Co(II), or Ni(II), }, and [M'(L₁)(L₂)]. where M' = {Cu(II), or Zn(II)}. The presence of the two coordinated water molecules in these complexes was indicated by IR spectra and (C.H.N) analysis of the complexes. The electronic absorption spectra and magnetic susceptibility measurements suggest the square planar geometry for the copper(II) ion, and tetrahedral geometry for the zinc(II) ion, but the other metal complexes show octahedral geometry.

Keywords: Preparation, Characterization , Schiff bases, Mixed ligand complexes.

1. Introduction

The condensation product of an amine and a ketone or aldehyde with general formula of R₂C=NR are well known Schiff base compound⁽¹⁾. A large variety of these compounds have been prepared and their complexation behaviors have been studied, due to the great flexibility and diverse structural aspects⁽²⁻⁴⁾. Many Schiff bases are known to be medicinally important and are used to design medicinal compounds^(5,6), as well as a wide range of Schiff bases are used as ligands in the coordinate chemistry field⁽⁷⁻¹⁰⁾. A lot of Schiff-base ligands derived from the condensation of Salicylaldehyde and its derivatives with various primary amines have been prepared and

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investigate⁽¹¹⁻¹⁵⁾. These Schiff bases may act as a bidentate mono-negative (N,O) donor Ligands⁽¹⁶⁻¹⁸⁾.

In the present work, we have prepared two Schiff base compounds, (PDIMP) and (TIMP). The structures of these compounds were studied by elemental analysis, IR, and UV-Vis spectra. Then, their Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes were prepared and the spectral, magnetic and molar conductances properties of these complexes were studied.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were obtained from commercial sources and used as received without further purification, except of 4-aminoazobenzene was prepared as reported procedure⁽¹⁹⁾. The melting points were determined by the open capillary method and are reported in °C, by using a Stuart melting point SMP10. The elemental analysis of the Schiff bases and their mixed ligands complexes were carried out on a C.H.N.O.S. EA 3000 elemental analyzer by the Central Laboratory University of Kufa. The metal contents of complexes were determined by atomic absorption technique by Shimadzu AA-6300 spectrophotometer. IR spectra were recorded on a Shimadzu FTIR 8400 spectrophotometer using KBr pellets between (4000-400 cm⁻¹). The electronic spectra were recorded in (10⁻³ M) ethanol solution on a Shimadzu UV-Vis 1700 spectrophotometer. Magnetic susceptibility measurements of the complexes were done on (MSB-MKI) balance at room temperature, the diamagnetic corrections were made by Pascal's constants. The conductance was measured in ethanol (10⁻³ M) by using Alpha Digital conductivity meter model 800 at room temperature.

2.2. Preparation of the Schiff bases ligands

A- Preparation of the azo Schiff base ligand (HL₁)

Hot solution (~ 50 °C) of salicylaldehyde (2.442 g, 20 mmol) was mixed with hot solution (~ 50 °C) of *p*-aminoazobenzene (3.944g, 20 mmol) in (200 mL) ethanol and two drops of glacial acetic acid. The resulting mixture was left under reflux for 1 hour and the formed red solid product was separated by filtration, purified by recrystallized from hot ethanol, and dried over anhydrous CaCl₂.

B- Preparation of the Schiff base ligand (HL₂)

Warm solution (~ 40 °C) of salicylaldehyde (4.884 g, 40 mmol) was mixed with warm solution (~ 40 °C) of (4.286 g, 40 mmol) of *p*-toluidine, in (100 mL) ethanol. The resulting mixture was left under reflux for 1 hour and the formed shine yellow crystals product was separated by filtration, purified by recrystallized from hot ethanol, and dried over anhydrous CaCl₂. The structure of both Schiff bases ligands (HL₁) and (HL₂) are shown in figure (1).

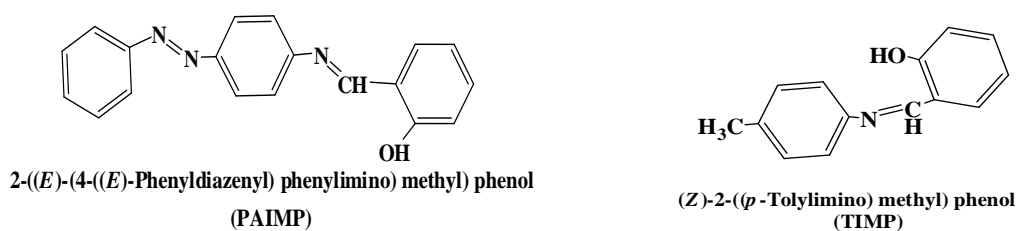


Fig.1: The structural formula of the (PDIMP) and (TIMP) ligands

2.3. Preparation of mixed ligand complexes

The mixed ligand complexes were prepared by adding the appropriate amount of the metal salt (1mmol), namely MnCl₂. 4H₂O, CoCl₂. 6H₂O, NiCl₂. 6H₂O, CuCl₂. 2H₂O, and ZnCl₂ dissolved in (4 mL) of distilled water slowly with constant stirring to a solution of (0.3013g, 1 mmol.) from 2-((E)-4-((E)-phenyl-diazenyl) phenylimino) methyl) phenol (HL₁) and (0.2113g, 1 mmol.) from (Z)-2-((p-Tolylimino)methyl) phenol (HL₂) in (50 mL) ethanol. The pH of the mixture solution was raised by addition of ethanolic potassium hydroxide until (pH=7). The resulting mixture was refluxed for 1 hour. The metal complexes thus formed were filtered out, washed with (1 : 3) aqueous alcohol mixture followed by recrystallized from hot ethanol, and dried over anhydrous CaCl₂.

3. Results and discussion

3.1. Characterization of the Schiff bases ligands and their metal complexes

The Schiff bases ligands (PDIMP) and (TIMP) were red and shine yellow crystals respectively, but the complexes of these ligands vary in color depended of metal ions. The Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes with their analytical data and some physical characteristics are listed in Table 1. The melting points of the compounds fall within the range of 118-191 °C with the exception of [Mn(L₁)(L₂)(H₂O)₂] which doesn't melted over at 300 °C. Elemental analyses gave

satisfactory agreement between observed and calculated values for carbon, hydrogen, nitrogen and metal ions compositions in the complexes. The results show that the compounds formed in ratio (1:1:1) of M(II) ion to (PDIMP) to (TIMP), corresponding to the molecular formulae proposed for the all mixed ligand complexes. The chelate complexes vary in color depended of metal ions, and are generally insoluble in water, but soluble in most organic solvents such as methanol, ethanol, acetone, chloroform, DMSO and DMF.

3.2. IR spectra

The important infrared frequencies exhibited by the (PDIMP) and (TIMP) Schiff base ligands and their mixed ligand complexes are given in Table 2. The formation of these two Schiff bases, was noted from the absence of (C=O) and (NH₂) peaks in the ligands⁽²⁰⁾. In order to determine the involvement of coordination sites in chelation, infrared spectra of the complexes were compared with those of the free ligands. The IR spectra of the free ligands (HL₁) and (HL₂) show a broad weak intensity band centered at around 3424 and 3402 cm⁻¹ respectively, due to the intra molecular hydrogen bond O–H ...N=C⁽²¹⁾. This band disappeared in the spectra of the complexes indicating probably the coordination through phenolic oxygen moiety^(22,23). A very weak intensity bands had been observed at 3020-3082 and 2980-2914 cm⁻¹ in the spectra of both Schiff bases and metal complexes are due to ν (C–H) aromatic and aliphatic respectively. Another strong bands appeared at 1620 and 1618 cm⁻¹ in the spectra of (HL₁) and (HL₂) ligands respectively, due to ν (C=N) group⁽²⁴⁾ which has been shifted towards lower region at around 1616-1595 cm⁻¹ in the spectra of complexes, this may suggest the linkage of metal ion with nitrogen atom of the azomethine group⁽²⁵⁾. IR spectrum of free azo-azomethine ligand (PDIMP) shows a medium absorption band at 1480 cm⁻¹ due to ν (–N=N–) group⁽²⁶⁾, there is no appreciable change in the complexes spectra which indicates that the nitrogen atoms of this group does not participate in coordination⁽²⁷⁾. A broad medium intensity band at 3444, 3335 and 3430 cm⁻¹ suggests the presence of coordinated water in Mn(II), Co(II) and Ni(II) complexes⁽²⁸⁾. The new bands at 543-501 cm⁻¹ and 461-426 cm⁻¹ have been assigned to ν (M–O) and ν (M–N), respectively⁽²⁹⁾. The IR spectra of the ligands and two representative mixed ligand complexes are shown in Figures,(2- 5).

3.3. Electronic Spectra and Magnetic Moments

The UV-vis spectra of ligands and their complexes have been taken in ethanol solution in the scan range 10000-50000 cm⁻¹. The values of band positions (cm⁻¹) together with the magnetic moment values are listed in Table 3. The UV-Vis spectra

of both two ligands showed bands at 40000 , 27027 and 31348 , 29586 cm^{-1} assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the molecule, these inner ligand transitions are common due to the presence of (C=N), (N=N) and (C=C) groups in the ligands' structures⁽³⁰⁾. In the metal complexes, new bands at higher wave numbers support the formation of strong (M–O) and (M–N) bonds⁽³¹⁾, which discussion as follow:-

1. The electronic spectrum of the Mn(II) complex shows two absorption bands at 16695 and 25316 cm^{-1} which ascribed to the transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ respectively. These transition are characteristic to the octahedral environment around Mn(II) ion⁽³²⁾. The magnetic moment (5.95 BM) is an additional evidence for an octahedral structure⁽³³⁾.
2. The spectrum of Co(II) mixed ligand complex occurs three absorption bands at 12739, 16260 and 21142 cm^{-1} characteristic of octahedral stereo absorption⁽³⁴⁾. They were assigned to the transition of ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{p})$ respectively. This complex has the room temperature magnetic moment of (4.88 BM), as expected for a octahedral Co(II) complex⁽³⁵⁾.
3. The UV-vis spectrum of Ni(II) complex exhibited three transitions bands at the 13333, 16000 and 21277 cm^{-1} due to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively with in octahedral spatial configuration⁽³⁶⁾. This complex exhibit magnetic moment of (3.21 BM), which can be a normal value for octahedral high-spin Ni(II) complexes⁽³⁶⁾.
4. The visible spectrum of the mixed ligand complex of Cu(II), exhibit one broad band at 20408 cm^{-1} which may be assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, respectively, corresponding to a square planer geometry around the Cu(II) ion⁽³⁷⁾. The magnetic moment value (1.66 BM) observed for this metal complex is comparable with the assignment of square planer stereochemistry⁽³⁸⁾.
5. The electronic spectrum of the Zn(II) complex do not show any d→d transition bands. The magnetic susceptibility show that this complex has diamagnetic moment for d^{10} ion. Both elemental analyses and magnetic moment value lead to suggest a tetrahedral geometry⁽³⁹⁾.

3.4. Molar Conductance Studies

The conductance of solutions of the complexes in DMSO (10^{-3} M) at room temperature are shown in Table 3. The low molar conductance values lying in the range (14.35 - 16.88) S. cm² mol⁻¹ confirmed the nonionic behavior of all the complexes⁽⁴⁰⁾.

4. Conclusion

The spectral, molar conductance and magnetic studies of the prepared mixed ligands complexes of (PDIMP) and (TIMP) Schiff base ligands reveals that Mn(II), Co(II) and Ni(II) metal complexes are having octahedral geometry and square planer stereochemistry of Cu(II) complex. But Zn(II) metal complex have tetrahedral geometry. According to the above data the structural formula of metal complexes may be proposed in Figures,(6&7).

تحضير وتشخيص معقدات مزيج الليكاند لبعض العناصر الانتقالية

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الخلاصة

تضمن البحث تحضير معقدات مزيج الليكاند لأيونات كل من المنغنيز(II) و الكوبلت(II) و النيكل(II) والنحاس(II) والخرصين(II) وذلك من مفاعلة أملاح كلوريداتها مع كل من قاعدتي شف [(PDIMP) = (HL₁)] 2-((E)-4-((E)-phenyl-diazenyl) phenylimino) methyl) phenol و [(TIMP) = (HL₂)] (Z)-2-((p-Tolylimino)methyl) phenol. شخّصت هذه المعقدات باستعمال الوسائل التحليلية و الطيفية المتاحة، منها التحليل الدقيق للعناصر وحساب النسبة المئوية للفلز في معقده، والتوصيل المولاري، وقياسات الحساسية المغناطيسية، المولاري و أطياف الأشعة فوق البنفسجية - المرئية و تحت الحمراء. وقد تبين أن كلا قاعدتي شف سلكت كليكاند ثنائية المخلّب أحادية الشحنة السالبة، ترتبط من خلال ذرة نيتروجين مجموعة الأزوميثين وذرة أوكسجين المجموعة الفينولية بعد إزالة بروتونها، كما تبين انعدام الصفة الأيونية لمحاليل المعقدات في مذيب ثنائي مثيل أوكسيد الكبريت. وبالاغتماد على النتائج التحليلية والطيفية فقد اتضح أن معقدات كل من المنغنيز(II) و الكوبلت(II) و النيكل(II) قد اتخذت الصيغة [M(L₁)(L₂)(H₂O)₂] بينما عادت الصيغة [M'(L₁)(L₂)] لمعقدي النحاس(II) والخرصين(II). وأستناداً إلى نتائج تحليل العناصر و أطياف الأشعة تحت الحمراء فقد تم التثبت من وجود جزيئتي الماء المتناسقة. أما الأشكال الفراغية لهذه المعقدات فقد تم اقتراحها بالاستناد إلى معطيات التحليل الدقيق للعناصر و قياسات الحساسية المغناطيسية و التوصيل الكهربائي المولاري و أطياف الأشعة تحت الحمراء و الأطياف الالكترونية.

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**Table 1. Some physical properties and analytical data of Schiff bases
ligand and their metal complexes**

Compounds (Formula)	Yield %	M.P., °C	Color	Found (Caled) %			
				C	H	N	M
HL ₁ = (PDIMP) C ₁₉ H ₁₅ N ₃ O	79	158- 159	Red	75.73 (75.52)	5.02 (5.00)	13.94 (14.15)	-----
HL ₂ = (TIMP) C ₁₄ H ₁₃ NO	83	98-99	Yellow	79.59 (79.17)	6.20 (6.11)	6.63 (6.75)	-----
[Mn (L ₁) (L ₂) ₂ (H ₂ O) ₂] C ₃₃ H ₃₀ N ₄ O ₄ Mn	74	>300	Red	65.89 (65.61)	5.03 (4.92)	9.31 (9.52)	9.13 (8.89)
[Co (L ₁) (L ₂) ₂ (H ₂ O) ₂] C ₃₃ H ₃₀ N ₄ O ₄ Co	70	135- 136	Red	65.45 (65.19)	4.99 (4.88)	9.25 (9.49)	9.73 (9.50)
[Ni (L ₁) (L ₂) ₂ (H ₂ O) ₂] C ₃₃ H ₃₀ N ₄ O ₄ Ni	73	145- 146	Red	65.48 (65.19)	3.52 (3.65)	10.02 (10.23)	6.42 (6.84)
[Cu (L ₁) (L ₂) ₂] C ₃₃ H ₂₆ N ₄ O ₂ Cu	76	118- 120	Deep red	45.19 (45.31)	5.00 (4.89)	9.26 (9.52)	9.73 (9.43)
[Zn (L ₁) (L ₂) ₂] C ₃₃ H ₂₆ N ₄ O ₂ Zn	78	190- 191	Red	69.04 -----	4.56 -----	9.76 -----	11.07 (10.81)

Table. 2: Characteristic IR frequencies (in cm^{-1}) of Schiff bases and their mixed ligand complexes

Compounds	$\nu(\text{O-H})$	$\nu(\text{C-H})$ Ar.	$\nu(\text{C-H})$ Alph.	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
$\text{HL}_1 = (\text{PDIMP})$	3424 w	3055 w	2920 w	1597 s	1480 w	-----	-----
$\text{HL}_2 = (\text{TIMP})$	3402 w	3024 w	2922 w	1597 m	-----	-----	-----
$[\text{Mn}(\text{L}_1)(\text{L}_2)(\text{H}_2\text{O})_2]$	3444 w	3035 w	2922 w	1597 s	1481 w	501 w	433w
$[\text{Co}(\text{L}_1)(\text{L}_2)(\text{H}_2\text{O})_2]$	3335 m	3047 w	2925 w	1594 s	1491 w	515 w	445 w
$[\text{Ni}(\text{L}_1)(\text{L}_2)(\text{H}_2\text{O})_2]$	3430 w	3020 w	2919 w	1597 s	1471 w	520 w	426 w
$[\text{Cu}(\text{L}_1)(\text{L}_2)]$	-----	3082 w	2914 w	1597 s	1482 w	531w	448 w
$[\text{Zn}(\text{L}_1)(\text{L}_2)_2]$	-----	3066 w	2962w	1597 s	1482 w	543 w	461 w

s= strong, m = medium, w = weak.

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

Metal complexes	Absorption bands (cm^{-1})	Transition	Conductivity $\text{S. cm}^2 \cdot \text{mol}^{-1}$	μ_{eff} (B.M)
$[\text{Mn}(\text{L}_1)(\text{L}_2)_2(\text{H}_2\text{O})_2]$	16695	${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	16.32	5.95
	25316	${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{G})$		
$[\text{Co}(\text{L}_1)(\text{L}_2)_2(\text{H}_2\text{O})_2]$	12739	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F}) (\nu_1)$	16.85	4.88
	16260	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F}) (\nu_2)$		
	21142	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F}) (\nu_3)$		
$[\text{Ni}(\text{L}_1)(\text{L}_2)_2(\text{H}_2\text{O})_2]$	13333	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1)$	16.88	3.21
	16000	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$		
	21277	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$		
$[\text{Cu}(\text{L}_1)(\text{L}_2)_2]$	20408	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	14.35	1.66
		${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$		
$[\text{Zn}(\text{L}_1)(\text{L}_2)_2]$	24691	-----	15.16	Dia

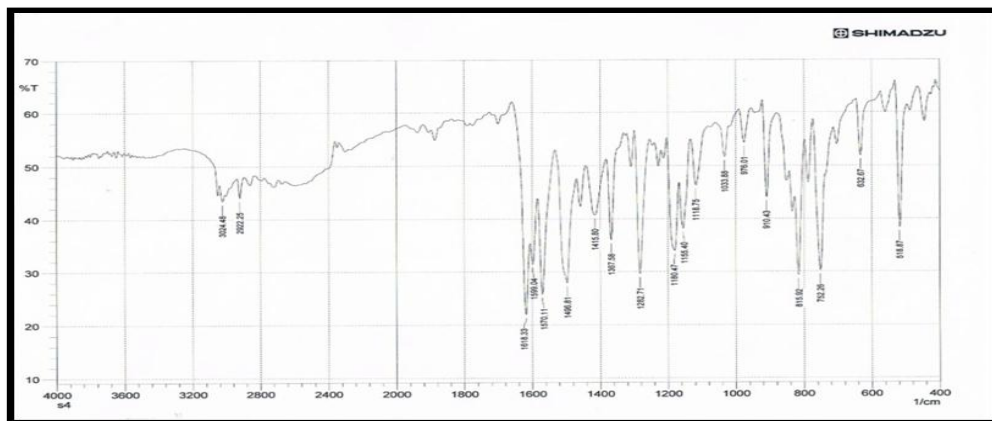


Fig. 2: IR Spectrum of (PDIMP) Schiff base ligand

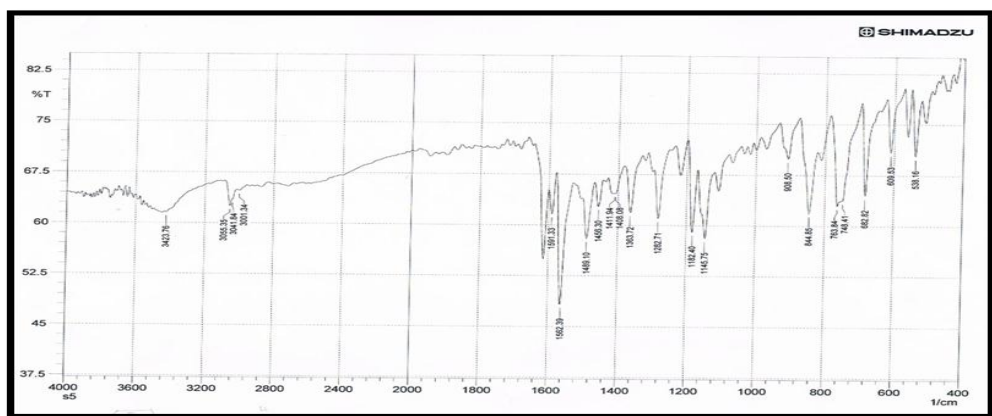


Fig. 3: IR Spectrum of (TIMP) Schiff base ligand

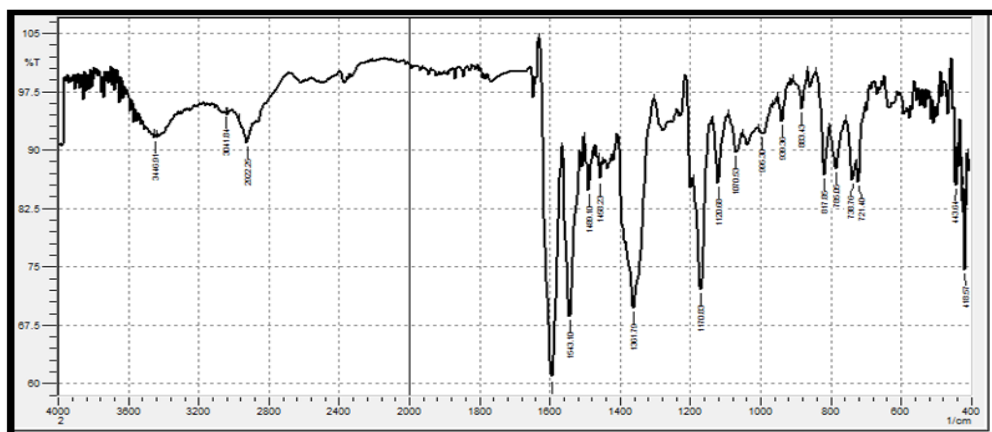


Fig. 4: IR Spectrum of Mn(II) mixed ligand complex

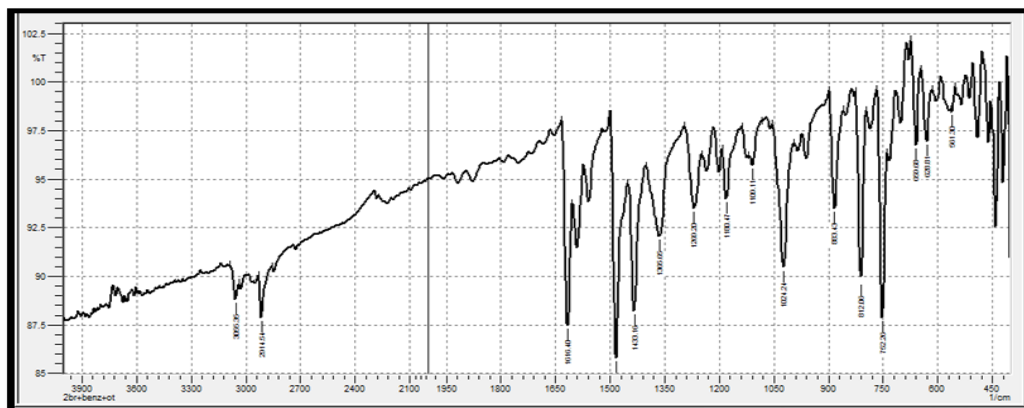


Fig. 5: IR Spectrum of Cu(II) mixed ligand complex

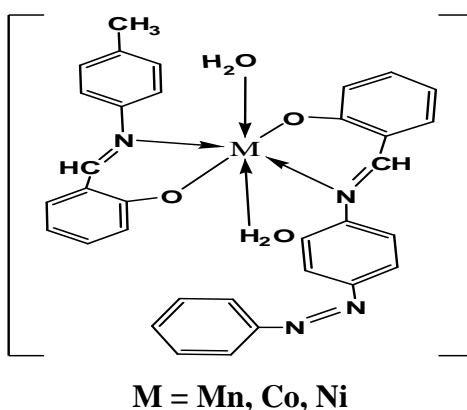


Fig. 6: Proposed structure for Mn(II), Co(II) and Ni(II) mixed ligand complexes

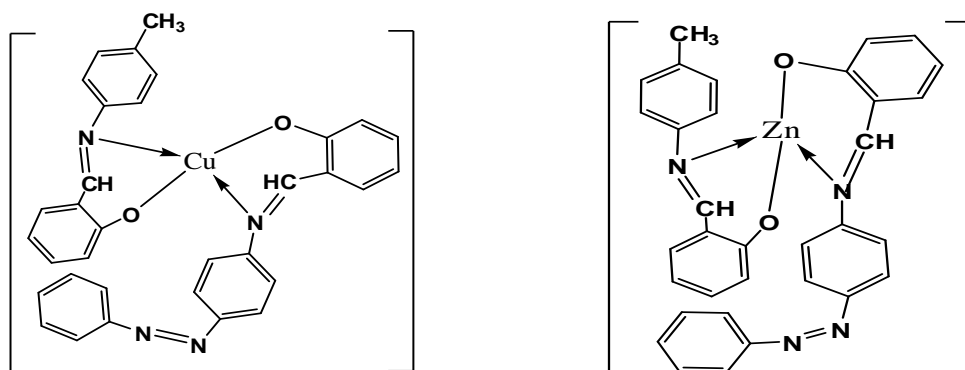


Fig. 7: Proposed structure for the mixed ligand complexes of Cu(II) and Zn(II)