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Original Research Article

Synthesis, Characterization and Antibacterial Activity Studies of Some Transition Metal Chelates of Mn(II), Ni(II) and Cu(II) with Schiff Base Derived from Diacetylmonoxime with *O*-phenylenediamine

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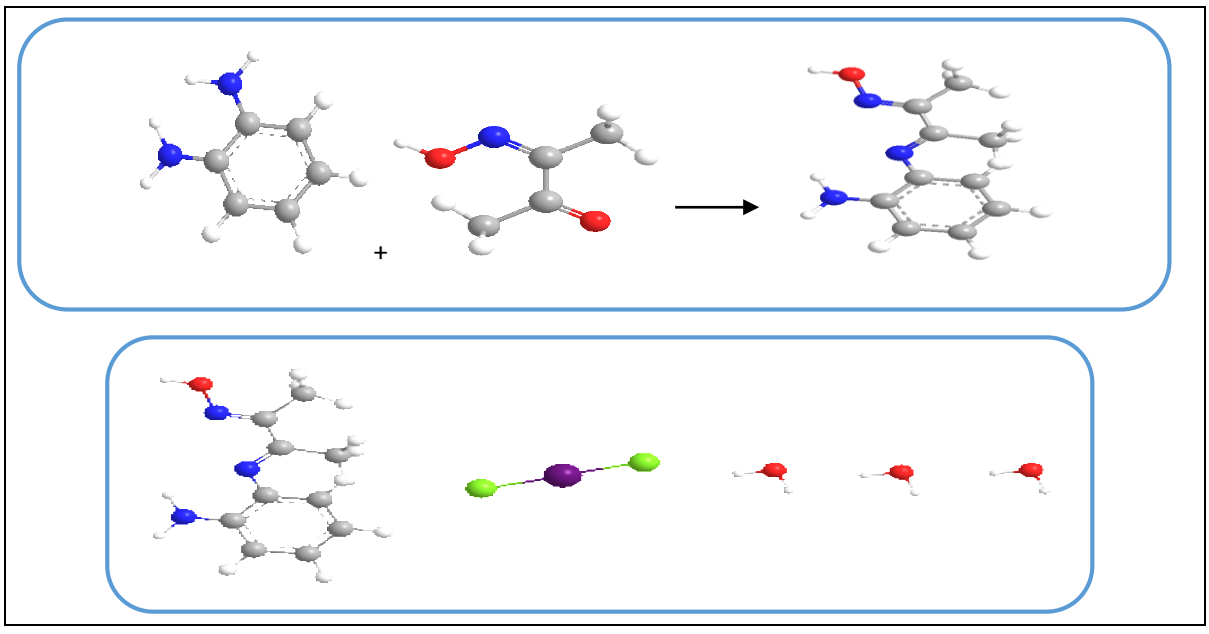
ABSTRACT

In this study, the transition metal chelates of Mn(II), Ni(II) and Cu(II) with Schiff base were synthesized and characterized. The elemental analysis data showed that, the isolated chelates are in 1:1 [M:L] ratio. The molar conductance values revealed that the chelates are none electrolyte in nature. The results of magnetic moment measurements demonstrated that, the chelates of Mn(II) and Cu(II) have unpaired electrons and chelates of Ni(II) is diamagnetic. The infrared spectral data displayed the main coordination sites of (2E, 3E)-3-((2-aminophenyl)imino)butan-2-one oxime towards Mn(II), Ni(II) and Cu(II) ions. The electronic spectrum results of the Schiff base ligand and its chelates suggest that the Mn(II) and Cu(II) chelates have octahedral structure and Ni(II) chelate is square planar.

GRAPHICAL ABSTRACT



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Introduction

Schiff bases compounds are the contain azomethine group (-HC=N-), and were first reported by Hugo Schiff in 1864 [1]. These compounds are also known as anils, imines or azomethines. It is usually formed by condensation of ketone or an aldehyde with a primary amine [2]. Schiff bases are the most widely used organic compounds. They have been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. This study summarizes the synthesis and biological activities of Schiff bases and their chelates [3]. Ligand oxime has been synthesized by condensation 3,3'-diaminobenzedine and phthaldehyde monoxime. The Mn(II), Co(II), Ni(II) and Cu(II) chelates, of this ligand have been prepared and characterized using elemental analysis, molar conductance studies, IR, UV, NMR, EPR and magnetic studies. The ligand and chelates, have been screened for their antimicrobial activity against two gram-negative bacteria and fungi, two gram-positive bacteria. The metal chelates were found to possess potent antimicrobial, antifungal activity better than ligand alone [4]. The oxime ligands can exhibit three coordination modes: coordination through N, coordination through O after deprotonation and coordinate on through N after deprotonation [5]. Schiff bases and their metal chelates play an important role in the development of coordination chemistry, resulting in an enormous number of publications, has been studied extensively, and have gained much importance recently due to their chelating ability, antimicrobial, anti-inflammatory activitiesand anticorrosion [6-9]. Schiff bases used in the fields of industry, medicine, and organic synthesis, analytical, inorganic and chemistry, they used in optical and electrochemical sensors, transition metal complexes of Schiff bases are used in dyes industry for food, leathers, and wood [10,11]. Tetra dentate Schiff bases ligand with a N_2O_2 donor atom set are well known to coordinate with various metal ions, and this has attracted the interest of many authors. Chelates of Schiff base ligands studied for their oxidative catalysis [12].

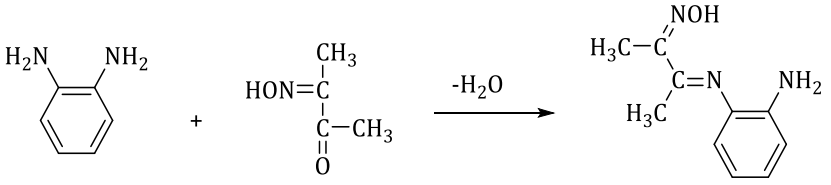
Experimental

Materials

All the chemicals used in this study were reagent of BDH or Aldrich including, diacetylmonoxime, *o*-phenylenediamine, ethanol, diethyl ether and dimethyl formamide.

Synthesis of Schiff base

The Schiff base L was synthesized by adding (5.055 g, 0.05 mmole) of diacetylmonoxime dropwise to *o*-phenylenediamine (5.408 g, 0.05 mmole) in 50 mL of absolute ethanol. The reaction mixture was refluxed for three hours. Then the product obtained was allowed to cool at room temperature, filtered and recrystallized from ethanol, and then dried under vacuum to get yellow precipitate (m.p. 199 ºC; yield 89%). The Schiff base formation can be explained as shown in Scheme 1.



Scheme 1. Synthesis of Schiff base (L)/Reaction condition: Diacetylmonoxime (5.055 g, 0.05 mmol), *o*-phenylenediamine (5.408 g, 0.05 mmol), absolute ethanol (50 mL)

Synthesis of chelates

The Schiff base chelates under investigation were synthesized by adding (2E,3E)-3-((2-aminophenyl)imino)butan-2-oneoxime (1.92 g; 0.01 mmole) in 30 mL absolute ethanol to 0.01 mmole of $MnCl_2.6H_2O$ (2.34 g), $NiCl_2.6H_2O$ (2.38 g) and $CuCl_2.2H_2O$ (1.70 g) salts in the same amount of the absolute ethanol. The reaction mixtures were heated under reflux for 3 hours. The chelates were filtered off recrystallized from ethanol and finally kept in a desiccator over silica gel.

Antibacterial activity

The synthesized complexes were screened for antibacterial activity against *Slamonalla typhi*., *E. coil* and *Staphylococcus aures* using cup plate method [13,14]. The test medium (Muller Hinton agar) poured in Petri dishes and allowed solidify at room temperature. The tested bacteria species suspension prepared in sterile distilled water and streaked on the surface of the agar medium. All the compounds were placed in the wells made by sterile cork borer using 100 µL micropipette and allowed to diffuse. The plates were incubated at 37 ºC for 24 h. The inhibition zone formed around the cups were measured in mm.

Wt. of sample in gram=M. wt.×M×V mL/1000

Wt. of sample in gram=M. wt.×0.1×1 mL/1000

Results and discussions

The reaction between the diacetylmonoxime and *o*-phenylenediamine yields only one product (Scheme 1).

Table 1. Elemental analysis and some physical properties of the Schiff base (L) and its chelates

Compound/Chelates	Colour	M. wt.	M.P. °C	%Calc. (Found) C%	H%	N%	Λ (μs)	BM
L ($C_{10}H_{13}N_3O$)	Yellow	191.23	199	62.81 (62.01)	6.85 (7.07)	21.97 (22.29)	-	-
$[MnL(H_2O)_2Cl_2]H_2O$	Yellowish brown	371.12	250>	32.36 (32.40)	5.16 (4.71)	11.32 (11.14)	13	5.56
$[NiLCl_2](H_2O)_3$	Red	374.87	245	32.04 (32.67)	5.11 (4.71)	11.21 (11.14)	21	0.0
$[CuL(H_2O)_2Cl_2](H_2O)_2$	Dark brown	379.74	232	31.63 (31.51)	5.04 (4.72)	11.07 (10.57)	27	1.87

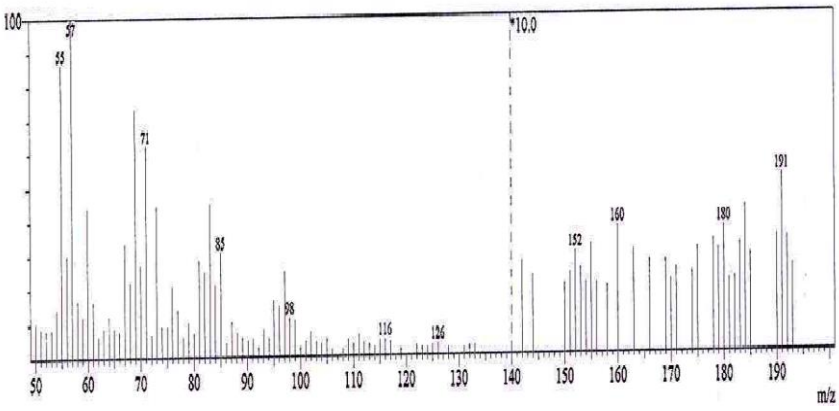


Figure 1. Mass spectrum of Schiff base

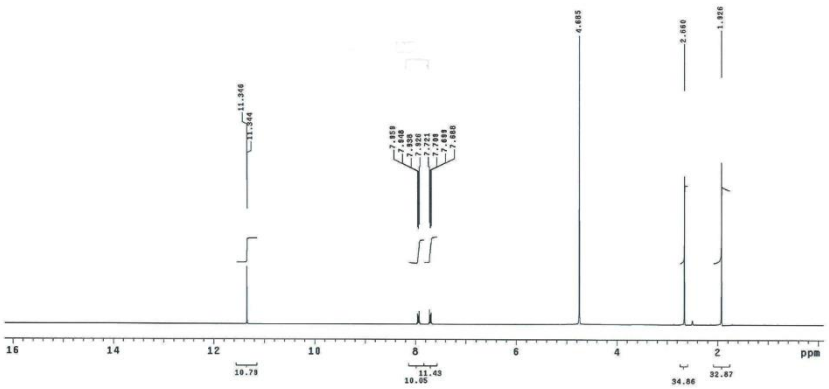


Figure 2. ^{1}H NMR spectrum of the Schiff base

Microanalysis and molar conductance measurements

Some physical properties and elemental analysis data of the Schiff base and its chelates are summarized in Table 1**,** where the results confirm the proposed composition. The synthesized chelates were formed in 1:1 (M:L) ratio. The obtained molar conductance values of the complexes in DMF solvent lie in the range of 13-27 ohm^{-1}/cm^{2}/mol^{-1} indicating their chelates of Mn(II), Ni(II) and Cu(II) are non-electrolytic [15].

Mass spectrum of Schiff base

The mass spectral data of the Schiff base ligand are demonstrated in Figure 1. Molecular ion showed peaks, which were in good agreement with the expected values [16]. The mass spectrum of the Schiff base gives a peak at 191 *m/z*.

Proton nuclear magnetic resonance spectrum of ligand

Proton nuclear magnetic resonance spectrum of L

The ^{1}H-NMR spectrum recorded in d_6-DMSO solvent on a Jeol-90 Fourier Transform (200 MHz). Shows some singlet signals (Figure 3) at 11.346, 7.959-7.688, 4.685, 2.660 and 1.926 ppm, downfield of TMS, assignable to the protons of OH(NOH), phenyl ring, υNH2, υCH3 and υCH3 respectively [17].

Electronic spectra

The electronic absorption spectra of the Schiff base and its chelates under investigation were recorded using Nujol mull on a Unicom model UV2 spectrophotometer. The electronic spectral data of the schiff base and its chelates under study are shown in (Figures 3-6). The Schiff base ligand spectrum exhibits two absorption signals at 40733 cm^{-1}, 39138 cm^{-1}, attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively [18]. The electronic absorption spectrum of Mn(II) chelate show two bands at 48899 cm^{-1}, 39062 cm^{-1} attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, and two bands at 24270 cm^{-1} and 16124 cm^{-1} which is due to d-d transition for octahedral geometry [19,20]. The electronic absorption spectrum of Ni(II) show a band at 38986 cm^{-1} attributed to $\pi\rightarrow\pi^*$ transitions and two bands at 19607 cm^{-1} and at 16260 cm^{-1} due to 3A2g (F)→3T1g (F) and 3A2g (F)→3T1g (P) (d-d) transitions which suggest an octahedral geometry [21]. Cu(II) chelate spectrum exhibits two absorption bands at 47505 cm^{-1} and 39138 cm^{-1} attributed $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, and show bands at 24390 cm^{-1} and at 16129 cm^{-1} mainly due to 2Eg→2T2g transition. The observed data gave evidence for the octahedral geometry [22] of the chelate.

Table 2. IR and electronic spectral data of the Schiff base and its chelates

Ligand/ chelates	IR (cm^{-1})					UV – Vis
	υOH	υNH2	υC=N	υM-N	υM-O	λ_{max} (cm^{-1})
L ($C_{10}H_{13}N_3O$)	3443	3348	1619	-	-	39138, 40733
$[MnL(H_2O)_2Cl_2]H_2O$	3476	3416	1630	595	531	48899, 39062, 16124, 24270
$[NiLCl_2](H_2O)_3$	3474	3412	1624	623	585	38986, 19607 16260
$[CuL(H_2O)_2Cl_2](H_2O)_2$	3413	3326	1615	602	538	47505, 39138 24390, 16129

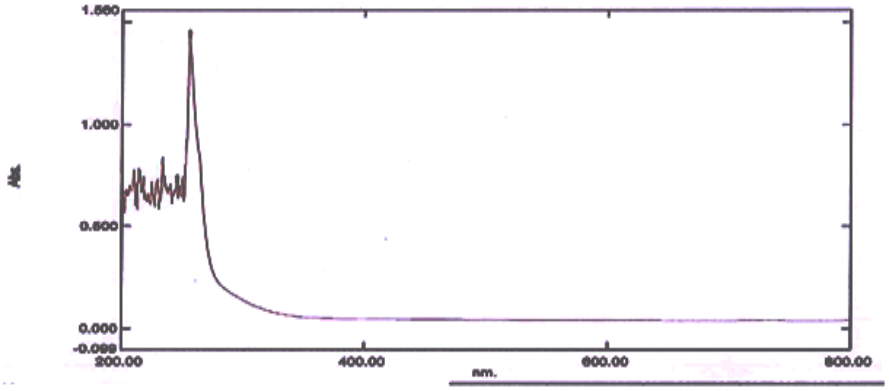


Figure 3. UV spectrum of the free ligand L

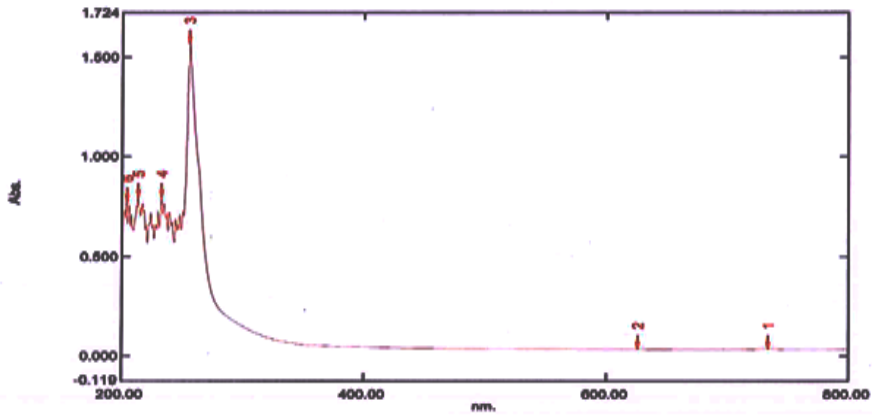


Figure 4. Electronic spectrum of $[MnL(H_2O)_3]Cl_2$

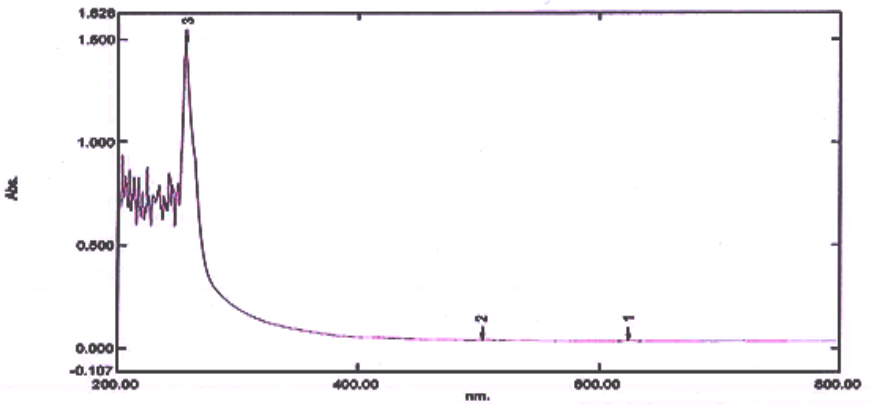


Figure 5. Electronic spectrum of $[NiL(H_2O)_3]Cl_2$

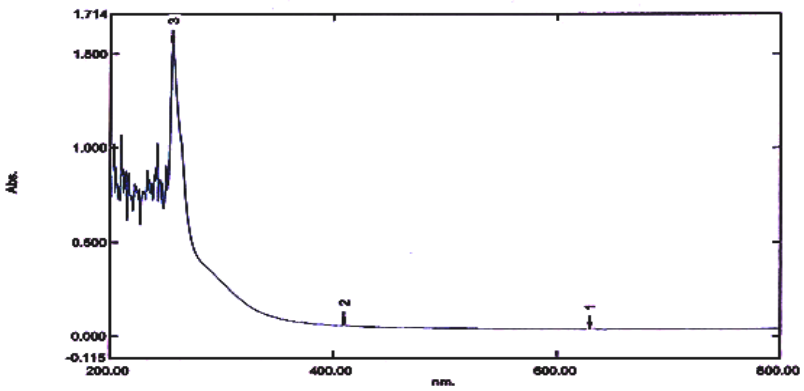


Figure 6. Electronic spectrum of $[CuL(H_2O)_2Cl](H_2O)Cl$

Magnetic susceptibility measurements

The magnetic moment of Mn(II) chelate was 5.65 BM, suggesting the high spin six-coordinated octahedral arrangement of the ligand around the metal ion [23,24]. The Ni(II) chelate has magnetic moment value of 0.00 BM indicating a square planar configuration [25]. The magnetic moment value of Cu(II) chelate is 1.79 BM which suggests a distorted octahedral geometry around the metal ion [26].

IR spectra

The IR spectra of the ligand and its chelates with Mn^{2+}, Ni^{2+} and Cu^{2+} were recorded in the solid state in the rang 400-4000 cm^{-1} using KBr disc on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer (Figures 7-10). The IR spectral data are present in Table 2. A verification of the structures of the metal chelates can be easily achieved by comparing the IR spectrum of the free ligand with those of chelates [27]. When a Schiff base ligand is coordinated to metal ion at least one additional atom is introduced into the ligand vibrating system. It is thus expected that bond lengths, angles and interacting forces within the ligand would be altered even at least slightly. The IR spectrum of the Schiff base display three bands at 3443 cm^{-1} attributed to OH group, 3348 cm^{-1} attributed NH2 group and a band at 1619 cm^{-1} attributed to C=N group [28-30]. The shifting of υ(C=N) group vibration in all chelates indicates the participation of nitrogen atom during chelates [31,32]. Chelates IR spectrum revealed broad bands at the range of 3413-3476 cm^{-1} that attributed to stretching vibration OH of coordinated water molecules banding with chelates formation [33]. The NH2 group is not participating in coordination 34. New bands observed at 538-585 cm^{-1} and at 595-623 cm^{-1} which could be attributed to υ(M-O) and υ(M-N) vibrations [35,36].

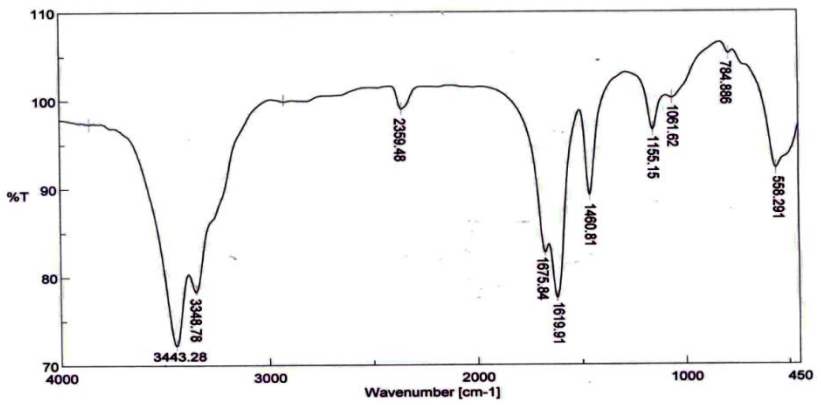


Figure 7. IR spectrum of the Schiff base

Figure 8. IR spectrum of $[MnL(H_2O)_3]Cl_2$

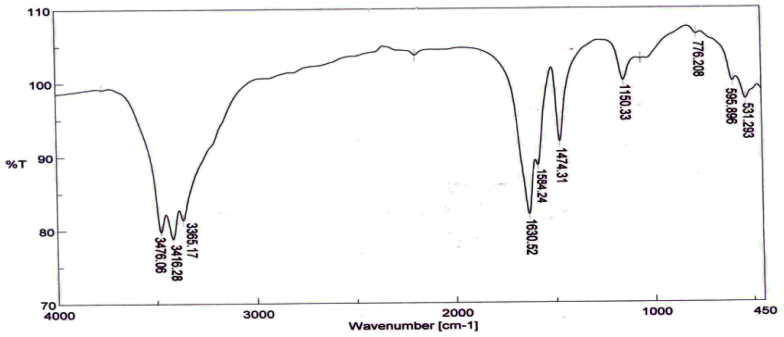


Figure 9. IR spectrum of $[NiL(H_2O)_3]Cl_2$

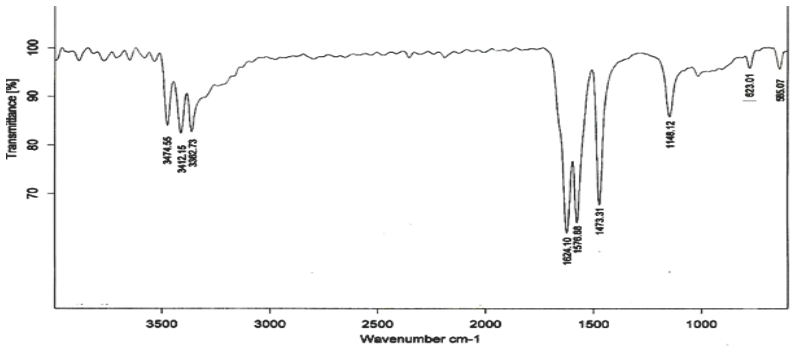


Figure 10. IR spectrum of $[CuL(H_2O)_2Cl](H_2O)Cl$

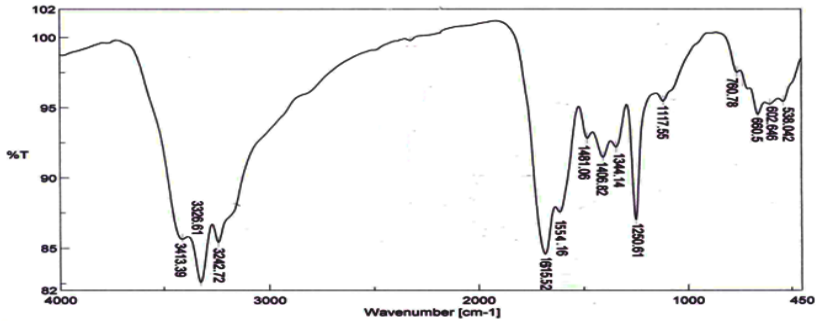
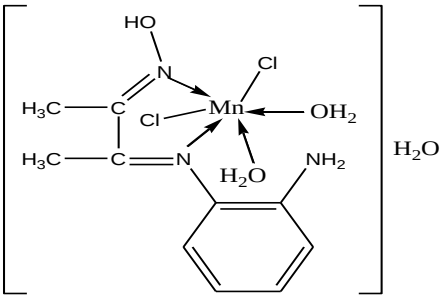


Table 3. Antibacterial activity results (mm) for the Schiff base and its complexes

Ligand and its chelates	Bacteria, inhibition zone (mm)		
	Slamonalla typhi	*E. Coli*	*Staphylococci*
L ($C_{10}H_{13}N_3O$)	15	18	-
$[MnL(H_2O)_3]Cl_2$	9	13	19
$[NiL(H_2O)_3]Cl_2$	13	23	15
$[CuL(H_2O)_2Cl](H_2O)Cl$	13	12	11

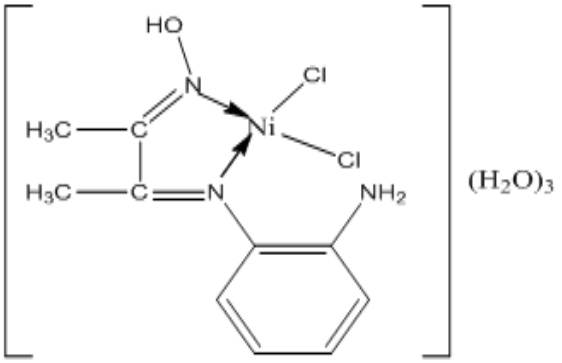
Scheme 2. $[MnL(H_2O)_2Cl_2]H_2O$
Reaction condition: (2E, 3E)-3- ((2-amino phenyl) imino) butane-2-one oxime (1.92 g, 0.01 mmole), MnCl2.6H2O (2.34 g, 0.01 mmole), absolute ethanol (60mL)



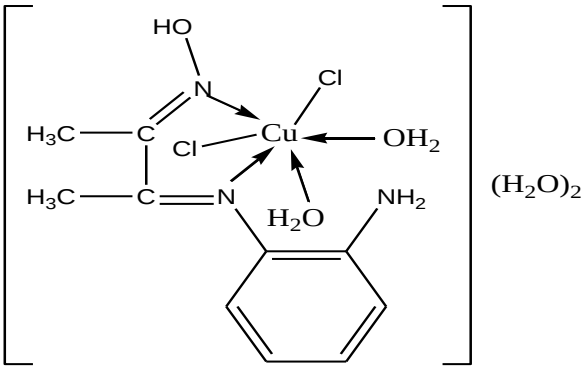
Anti-bacterialactivity results

The ligand (2E.3E)-3-((2 aminophenyl)imino)-butan-2-one oxime (L) and its synthesized chelates were screened for their possible antibacterial activities against three types of bacteria, *Slamonalla typhi, E. Coli*, and *Staphylococci*. The ligand and its chelates showed moderate to good antibacterial activities against all used types of bacteria these activities were performed by cup plate method. Inhabitation zone were recorded by measuring the diameter of inhabitation zone in mm at the end of 24 h [37]. At room temperature, the results of antibacterial study are tabulated in Table 3. The widest inhabitation zone was formed around *E. coil* (23 mm), followed by (19 mm) for *Staphylococci* and the least inhibitory effects were observed for *Slamonalla* typhi and *Staphylococci* (9 mm). The (-) means no inhibition [38].

Scheme3. $[NiLCl_2](H_2O)_3$
Reaction condition: (2E, 3E)-3-((2-amino phenyl) imino) butane-2-one oxime (1.92 g, 0.01 mmole), $NiCl_2.6H_2O$ (2.38 g, 0.01 mmole), absolute ethanol (60 mL)



Scheme 4. $[CuL(H_2O)_2Cl_2](H_2O)_2$
Reaction condition: (2E, 3E)-3-((2-amino phenyl) imino) butane-2-one oxime (1.92 g, 0.01 mmole), $CuCl_2.6H_2O$ (1.70 g, 0.01 mmole), absolute ethanol (60 mL).



Conclusion

In this research study, we describe the synthesis, chraracterization and antibacterial properties of the complexes. Three novel transition metal complexes of Mn(II), Ni(II) and Cu(II) with Schiff base derived from diecetylemonoxime with *o*-phenylenediamine were synthesized by condensation process. The synthesized compounds were characterized using several techniques: Elemental analysis, Magnetic moment measurements, Molar conductivity measurements, Mass spectral, H-NMR spectroscopy, UV-Vis spectroscopy and IR spectrometer. Based on the analytical data the synthesized compounds Mn(II), Ni(II) and Cu(II) Schiff base chelates suggests 1:1 {M:L} molar ratio and exhibits an octahedral structure for Mn(II), Cu(II) complexes and squar planer structure for Ni(II) complex as shown above (Schemes 2-4). The synthesized compounds were screened against three types of bacteria showing moderate to good activities against all used types of bacteria.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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