Original Article

Synthesis, characterization and antibacterial activity studies of some transition metal complexes of Mn(II), Ni(II) and Cu(II) with Schiff base derived from (2Z,3Z)-3-((4-(((2E,3E)-3-(hydroxyimino)butan-2-ylidene)amino(phenyl-imino)butan-2-one oxime

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Abstract

Newly discovered transition metal Schiff base complexes of Mn(II), Ni(II), and Cu(II). (2Z,3Z)-3-((4-(((2E,3E)-3-(hydroxyimino) butan-2-ylidene)amino)- phenyl imino)buttan-2-one oxime ligands were synthesized from diacetylemonoxime with p-phenylenediamine and characterized on the basis of physical characteristics, molar conductivity, UV–Vis spectrum data, 1H-NMR, magnetic moment measurements, mass spectra, microanalytical data (C.H.N.), and IR. The elemental analysis data showed that the isolated complexes are in a 1:1 [M: L] MnL and 2:1 [2M:L] NiL and CuL ratio. The molar conductance values revealed that the complexes are none electrolytes in nature. The results of magnetic moment measurements showed that the complexes of Mn(II) and Cu(II) have unpaired electrons and that the complex of Ni(II) is diamagnetic. The infrared spectral data displayed the main coordination sites of (2Z,3Z)-3-((4-(((2E,3E)-3-(hydroxyimino)butan-2-ylidene)amino-phenyl)imino)buttan-2-one oxime towards Mn(II), Ni(II) and Cu(II) ions. The electronic spectrum results of the Schiff base ligand and its complexes suggest that the Mn(II) and Cu(II) complexes have octahedral structures and that the Ni(II) complex is square planar.

***Key words*:** Schiff base, complexes, (*2Z,3Z*)-3-((4-(((*2E,3E*)-3-(hydroxyimino)butan-2-ylidene)- (amino-phenyl) imino-buttan-2-one oxime.

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Introduction

The most frequently used organic compounds are Schiff bases. A wide range of biological activities, such as antifungal, antibacterial, antimalarial, anti-ant proliferative, anti-inflammatory, antiviral, and antipyretic properties, have been demonstrated. This review summarizes the biological functions of Schiff bases and their chelates1,2 as well as their synthesis. Hugo Schiff first described azomethine group-containing Schiff base compounds in 18643. These compounds are also known as anils, imines or azomethines. It is usually formed by the condensation of a ketone or an aldehyde with a primary amine4. New complexes of Ni(II) and Pd(II) with Schiff base ligands derived from 5-nitro isatin with 4-phenyl-3-thiosemicarbazide have been synthesized in absolute ethanol. The solid products were characterized by elemental analysis and spectral (FT-IR, 1 H NMR and UV–Vis) measurements. Single-crystal XRD was used to further characterize the Schiff base ligand. It has been found that the Schiff base ligand behaves as a tridentate ligand forming chelates with 1:2 (metal: ligand) in the case of the Ni-complex and 1:1 (metal: ligand) in the case of the Pd-complex. Octahedral geometry has been suggested for the Ni(II) chelate, while square-planar geometry has been suggested for the Pd(II) chelate5. Precursor techniques can be used to introduce and justify the coordination behavior of Schiff bases synthesized from phenylenediamine and carbonyl compounds in a variety of applications. Such Schiff bases have been the subject of investigations and studies due to their chemistry interest and other applications, including titration analysis, anticorrosion, and biological activity6, in addition to coordination chemistry, metal ion uptake, or dye techniques. In the current study, new metal complexes of the ligand diacetylmonoxime-N(4) antipyrinyl thiosemicarbazone were created, and their antitumour activity was assessed. We synthesized new complexes containing iron, cobalt, nickel, and copper ions. Elemental analysis (C, H, N, O), 1H nuclear magnetic resonance, mass spectrometry, electron paramagnetic resonance, Fourier transform infrared spectroscopy, andultraviolet–visible and thermogravimetric analyses were used to characterize the obtained complexes7.

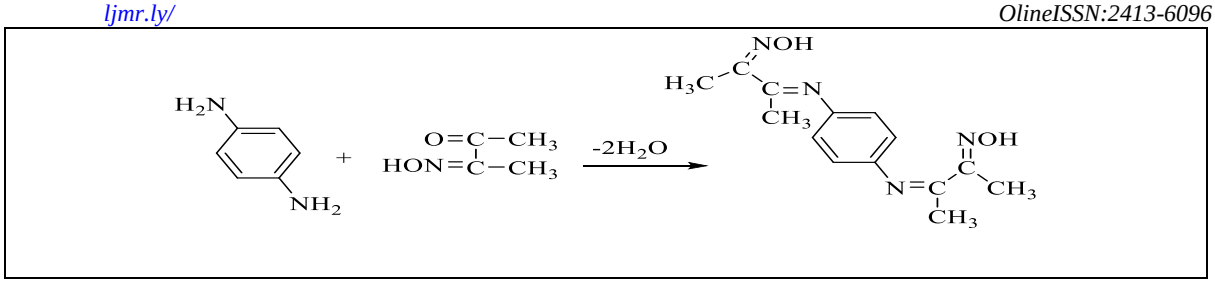
1. Experimental

1.1. Materials

All of the chemicals used in this study, including p-phenylenediamine diacetylmonoxime, DMF, EtOH, and ether, were Aldrich or BDH reagents.

1.2. Synthesis of Schiff base

Schiff base L was synthesized by adding (5. 055 g, 0.05 mmol) diacetyl monoxime dropwise to p-phenylenediamine (5.408 g, 0.05 mmol) in 50 cm3 of absolute ethanol. The reaction mixture was refluxed for 3 hours. Then, the product obtained was allowed to cool at room temperature, filtered and recrystallized from ethanol, and then dried under vacuum to obtain a pale brown precipitate (m. p. 187 ºC; 74% yield). The Schiff base formation can be explained as shown in **Scheme 1**.



Scheme 1: Synthesis of Schiff base (L)

1.3. Synthesis of complexes

The Schiff base Complexes under investigation were synthesized by adding (2Z,3Z)-3-((4-(((2E,3E)-3-(hydroxyimino) butan-2-ylidene)amino)-phenyl)imino)buttan-2-one oxime ligand (2.74 g; 0.01 mmole) in 30 ml absolute EtOH to 0.01 mmole of MnCl2.6H2O (1.97 g), NiCl2.6H2O (2.37 g) and CuCl2.2H2O (1.70 g) salts in the same amount of absolute EtOH. The reaction mixtures were heated under reflux for 3 hours. The chelates were filtered off, recrystallized from the suitable solvent and finally kept in a desiccator over silica gel.

3. Results and Discussion:

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

3.1. Microanalysis and molar conductance measurements

The elemental analysis data (C.H.N) and some physical properties of the Schiff base and its complexes are summarized in Table 1, where the results confirm the proposed composition. The synthesized complexes were formed in a 2:1 (2 M:L) ratio. The obtained molar conductance values of the complexes in DMF solvent lie in the range of 11 - 19 ohm-1 cm2 mol-1, indicating that their complexes of Mn(II), Ni(II) and Cu(II) are nonelectrolytic8.

Table (1): Physical and elemental analysis of the Schiff base (L) and its complexes

Ligand/Complexes	M. wt	M.P. ^{0}C	%Calc. (Found)			Λ (µs)	BM
			C%	H%	N%		
L_2 ($C_{14}H_{18}N_4O_2$)	274.32	187	61.30 (61.82)	6.61 (5.91)	20.42 (19.78)	-	-
$C_{14}H_{22}Cl_2Mn_2N_4$	436.19	>250	38.35 (39.51)	5.08 (4.32)	12.84 (13.61)	15	5.51
$C_{14}H_{18}Cl_4Ni_2N_4$	533.52	245	31.52 (32.64)	3.40 (3.87)	10.50 (11.77)	19	0.0
$C_{14}H_{34}Cl_4Cu_2N_4$	545.53	232	30.82 (30.51)	6.28 (2.89)	10.27 (10.57)	11	1.89

3.2. Infra-Red spectra

A Perkin-Elmer 1430 ratio recording infrared spectrophotometer was used to record the IR spectra of the ligand and its complexes with Mn2+, Ni2+, and Cu2+ in the solid state between 400 and 4000 cm-1 (Figs. 1-4). Table 2 displays the IR spectral

data. By contrasting the IR spectra of the free ligand and the complexes, it is simple to verify the structures of the metal complexes. 910. When a Schiff base ligand is coordinated to a 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 slightly11. The IR spectrum of the Schiff base displays three bands at 3443 cm-1 attributed to the OH group, 3348 cm-1 attributed to the NH2 group and a band at 1619 cm-1 attributed to the C=N group12. The shifting of the ν(C=N) group vibration in all complexes indicates the participation of nitrogen atoms during chelation13-15. The complex IR spectrum displays broad bands in the range of 3413 – 3476 cm-1 that are attributed to the stretching vibration OH of coordinated water molecules banding with complex formation16. The NH2 group does not participate in coordination. New bands were observed at 538-585 cm-1 and at 595-623 cm-1, which could be attributed to υ(M-O) and υ(M-N) vibrations17.

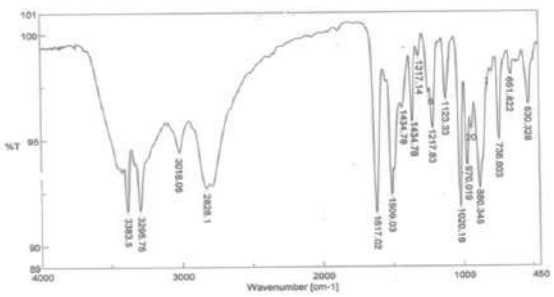


Fig. (1): IR spectrum of the Schiff base

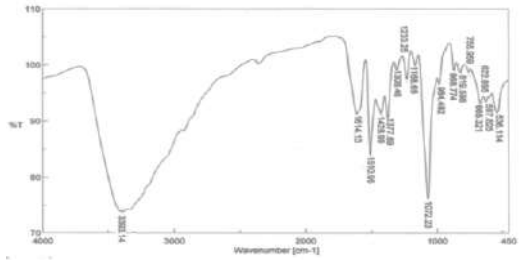


Fig. (2): IR spectrum of $[MnL(H_2O)_3]Cl_2$

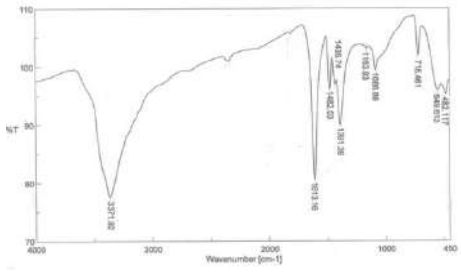


Fig. (3): IR spectrum of $[NiL(H_2O)_3]Cl_2$

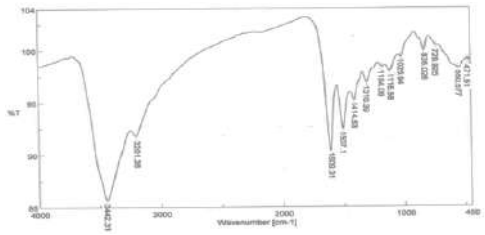


Fig. (4): IR spectrum of $[CuL(H_2O)_2Cl](H_2O)Cl$

3.3 Mass spectrum of the Schiff base ligand

The molecular ion showed peaks in Figure 5, which were in good agreement with the expected values18. The mass spectrum of the Schiff base gives a peak at 274 m/z.

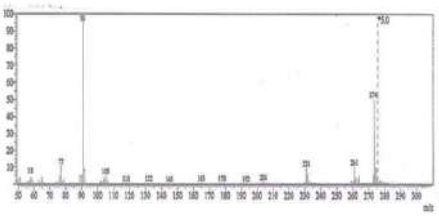


Fig. (5): Mass spectrum of Schiff base

3.4. Proton nuclear magnetic resonance spectrum of the ligand

The 1H-NMR spectrum was recorded in d6 DMSO solvent on a Jeol-90 Fourier transform (200 MHz). 4-(2-

Hydroxbenzylideneamino)-3-hydroxnaphtalene-1-sulfonic acid shows some singlet signals (figure 6) at 11.739, 11.612, 6.360 – 6.795, 3.392 and 2.042 ppm, downfield of TMS, assignable to the protons of υOH(NOH), υOH(NOH), phenyl ring, υCH3 and υCH3, respectively19.

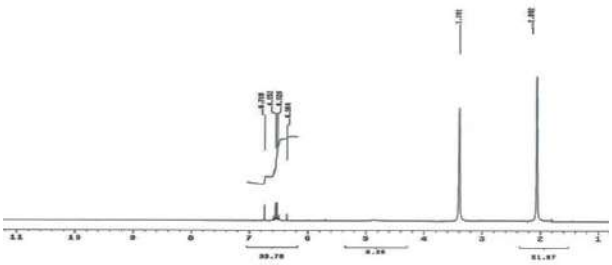


Fig. (6): ^{1}H NMR spectrum of the Schiff base

3.4. Electronic spectra

The electronic absorption spectral data and magnetic moment values and the electronic spectra of the Schiff base ligand and its metal complexes are presented in Figures (7-10) and given in Table 4. The electronic spectra of the Schiff base ligand show strong absorption bands at 28169 and 35089 cm-1, which are attributed to n → π* and π → π* transitions, respectively20. The Mn(II) complex shows three absorption peaks at 17953 cm-1, 24390 cm-1 and 36363 cm-1 corresponding to the 6A1g → 4T2g(G), 6A1g → 4A1g and CT transitions, respectively, suggesting octahedral geometry21. Furthermore, the octahedral geometry is proposed based on the magnetic moment. The magnetic moment of the complex is found to be 5.76 BM, which falls within the range expected for octahedral geometry22. The electronic spectrum of the nickel complex shows two bands at 18868 cm–1 and 14925 cm–1, which are attributed to the 1A1g → 1A2g and 1A1g → 1B2g transitions23. These transitions, as well as the measured value of the magnetic moment (μeff = 0), suggest a square-planar stereochemistry of the compound.24 The observed magnetic momentum value of the Cu(II) complex is 2.23 BM, which falls within the range observed for octahedral geometry25. Furthermore, the electronic spectra of the Cu(II) complex show two broad peaks at 13889 and 18867 cm-1 due to a transition between 2Eg → 2T2g and 3A2g(F) → 3T2g(F), indicating octahedral geometry26.

Table (2): IR and electronic spectral data of the Schiff base and its chelates

Ligand/chelates	IR (cm^{-1})					UV – Vis
	υOH	υC=N	CH_3	υM-N	υM-O	λ_{max} (cm^{-1})
$L_2(C_{14}H_{18}N_4O_2)$	3262	1626	1328	-	-	35089, 28169
$C_{14}H_{22}Cl_2Mn_2N_4$	3405	1621	1330	517	745	24390, 36363
$C_{14}H_{18}Cl_4Ni_2N_4$	3432	1616	1313	517	745	18868, 14925
$C_{14}H_{34}Cl_4Cu_2N_4$	3833	1626	1322	470	583	13889, 18867

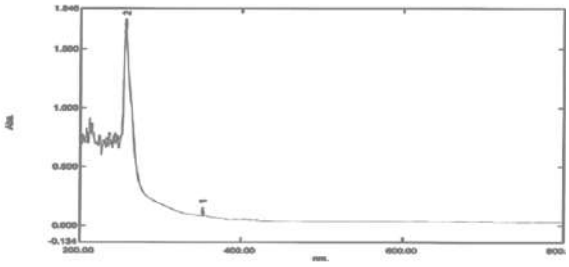


Fig. 7: UV spectrum of the free ligand L

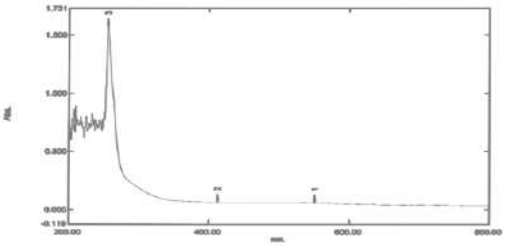


Fig. (8): Electronic spectrum of $[MnL(H_2O)_3]Cl_2$

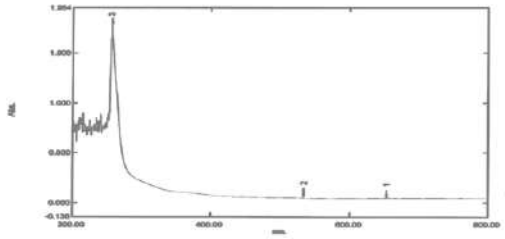


Fig. (9): Electronic spectrum of $[NiL(H_2O)_3]Cl_2$

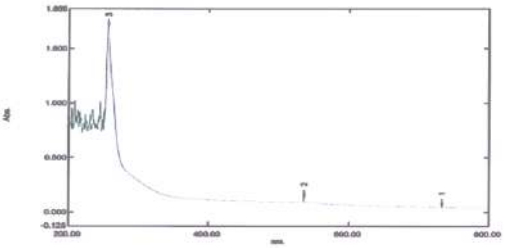


Fig. 10: Electronic spectrum of $[CuL(H_2O)_2Cl](H_2O)Cl$

3.5. Magnetic susceptibility measurements

The magnetic moment of the Mn(II) complex is 5.55 BM, which suggests the high spin six-coordinated octahedral arrangement of the ligand around the metal ion27. The Ni(II) complex has a magnetic moment value of 0.00 BM, indicating a square planar configuration28. The magnetic moment value of the Cu(II) chelate is 1.79 BM, which suggests a distorted octahedral geometry around the metal ion29.

4. Antibacterial activity results

The (2Z,3Z)-3-((4-(((2E,3E)-3-(hydroxyimino)butan-2-ylidene)amino(phenyl-imino)butan-2-one oxime (L) and its synthesized chelates were screened for their possible antibacterial activities against three types of bacteria, Slamonella typhi, E.Coli, and Staphylococci. The ligand and its chelates showed moderate to good antibacterial activities against all used types of bacteria, and these activities were determined by the cup plate method. By measuring the diameter of the habitation zone in mm after 24 hours and 30 minutes, the habitation zone was identified. The antibacterial study's findings are summarized in table (3) at room temperature. Around formed the largest habitation zone. E. Coli (23 mm), followed by Staphylococci (19 mm) for Staphylococci, and the least inhibitory effects were observed for Slamonalla type and Staphylococci (9 mm). The (-) means no inhibition.

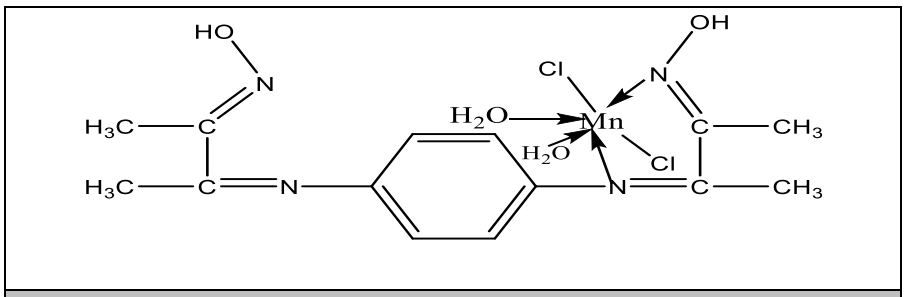
Table (3): Antibacterial activity results (mm) for the Schiff base and its complexes.

Ligand and its chelates	Bacteria, inhibition zone (mm)		
	Slamonalla typhi	*E. Coli*	*Staphylococci*

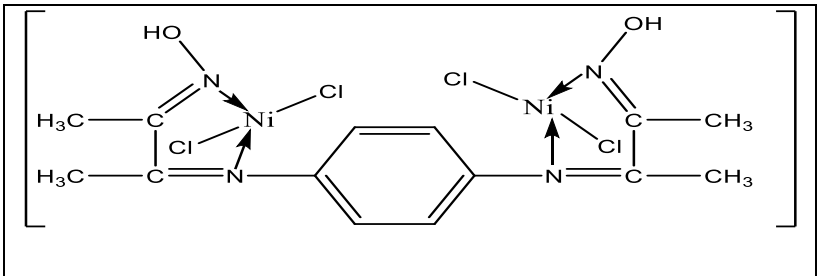
L ($C_{10}H_{13}N_3O$)	16	23	12
$[MnL(H_2O)_3]Cl_2$	-	-	-
$[NiL(H_2O)_3]Cl_2$	14	16	15
$[CuL(H_2O)_2Cl](H_2O)Cl$	13	11	09

5. Conclusion

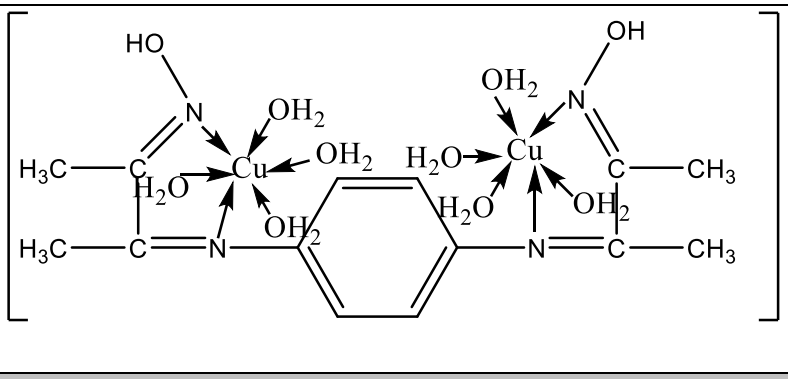
On the basis of the spectral and analytical data, the synthesized manganese(II), nickel(II) and copper(II) Schiff base (L) complexes suggest 1:1 and 2:1 [M:L] metal to ligand stoichiometry and exhibit octahedral structures, and the ligand is coordinated to the metal ions as a tridentate. The following geometrical structures of the synthesized complexes were suggested.



.**Scheme 2.** $C_{14}H_{22}Cl_2MnN_4O_4$



.**Scheme3.** $C_{14}H_{18}Cl_4Ni_2N_4O_2$



.**Scheme 4.** $C_{14}H_{34}Cu_2N_4O_{10}$

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