



Synthesis, Characterisation and Antimicrobial Studies of Schiff Base and Its Metal Complexes

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Authors' contributions

This work was carried out in collaboration among all authors. Author FAA designed the study, conducted the lab work, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors HMAH and RAB provided literature support and reviewed. All authors read and approved the final manuscript.

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ABSTRACT

Four metal complexes of Co(II), Pb(II), Ni(II) and Fe(II) ions with a Schiff base derived from (3-methoxy-4-hydroxy-benzaldehyde with leucine) have been synthesized and characterized using several physical techniques, in particular; molar conductance measurements, colour, melting point, infrared and electronic spectra. The molar conductance values reveal a non-electrolytic nature. The infrared spectral data display the coordination behaviour of the Schiff base toward Co(II), Pb(II), Ni(II) and Fe(II) ions. The electronic absorption spectra of the Schiff base and its complexes show $\pi \rightarrow \pi^*$ (phenyl ring) and, $n \rightarrow \pi^*$ (HC=N) and the expected geometrical structure for the prepared complexes. The Schiff base and its complexes were tested for antimicrobial activity against gram-positive bacteria; *Staphylococcus aureus*; *E. Coli* and *Klebsiella*, in addition Rizopus as fungal. The effect of the Schiff base leucine complex on bacteria was recorded only against *Staphylococcus aureus* and *Escherichia coli*.

Keywords: Schiff Base; vanillin; leucine; complexes.

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1. INTRODUCTION

Leucine is a branched-chain α -amino acid, classified hydrophobic due to the isobutyl side chain. Its chemical formula is $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{CH}(\text{CH}_3)_2$. L-Leucine is a major component of the subunits in ferritin, astacin, and other 'buffer' proteins. L-Leucine is an essential amino acid, meaning that the human body cannot synthesize it, and it therefore must be ingested [1]. Vanillin is a phenolic aldehyde, which is an organic compound with the molecular formula $\text{C}_8\text{H}_8\text{O}_3$. Its functional groups include aldehyde, hydroxyl, and ether [2]. Also vanillin has been used as a chemical [3], intermediate in the production of pharmaceuticals and other fine chemicals.

Noorjahan et al. [4] studied the spectroscopic characterization and biological evolution of ortho vanillin pramipexole Schiff base metal complexes. The synthesis of Schiff base ligand resulted from the condensation of Pramipexole(N6-propyl-4,5,6,7-Tetrahydro-,1,3-benzothiazole-2,6-diamine) with O-Vanillin (2-hydroxy-3-methoxy benzaldehyde). Using this bidentate ligand, complexes of Cu(II), Ru(II) with general formula ML_2 have been synthesized and its complexes were synthesized and characterized using different physico-chemical studies as elemental analysis, FTIR, ^1H NMR, conductivity, magnetic properties, thermal analysis, and their biological activities. The elemental analysis data suggest that stoichiometry to be 1:2 [M:L]. All the complexes are non electrolytic in nature as suggested by molar conductance measurements. Infrared spectral data indicate the co-ordination between ligand and central metal ion through deprotonated phenolic oxygen and azomethine nitrogen. In addition the authors have been screened the compounds for biological activity. It was found that the compounds have shown activity against the organisms like Escherichia coli, Klebsiella and Bacillus subtilis. Parashuram Mishra [5] investigated the Kinetics and Mechanisms of Oxidation of 4-hydroxy -3-methoxy benzaldehyde (Vanillin) by Bi (V) in Aqueous Alkaline medium, they found The title reaction was investigated in aqueous alkaline medium. A first dependence in Bi (V) concentration and a order in both Vanillin and alkali were obtained at the concentration studied. The effect of added products and the ionic strength of the reaction medium have no significant effect on the reaction rate. Effect of temperature on the rate of reaction has also

been studied and Eyring's activation parameters have been evaluated. A mechanism based on the experimental results is proposed and the rate law is derived.

The aim of this work is to synthesize, characterize and biologically evaluate the complexes of the Schiff base derived from vanillin and leucine.

2. EXPERIMENTAL

2.1 Materials

All chemicals used in this study were laboratory grade of BDH or Aldrich. They are which including: $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{PbCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and leucine, potassium hydroxide [KOH], Ethanol, vanillin (3-methoxy-4-hydroxy-benzaldehyde).

2.2 Synthesis of the Schiff Base

The (6.5 mmol) of amino acids leucine, was dissolved in aliquot quantity of EtOH (10 ml), then added slowly with constant stirring to an alcoholic solution (20 ml) containing KOH (0.36 g, 6.5 mmol). The solution was stirred for a one hour then filtered. To the filtrate the vanillin(6.5 mmol) dissolved in EtOH (20 ml) was added drop-wise with constant stirring. The resulting yellowish solution was evaporated under reduced pressure and kept at room temperature for three days.

Vanillin and Leucine which have chemical structure as shown in Equation (1).

2.3 Synthesis of the Complexes

The following solution, every one of $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ (0.273 g, 1.0 mmol), $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (0.19 g, 1.0 mmol), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.24 g, 1.0 mmol), $\text{PbCl}_2 \cdot 4\text{H}_2\text{O}$ (0.14 g, 1.0 mmol). In EtOH (15ml) was added drop-wise to an Ethanolic solution (25 ml) of Schiff base (0.283 g, 1.0 mmol) and stirred at room temperature and heating, Equation 2.

2.4 Bacterial Culture

Plate cultures of nutrient agar (OXID) medium were used for culture of bacteria. The medium was prepared by dissolving of powder in 1liter of sterile distilled water. Then the medium was sterilized by autoclaving at 121°C for 15 minutes. The bacteria were cultured and

incubated at 37 °C for 24h. The antibacterial tests were assayed according to the diffusion method. The strains of bacteria used were Gram-positive bacteria (*Staphylococcus aureus*). All strains were isolated from patients in medicine academe. The identity of all the strains was confirmed. A bacterial suspension was prepared and added to the sterilized medium before solidification under aseptic condition.

Different weights of amino acid Schiff base complexes, Co(II), Fe(II), pb(II), Ni(II), (0.1 g from complex in 1 litter) were placed on the surface of the culture and incubated at 37 °C for 24 h. After incubation the average of inhibition zones recorded (μm).

2.5 Anti Fungi Test

Plate cultures of separated agar medium were used for culture of fungi. the medium was prepared by dissolving 32 g of powder in 1litter of sterile distilled water. Then the medium was sterilized by autoclaving at 121 °C for 15 minutes. The fungi were cultured and incubated at 28 °C from 2 to 3 days. The anti fungi tests were assayed according to the diffusion method. used were fungal species yeast (*Rizopa*). All strains were isolated from patients in medicine academe. The identity of all the strains was confirmed. A fungi suspension was prepared and added to the sterilized medium before solidification under aseptic condition.

Different concentrations of Schiff base complexes were placed on the surface of the culture and incubated at 28 °C from 2 to 3days. After incubation, the average of inhibition zones recorded (μm).

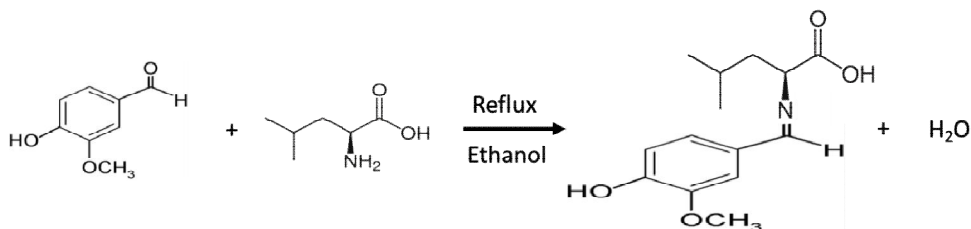
2.6 Measurements

The conductivity values of the prepared complexes were measured by using (conduct meter) type HANA conductometer at central Lab of the Faculty of Science, Omar El-Mukhtar University. The melting point was measured by using machines type (Melting point Apparatus SMP3). The infrared spectra of the Schiff base and their metal complexes were taken in potassium bromide discs using the I.R (Type thermo FT-IR 380Nicolet company) spectrophotometer covering the range from 500 to 4000 cm^{-1} . The electronic absorption spectra were measured using (spectrophotometer model 800 DU) covering range from 200 to 400 nm, the spectra of the ligand were measured by used quartz cell.

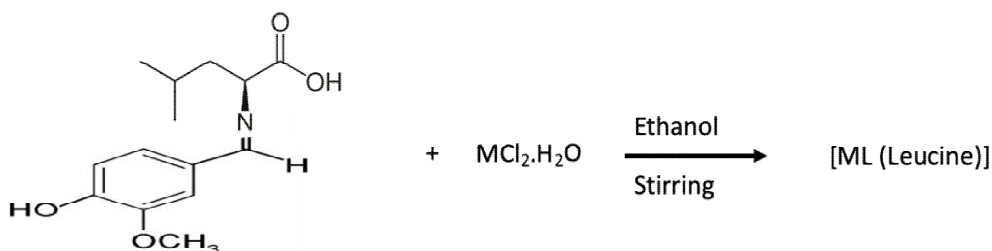
3. RESULTS AND DISCUSSION

3.1 The Physical Properties Schiff Base of the Complexes

Table 1 shows the colour and molar conductivity of the syntehsized Schiff base and the complexes.



Equation 1. Synthesis of the Schiff base



Equation 2. Reaction of formation of complexes between Schiff Base ligand with metal salts
Where M refers to the metal ion (i.e. Co, Ni, Fe and Pb)

Table 1. Physical properties and molar conductance of the Schiff base complex vanillin with leucine

Complex	Color	M.P. (°C)	E .c $\text{sm}^2 \text{mol}^{-1}$
Schiff base of leucine	Dark brown	<350	23.1
Co(II)	Dark green	<350	22.49
Pb(II)	Brown	237	24.27
Ni(II)	Brown	233	24.21
Fe(II)	Black	225	25.06

Table 1 showed the colour of ligand was change from brown colour of free ligand to several different shades of colour of the complexes according to the type metal, this change mainly due to the effect the linkage between the Schiff base and for to the different of electrons in 3d orbital's, where during the attracting between the Schiff base and the metal the electrons which are in d orbital and portion them for group the high and less in energy ,the magnetic frequency beam is proportion with the different in energy between the two states energy in atom. Some electrons rise into energy high level. And ability nothingness the atom on absorb several from the beam frequencies, the colour of the complex depended on: Number electrons in orbital d for metal and nature ligand whenever increase strongly ligand increasing the difference in energy between the two groups 3d the separated [6].

The results of the melting point of the studied complexes showed different values between the free ligand and complexes, this different mainly attributed to the bounded between the metals and the ligand [7]. The E.C values in the most of the studied complexes are low and ranged between (0.17-1.86 μS), it was reported that, the conductivity of the complexes depended on the free electrons which non conjugation in the last orbital's, where the conductivity become less when conjugating occur between the metal and the ligand and this mean these electrons are bounded [6]. The (I.R) spectra technique is one of the important methods to study the characterization of complexation between the ligand and the metal salts, because the metal salts don't give spectra, but when the metals conjugated with ligands, the complex give I.R spectra. The IR spectra was used to describe the structure of the prepared complexes, the IR spectra assignment of the metal complexes was achieved by comparing their vibration frequencies with those of the ligand: for comparative purposes and in order to facilitate the spectra assignment of the complexes, the IR

spectrum of I-Schiff base of valine was recorded. The obtained data are presented in Table 2.

Table 2. IR spectra bands of the schiff base

Functional group	Number wave length cm^{-1}
C-H Aromatic	3252
C-H Aliphatic	2860, 2954, 2999
O-H Carboxylic	3600
C=N	1663
C=O	-
C-O	1127
C-N	1340
CH ₂	1462
CH ₃	1397
N-H	3252
C=C	-

For the of Schiff base leucine IR spectra were shown in the Figs. 1-5 and presented in Table 2.

- 1- The band of Schiff base leucine located at 3252cm^{-1} are assigned to C -H Aromatic the first band of Schiff base leucine is shift to higher frequency is all complexes excepted Ferrous complex and Cobalt complexes are disappeared.
- 2- The band C-H Aliphatic located at 2999cm^{-1} are shifted to lower frequency in all complexes.
- 3- The band OH carboxylic appear in 3700cm^{-1} are shifted to higher in frequency in all complexes excepted Nickel complex.
- 4- The N-H band located at 3252cm^{-1} are shifted to higher frequency in case Nickel complex, Lead complex, Cobalt complex are disappeared in case Ferric complex .
- 5- The band C-N located at 1340cm^{-1} shifted to lower frequency in all complexes except Ferrous complex, Cobalt complex are disappeared.
- 6- The band C=N appear in 1663cm^{-1} shifted to lower frequency in all complexes except in case Ferric complex are shifted to higher are disappeared in case Cobalt complex.

- 7- The band C=O are disappeared all complexes except Copper complex located at 1671 cm^{-1} .
- 8- The band C=C appear are disappeared in case Schiff base leucine but for the another located in all complexes.
- 9- The band CH_2 located at 1462 cm^{-1} are shifted to higher frequency in case of Lead complex, Cobalt complex are shifted to lower frequency in case Nickel complex, Ferric complex.
- 10- The band CH_3 appear in 1397 cm^{-1} are completely disappeared in all complexes.

3.2 UV Spectrophotometric Studies

In polar or hydrogen bonding solvents with permanent dipole moment for polar solute, blue shift occurs of λ_{max} with increasing solvent polarity with the presence of "Frank Condon" phenomena. If the excited state-dipole moment is less than that of the ground state, blue shift of λ_{max} occurs with increasing solvent polarity.

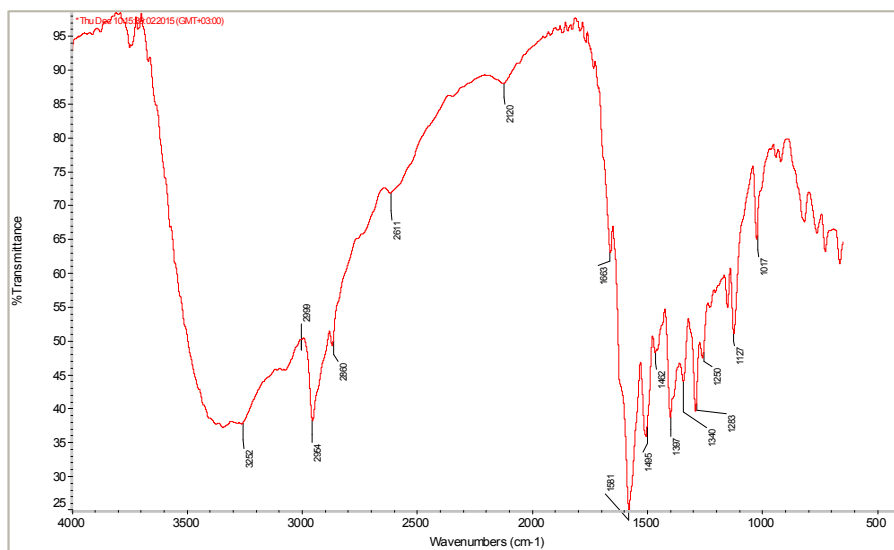


Fig. 1. Infrared spectra of Schiff base

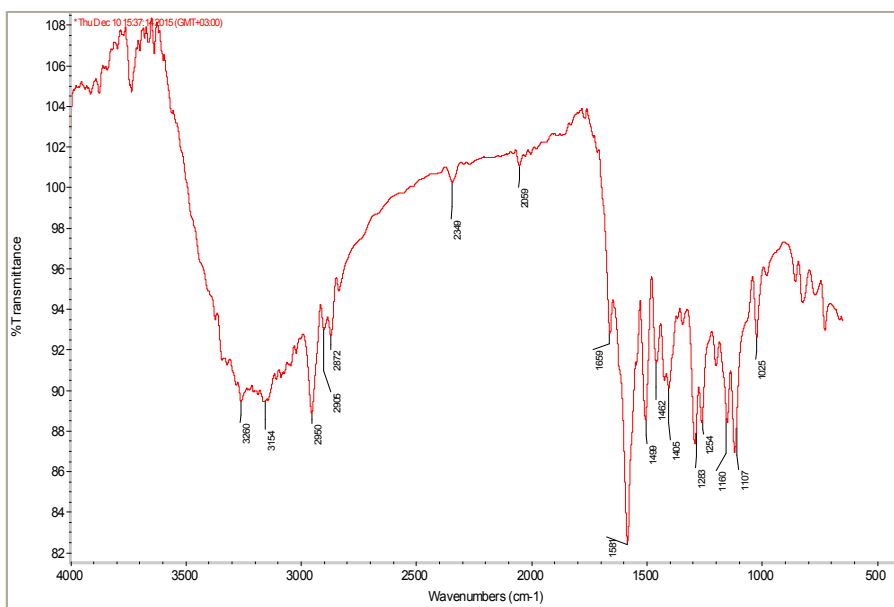


Fig. 2. Infrared spectra of Ni (II) complex

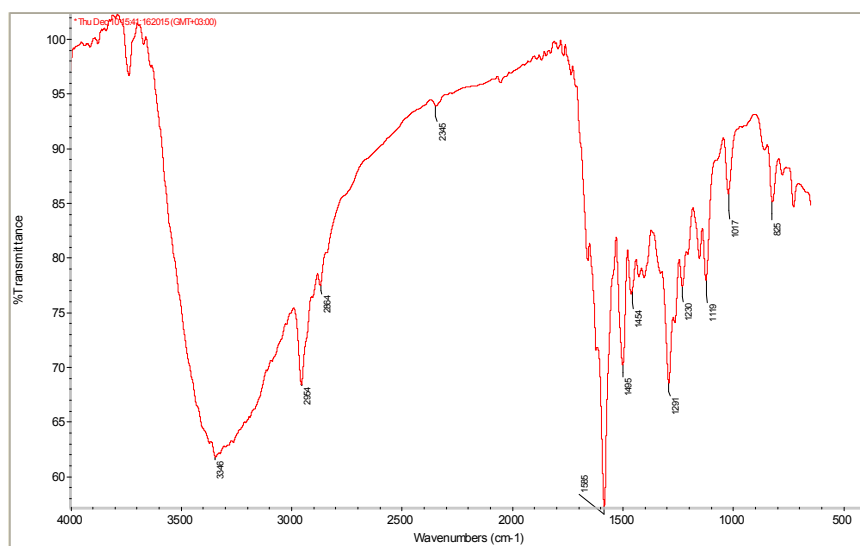


Fig. 3. Infrared spectra of Co(II) complex.

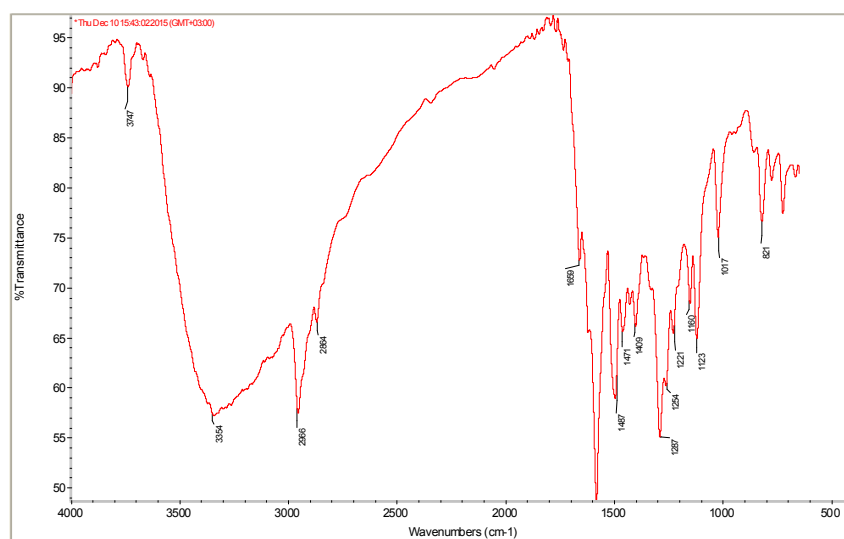


Fig. 4. Infrared spectra of complex

Table 3. IR spectra of complexes

Complex group	Co(II)	Pb(II)	Ni(II)	Fe(II)
C-H aromatic	-	3354	3260	-
C-H aliphatic	2864,2945	2864,2966	2872	2868,2962
OH Carboxylic	3700	3747	3700	3730
N-H	3346	3354	3260	-
C-H	-	1287,1254,1121	1283	-
C=N	-	1659	1658	1667
C-O	1119	1123	1107	1123
C=O	-	-	-	-
C=C	1454,1495	1409,1471,1487	1499	1434
CH ₂	1454	1471	1462	1434
CH ₃	-	-	-	-

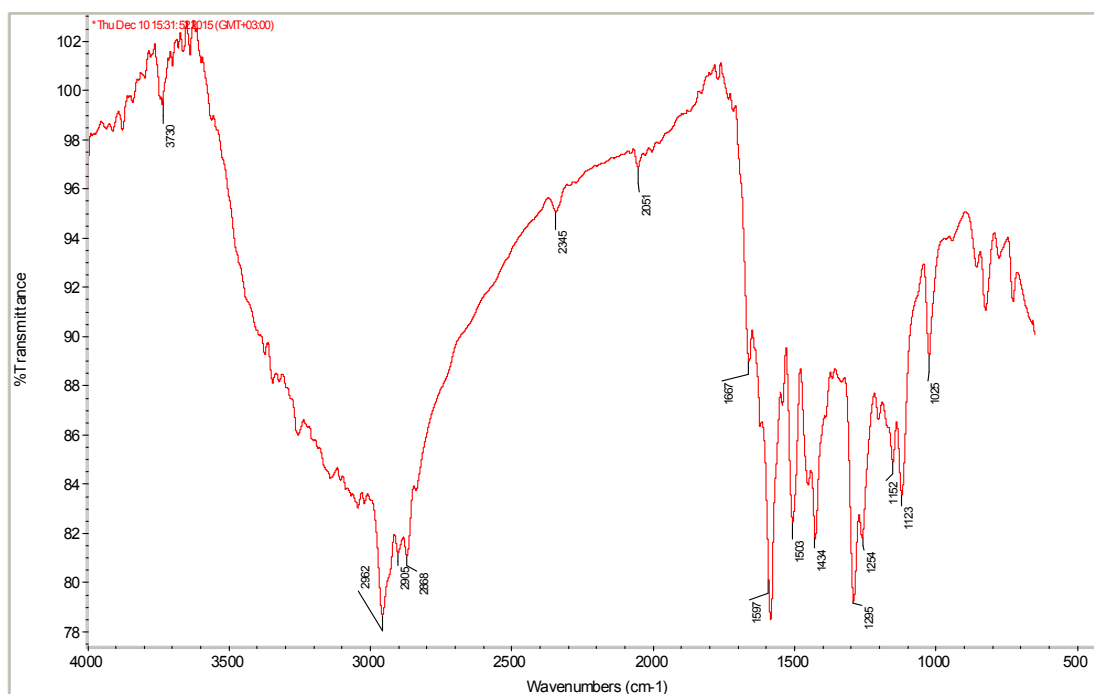


Fig. 5. Infrared spectra of Fe(II) complex

This explains the shift of $n-\pi^*$ transition on hydrogen bonding, relative to hydrocarbon solvent. In general, the functional group with high bond moments are involved in H-bond formation [8]. The process of the reaction in the first case leads to a blue shift of the maximum absorption and in the second case a red shift occurs. It is expected that in the presence of polar solvent, accumulation of H-bonding forces occurs depending on many factors: The magnitude of the charge in dipole moment during the electronic transitions, the solvent dipole moment value, and the size of solvent and solute molecules [9]. Many empirical single solvent polarity parameters have been introduced and have had varying degrees of success correlating solvent-dependant data. Nevertheless, little effort has been devoted to studying the various parameters in relation to each other. Katritzky et al. [10] had undertaken a comprehensive study of the effectiveness of the better known solvent polarity parameters over a wide variety of solvent-dependent phenomena (spectroscopic, kinetic and equilibrium) with the aim of determining the most successful measure of solvent "polarity". Since it transpires that no single parameter can deal effectively with all the types of phenomenon which vary with solvent.

Electronic spectra of Schiff base leucine and complexes in presence of different values of λ_{max} are illustrated in Figs. 6-9.

The λ_{max} of Schiff base leucine and band appear strongly red shifted are value 308nm, while all complexes are blue shifted in presence to be at Ni(II) 306nm and pb(II) are 305nm, and Fe(II) are 304 nm, due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

3.3 Antibacterial activities of the leucine Schiff base complex

Table 4 and Figs. 10-11 display the zone of bacterial growth inhibition of the Schiff base leucine of the divalent metal ion Co(II), pb (II), Ni(II), and Fe(II) complexes.

The effect of the Schiff base leucine complex on bacteria was recorded only against Escherichia coli and Staphylococcus aureus. No effect was observed against Klebsilla. The results show the reduction of inhibition zone with the reduction of the compounds weight placed on the bacterial culture. In contrast, no antibacterial effect was observed with leucine Schiff base and Co(II), pb(II), Ni(II) and Fe(II) complexes against all bacteria tested.

Table 4. The effect of leucine Schiff base complexes on bacterial growth of inhibition zone millimetre, (-) No growth

Sample	Schiff base leucine		Fe(II) complex		Co(II) complex		Ni(II) complex		pb(II) complex	
	0.1 mg	0.2 mg	0.1 mg	0.2 mg	0.1 mg	0.2 mg	0.1 mg	0.2 mg	0.1 mg	0.2 mg
bacterial	22 mm	7 mm	-	-	-	-	-	-	-	-
<i>Staphylococcus aureus</i>	-	-	-	-	-	-	-	-	-	-
<i>Rizopus</i>	-	-	-	-	-	-	-	-	-	-
<i>E.coli</i>	11 mm	-	-	-	-	-	-	-	-	-
<i>Klebsiella</i>	-	-	-	-	-	-	-	-	-	-

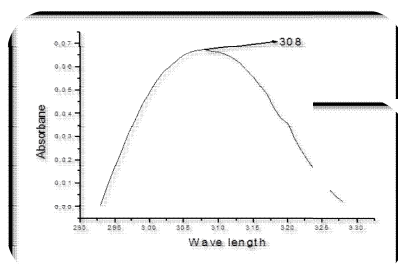


Fig. 6. The λ max of Schiff base (vanillin + leucine) Complex

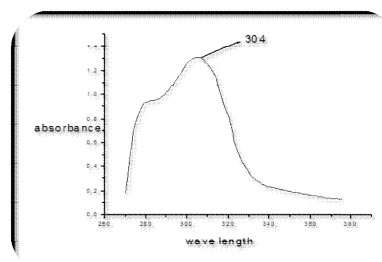


Fig. 7. The λ max of Schiff base (vanillin + leucine) with Fe(II) Complex

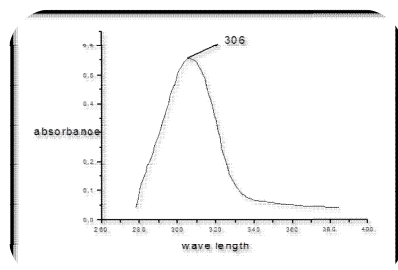


Fig. 8. The λ max of Schiff base (vanillin + leucine) with Ni(II) Complex

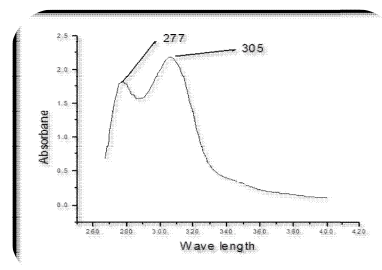


Fig. 9. The λ max of Schiff base (vanillin + leucine) with pb(II) Complex

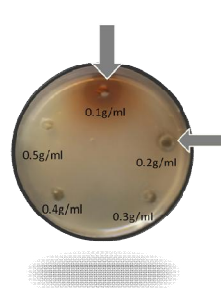


Fig. 10. Effect (1,2) of Schiff base leucine complex on *Staphylococcus aureus*

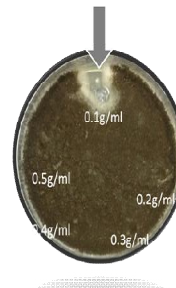


Fig. 11. Effect (1) of Schiff base leucine complex on *E. coli*

4. CONCLUSION

In this paper, we have reported the synthesis and characterization of some complexes of Co(II), Pb(II), Ni(II) and Fe(II) ions with a Schiff base derived from (3-methoxy-4-hydroxy-benzaldehyde with leucine). The structure of the complexes has been characterized on the basis of various spectroscopic techniques. molar conductance measurements, colour, melting point, infrared and electronic spectra. All the results indicate that the E.C. values in the most of the studied complexes are low and ranged between (0.17-1.86 μ S), reveal a non-electrolytic nature. the IR spectra assignment of the metal complexes was achieved by comparing their vibration frequencies with those of the ligand: for comparative purposes and in order to facilitate the spectra assignment of the complexes. The electronic spectra data of the Schiff base and its complexes displayed the proper transitions and the expected geometrical structure for the prepared complexes. The Schiff base and its complexes were tested for antimicrobial activity against gram-positive bacteria; Staphylococcus aureus, gram negative bacteria; E-Coli and Klebsiella, in addition Rizopus as fungal. The effect of the Schiff base leucine complex on bacteria was recorded only against staphylococcus aureus and Escherichia coli. No effect was observed against klebsilla. In contrast, no antibacterial effect was observed with leucine Schiff base and Co(II), pb(II), Ni(II) and Fe(II) complexes against all bacteria tested.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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