

Preparation , spectroscopic investigation and biological activity of a Schiff base metal complexes

HamadM.AdressHasan*, Fatimah A. Abdulsayid** and Roaa A. Bouagila*

*Chemistry department, Faculty of Science, Omar Al–Mukhtar University, Albaydha-Libya.

**Chemistry Department, Faculty of Science, Benghazi University, Alkufra-Libya.

Abstract: Some of complexes prepared by reaction between Schiff base (3-methoxy-4-hydroxy-benzaldehyde with Valine), the manufactured new complexes were characterized by I.R., colour and melting pointdetermination. Different biological applications were applied on the synthesized complexes.

Key words: Schiff base, vanillin, valine, Complexes

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I. Introduction

Vanillin compound belongs to the class of phenolic aldehyde, that class of organic compounds is characterized by the molecular formula $C_8H_8O_3$. Their functional groups comprise of hydroxyl, aldehyde and ether functional groups^[1]. Additionally, vanillin has been used as a chemical^[2] and as an intermediate in the manufacture of pharmaceuticals as well as other chemicals. In 1970s, over half of the world's vanillin production was mainly used in the synthesis of other chemicals, however, as of the year 2004, that traditional use has accounted for approximately 13% of the market for vanillin^[3]. The other compound **Valine** is an α -amino acid with the chemical formula $HO_2CCH(NH_2)CH(CH_3)_2$. L-Valine is one of 20 proteinogenic amino acids. It is an essential amino acid; hence it must be ingested, usually as a component of proteins. It is synthesized by plants via several steps starting from pyruvic acid^[4]. The synthesis and characterization of Schiff base complexes have been a source of interest to many chemists^[5-6]. Schiff bases can be usually synthesized from an amine moiety (aliphatic or aromatic) and a carbonyl compound via nucleophilic addition to form a hemiaminal, which in turn is subjected to dehydration to generate an imine. In a standard reaction, 4,4'-diaminodiphenyl ether reacts with o-vanillin^[7]. Yan Zhang et al^[8] investigated the nature of interaction between tryptophan-vanillin Schiff base and herring sperm's DNA, in their study, they investigated the kind of interaction of the Schiff base (K[HL]) with herring sperm DNA via fluorescence, UV-Vis absorption and viscosity methods in a physiological environment of pH 7.40. The Schiff base was derived from L-tryptophan and vanillin. A binding ratio of $n[K[HL]: nDNA = 5:1$, and an apparent molar absorption coefficient of $(K[HL]-DNA) = 4.98 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ were confirmed by the mole ratio method. Additionally, the binding constants of $KB (301K) = 1.94 \times 10^5 \text{ L mol}^{-1}$ and $KB (310 K) = 1.09 \times 10^5 \text{ L mol}^{-1}$ were obtained by the double reciprocal method. Sham WaliQurban^[9] investigated the synthesis and characterization of some Schiff base transition metal complexes derived from isonicotinic hydrazide and o-vanillin. They obtained a new series of transition metal complexes of Cu(II), Ni(II), Co(II), Cd(II), Zn(II) and VO(IV) that were synthesized from the Schiff base (L) derived from isonicotinic acid hydrazide and o-vanilline. Metal analysis helped to provide the structural features in addition to: molar conductance, magnetic susceptibility, IR and UV-Vis spectral studies. The obtained data showed that these complexes have the composition of ML₃ type for Cu(II), Co(II), Ni(II) while ML₂ type for Zn(II), Cd(II) and VO(IV). According to the UV-Vis and the magnetic susceptibility data of the complexes, an octahedral geometry was suggested for Cu(II), Ni(II) and Co(II) metal ions. It also showed a tetrahedral geometry for Cd(II) & Zn(II) metal ions, however, (IV) metal ion was depicted as a square pyramidal geometry. Rizwana et al.^[10] conducted some studies on Zn(II), Ni(II) and Cu(II) complexes of a Schiff base derived from o-vanillin and N-Allyl Thiourea in the form of synthesis, followed by characterization as well as antimicrobial studies. They observed that the present study, a new Schiff base ligand was synthesized by condensation of o-vanillin with allylthiourea in 1:1 molar ratio. The Schiff base metal complexes of Zn(II), Ni(II) and Cu(II) were prepared using the metal salts and the synthesized Schiff base ligand in 1:1 molar ratio. The metal complexes were characterized using molar conductivity, UV-Visible and IR spectra. The ligand and its metal complexes were screened for antibacterial activity against different types of bacteria such as: Klebsiella pneumonia, Bacillus cereus and Pseudomonas aeruginosa. Additionally, fungicidal activity against Aspergillus niger, Candida albicans and Candida kefyr was also investigated. The obtained results suggested that the prepared compounds showed higher potency against all the microbes under examination.

The main aims of the present paper was to firstly: prepare a Schiff base (derived from the reaction of vanillin and valine) and its complexes with Co(II), Pb(II), Ni(II), and Fe(II) ions and secondly, to illustrate their geometrical structures with the aid of different physical characterisation techniques.

II. Experimental

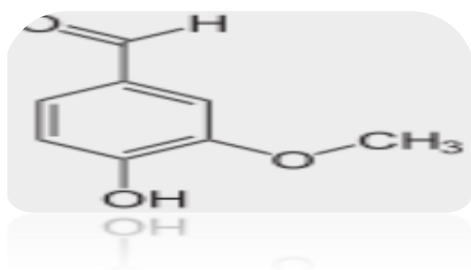
Materials

All the chemicals used in this study were of laboratory grade or equivalent. Materials used were: CoCl₂.4H₂O, NiCl₂.4H₂O, PbCl₂.4H₂O, FeCl₂.4H₂O, valine, potassiumhydroxide [KOH], ethanol, and vanillin (3-methoxy-4-hydroxy-benzaldehyde).

Preparation of the Schiff base

The (6.5mmol) of the amino acid valine was dissolved in aliquot quantity of EtOH (10 ml), then slowly added with a constant stirring to an alcoholic solution (20ml) that contained KOH (0.36g, 6.5mmol). The solution was then stirred for approximately one hour followed by subsequent filtration. To the filtrate, the vanillin(6.5mmol) dissolved in EtOH (20ml) and was added by dropwise with constant stirring. The resulting yellowish solution was left to evaporate under reduced pressure and was finally kept at room temperature for three days.

Figures (1-2) shows chemical structures of Vanillin and Valine, respectively.



Figure(1): Chemical structure of vanillin

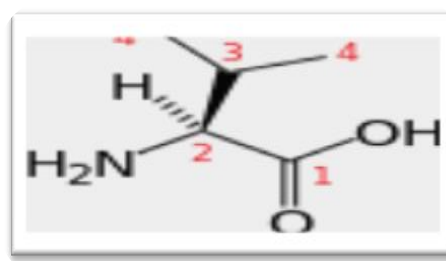


Figure (2): 2-amino-3-methylbutanoic acid (valine)

Preparation of the valine Schiff base complexes

1 mmol of Every one of the following solutions CoCl₂.4H₂O(1mmol,0.237g), NiCl₂.4H₂O(1mmol,0.19g), PdCl₂.4H₂O(1mmol,0.142g), and FeCl₂.4H₂O(1.0mmol,0.24g), in EtOH (15ml) was added dropwise to an Ethanolic solution (25ml) of Schiff base (0.269g, 1.0mmol) and stirred at room temperature and heated.

Bacterial culture

Plate cultures of nutrient agar (OXID) medium were used for culture of bacteria. The medium was prepared by dissolving powder in 1 liter of sterile distilled water. The medium was then 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 (Staphylococcus aureus). All strains were isolated from patients in the internal medicine department. The identity of all the strains was confirmed. A bacterial suspension was then prepared which was subsequently added to the sterilized medium before solidification under aseptic condition.

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

Anti-fungi test

Plate cultures of separated agar medium were used for the culture of fungi. The medium was prepared by dissolving 32g of powder in 1 liter 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 for 2 to 3 days. The anti-fungi tests were assayed according to the diffusion method, the used fungal species yeast was (Rizopa). All strains were isolated from patients in medicine Ward. The identity of all the strains was confirmed. A fungi suspension was

prepared and then added to the prepared sterilized medium before been subjected to solidification under aseptic condition. Different concentrations of Schiff base complexes were placed on the surface of the prepared culture and then incubated at 28⁰C for 2 to 3days. After incubation, the average of inhibition zones was recorded (μ m).

Measurements

The conductivity values of the manufactured complexes were measured using conductometer type HANA conductometer, 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 obtained in potassium bromide discs using the I.R (Type thermo FT-IR 380 Nicolet company) spectrophotometer covering the range from 500 to 4000 cm^{-1} . The electronic absorption spectra were measured using (spectrophotometer model 800 DU) covering the range of 200 to 400 nm, the spectra of the ligand were measured using quartz cell.

III. Results and Discussion

Physical properties of the Schiff base of the complexes

Table (1) gives the colour and molar conductivity of the prepared Schiff base and its complexes.

Table (1): Physical properties and molar conductance of the Schiff base complexes vanillin with valine

Complexes	Colour	m.p. ($^{\circ}$ C)	E.C $\text{sm}^2 \text{mol}^{-1}$
Schiff base of valine	Dark brown	316	.1125
Co(II)	Dark green	<350	23.79
Pb(II)	Brown	<350	23.31
Ni(II)	Green	337.7	25.31
Fe(II)	Black	337	23.65

The Colour

Tables (1) shows the colour of ligand was changed from brown colour of free ligand to several different colours according to the type of the metal, this change could be due to the effect of 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 high energy level and ability nothingness the atom on absorb several from the beam frequencies, the colour of the complex depended on: Number of 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^[11].

Melting point

The results of the melting point determination of the studied complexes showed different values between the free ligand and complexes, this difference could be attributed to the bounding between the metals and the ligand^[12].

Electrical Conductivity

The E.C. values in most of the studied complexes were low and ranged between (0.17-1.86^uS). It was reported that the conductivity of the complexes depended on the free electrons which are not in conjugation in the last orbital's, where the conductivity becomes less when conjugating occur between the metal and the ligand which could mean that these electrons are bounded^[11].

IR spectra studies:

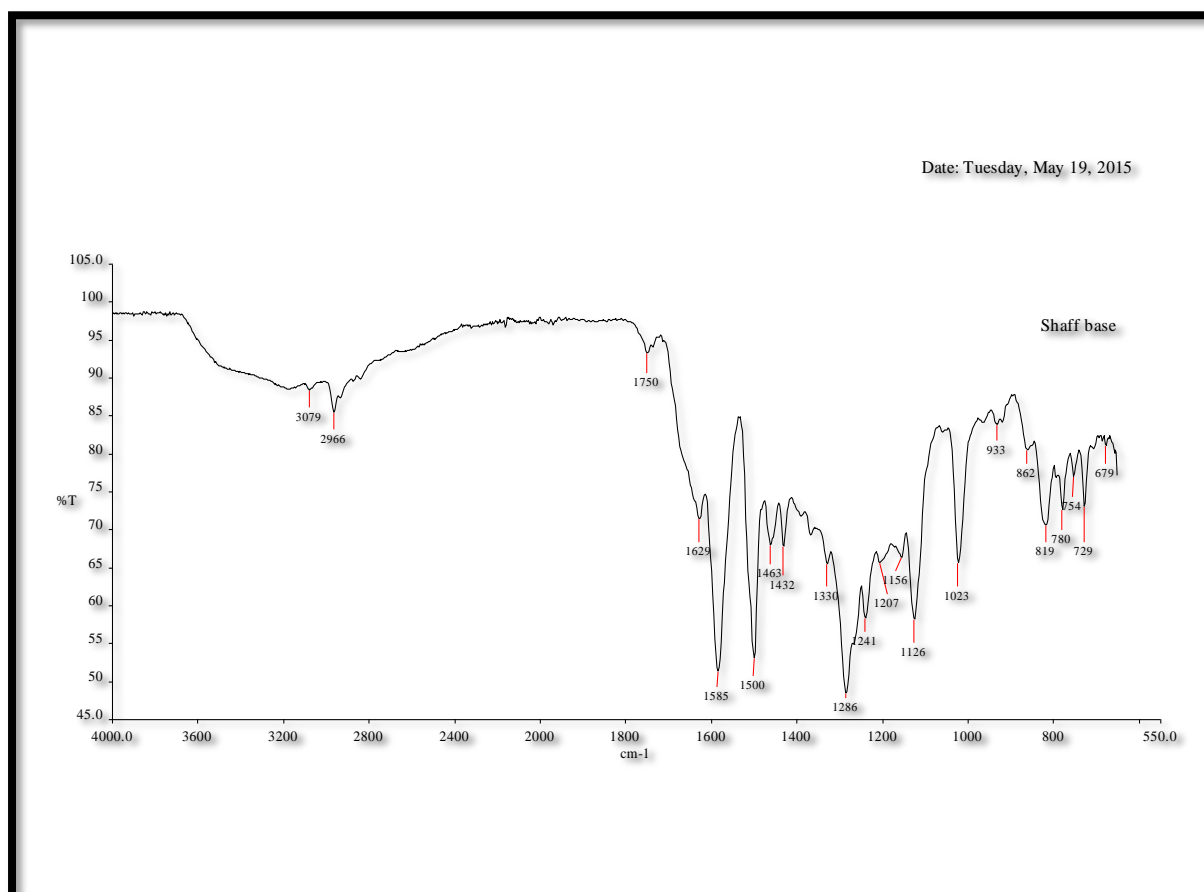
The (I.R.) spectra technique is one of the important methods to study the characterization of complexation between the ligand and the metal salts, because the metal salts do not give spectra, but when the metals conjugated with ligands, the complex give I.R. spectra.

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 the Schiff base of Valine was recorded. The obtained data are presented in table (2) below.

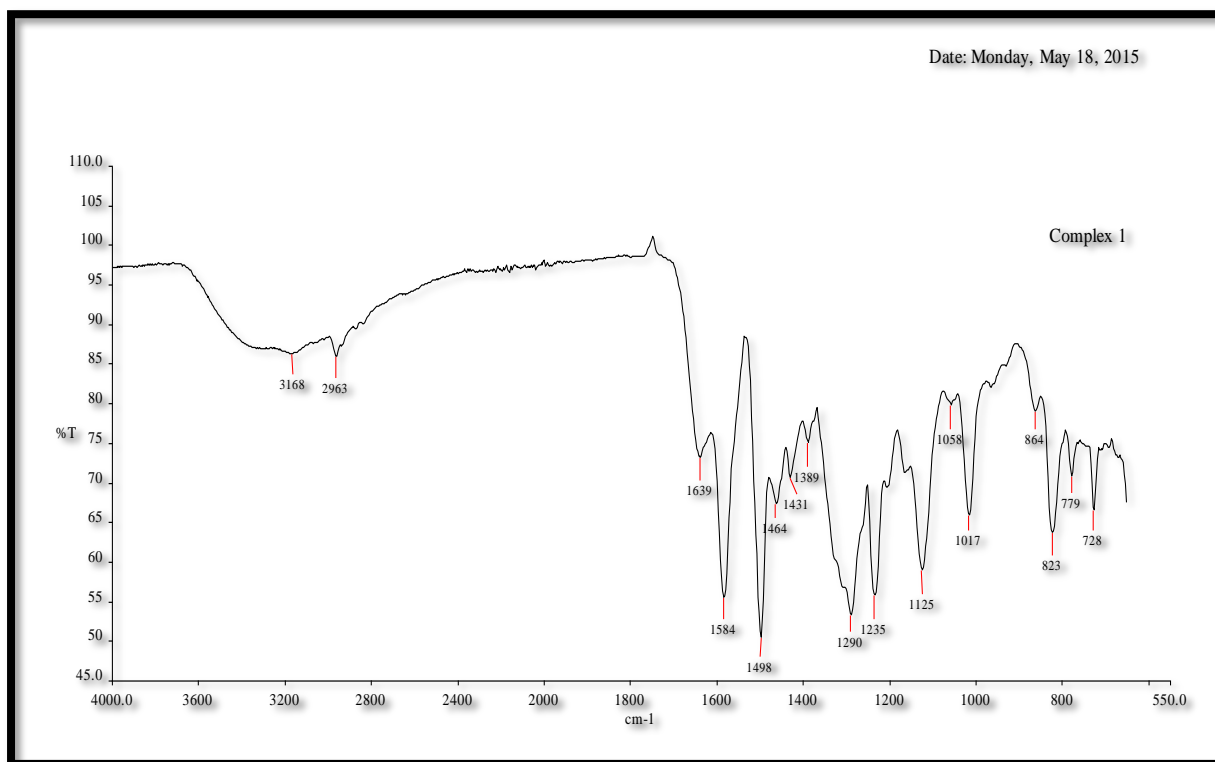
Table (2):The fundamental bands of the Schiff base of Valine

Functional group	Number wave cm ⁻¹ Schiff base of valine
C-H Aromatic	3079
C-H Aliphatic	2966
C=N	1629
C=O	1750
C=C	1585
CH ₂	1463
CH ₃	1330
C-O	1286
CN	1126

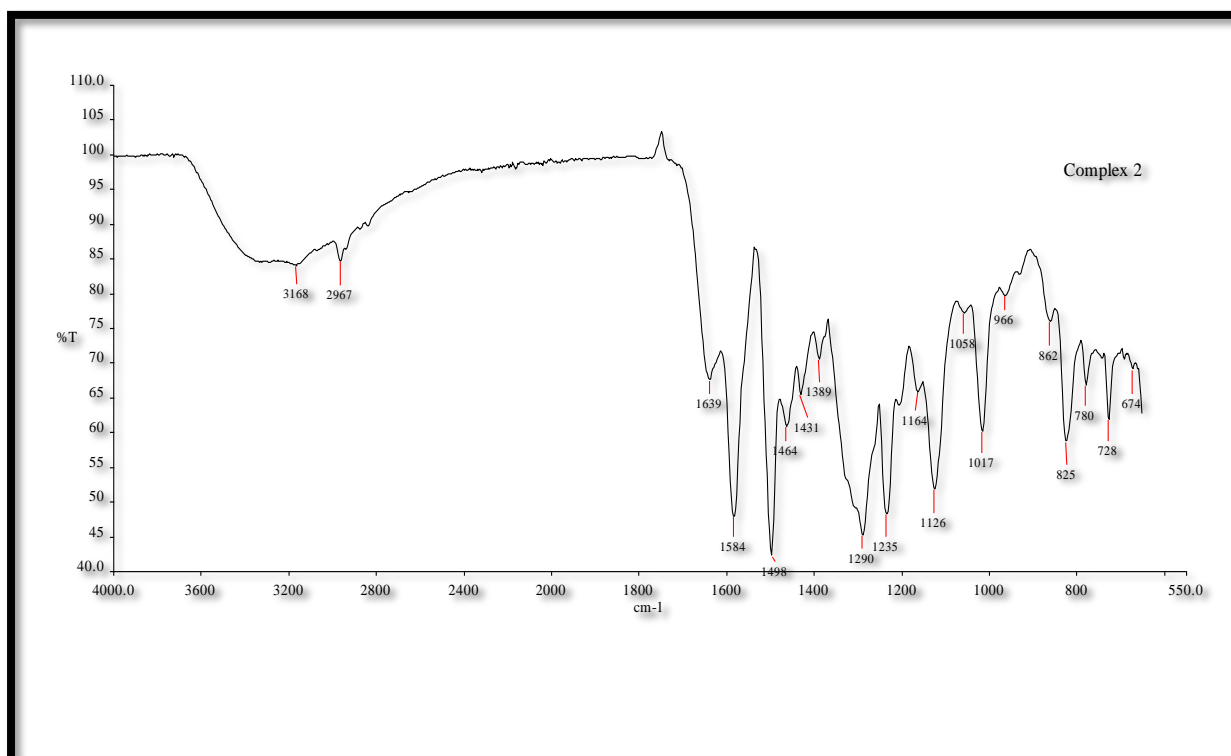
On the other side of the IR spectra of the Schiff base, valine complexes where presented in table (2)and shown in Figures (3-7).



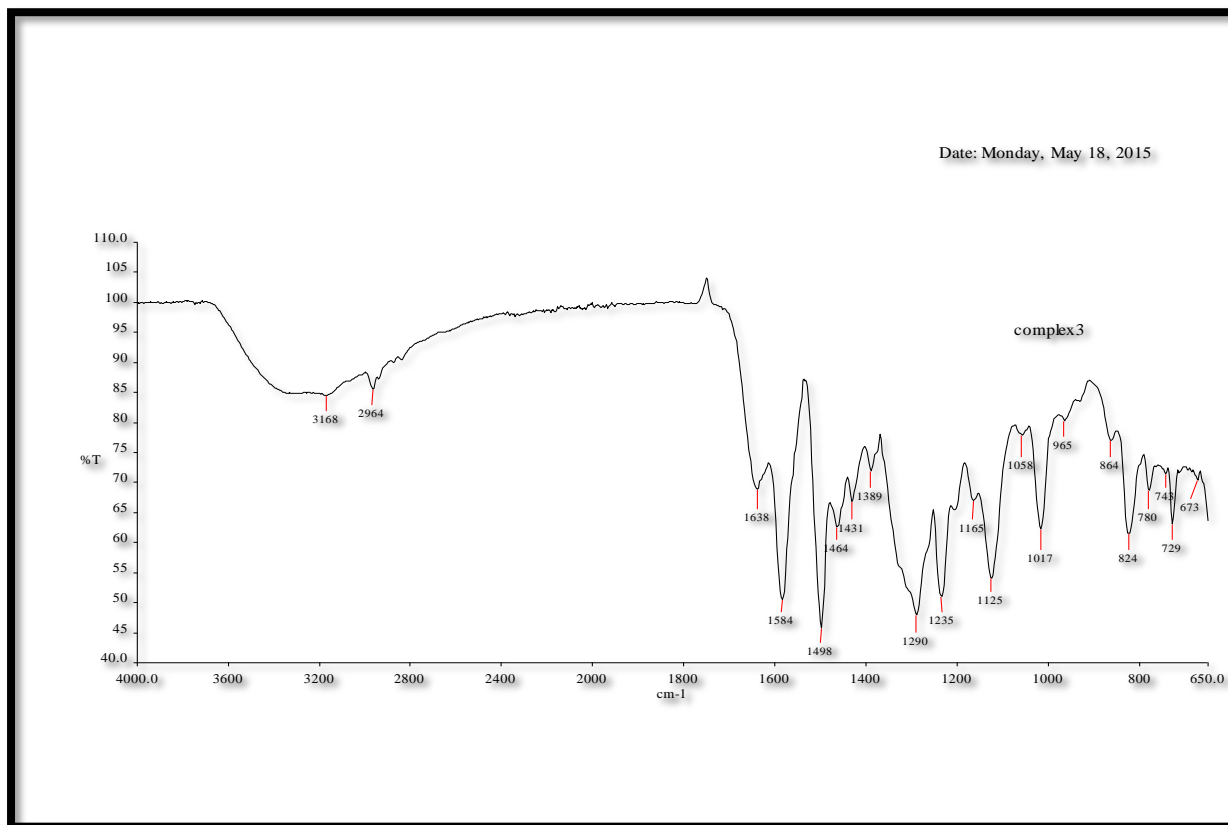
Figure(3):Infrared spectra Schiff base of Valine complex



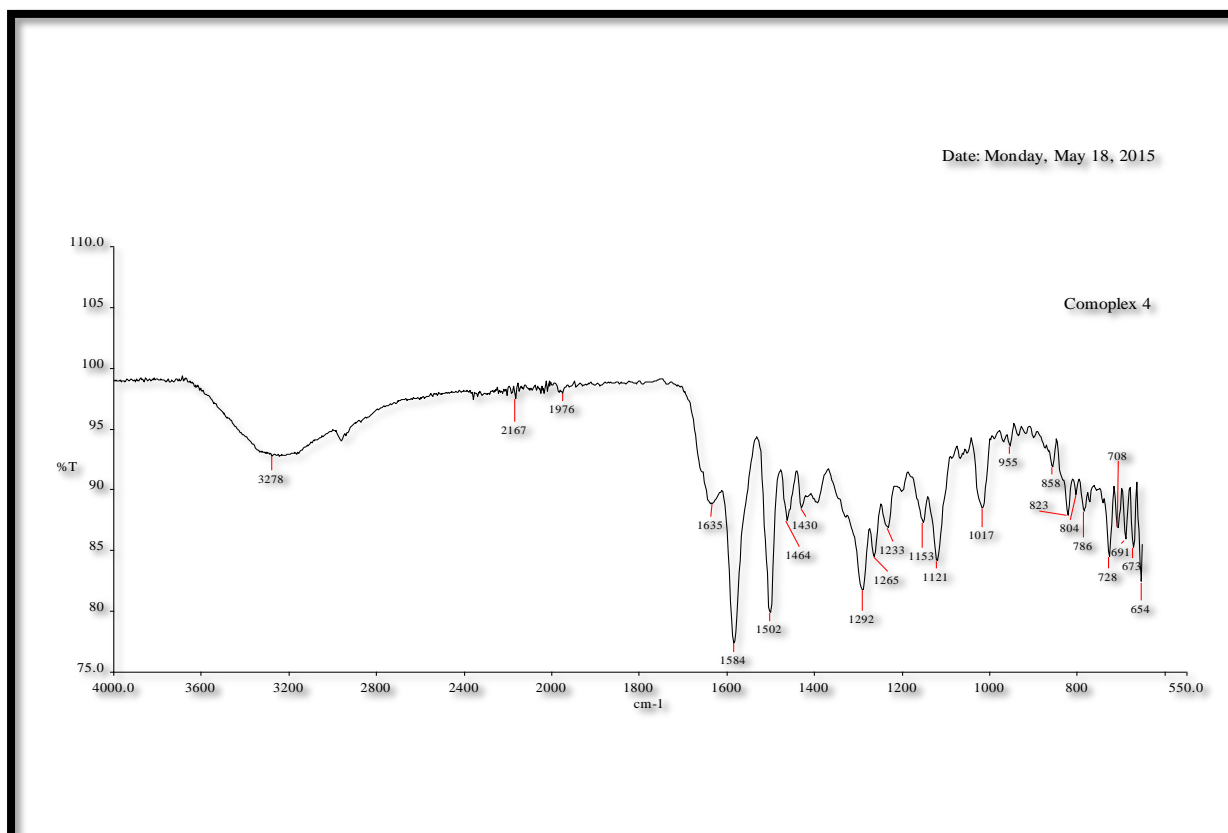
Figure(4):Infrared spectra of Co(II) from schiff base Valine complex.



Figure(5):Infrared spectra of pb(II) from schiff base of valine complex.



Figure(6):Infrared spectra of Ni(II) schiff base of valine complex.



Figure(7):Infrared spectra of Fe(II)from schiff base of valine complex.

Table(3): The I.R. spectra of the Schiff base Valine complexes.

Complexes group	Co(II)	Pb(II)	Ni(II)	Fe(II)
C-H	3168	3168	3168	3278
C-H	2963	2967	2964	2900
C=N	1639	1639	1638	1635
C=O	-	-	-	-
C=C	1498-1584	1498-1584	-	1584-1502
CH ₂	1464	1464	1464	1464
CH ₃	1389	1389	1389	1390
C-O	1290	1290	1290	1292
OH	-	-	-	-
C-N	1125	1126	1125	1121

1-The band of Schiff base valine at 3079 cm⁻¹ are assigned to C-H aromatic, respectively: the first band of the Schiff base valine shifted to higher frequency in Cobalt complex, Lead complex, Nickel complex and Ferric complex.

2-The band at 2966 cm⁻¹ of Schiff base valine are assigned to C-H aliphatic shifted to higher frequency in case of Lead complexes, but for the other complexes, shifted to lower as in the case of Cobalt complexes, Nickel complexes and Ferric complexes.

3-The band at 1629 cm⁻¹ of Schiff base valine assigned to C=N, the band are shifted to higher frequency in Cobalt complexes, lead complexes, Nickel complexes and Ferric complexes.

4-The band 1750 cm⁻¹ of Schiff base valine assigned to C=O in Ferric complexes, Nickel complexes, lead complexes, Cobalt complexes were disappeared.

5-The band C=C of Schiff base valine appear in 1585 and 1500 cm⁻¹ shift to lower frequency in cases Cobalt complexes, were disappeared in Nickel complexes.

6-The band CH₂ located at 1463 cm⁻¹ all complexes shifted to higher.

7-The band CH₃ appear at 1330 cm⁻¹ all complexes shifted to higher.

8-The band C-O located at 1286 cm⁻¹ all complexes shifted to higher.

UV-Visible Spectrophotometric studies

In hydrogen bonding or polar solvents with a permanent dipole moment for polar solute, blue shift usually occurs of λ_{max} with increasing solvent polarity at 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. This could explain the shift of n- π^* transition on hydrogen bonding, relative to hydrocarbon solvent. In general, the functional group with high bond moments are involved in H-bond formation^[13]. The process of the reaction in the first case leads to a blue shift of the maximum absorption, however, in the second case a red shift occurred. It could be expected that accumulation of H-bonding forces could occur in the presence of polar solvent, depending on many factors, such as: The solvent dipole moment value, the magnitude of the charge in dipole moment during the electronic transitions, and the size of solvent and solute molecules^[14]. Many empirical single solvent polarity parameters have been introduced which showed varying degrees of success in relation to solvent-dependent data. Nevertheless, to the best of our knowledge, a little effort has been taken to investigate deeper the various parameters in relation to each other. Katritzky et al^[15] had conducted a comprehensive study on the effectiveness of the better-known solvent polarity parameters over a wide variety of solvent-dependent phenomena (spectroscopic, kinetic and equilibrium) with the aim to determine the most successful measure of solvent "polarity". Since that no single parameter can deal effectively with all the types of phenomenon which vary with solvent.

The Schiff base (vanillin+valine) with complexes solvent of (DMF). Electronic spectra of Schiff base valine and complexes in presence of different values of λ_{max} are illustrated in Figures (8-12).

The λ_{max} of Schiff base valine gave band at 308 nm and pb(II) is due to n - π^* electronic transition^[16]. This band appeared strongly red shifted to at Co(II) 310 nm and 309 nm of Fe(II), Ni(II).

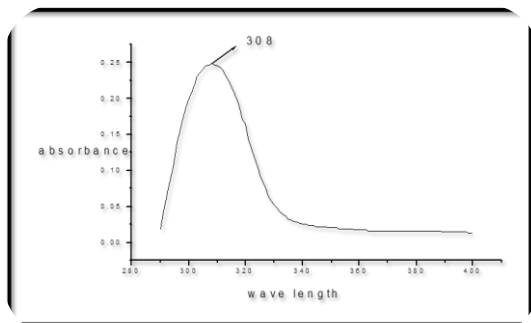


Figure (8): The λ_{max} of Schiff base (vanillin+valine) Complex

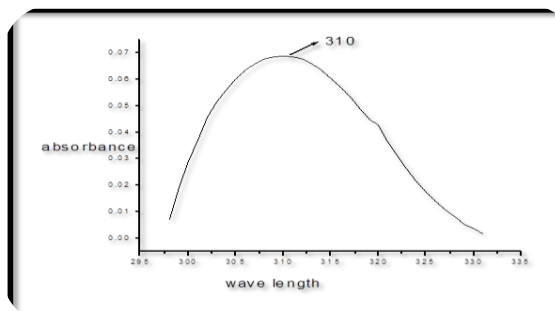


Figure (9): The λ_{max} of Schiff base (vanillin+valine) with Co(II) Complex.

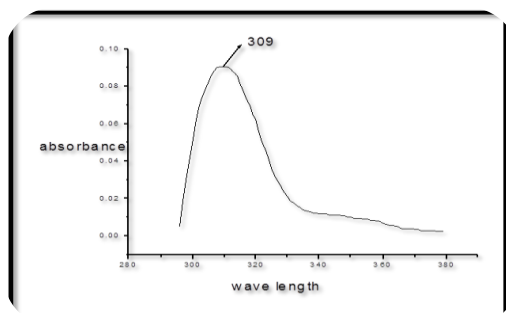


Figure (10): The λ_{max} of Schiff base (vanillin+valine) with Fe(II) Complex.

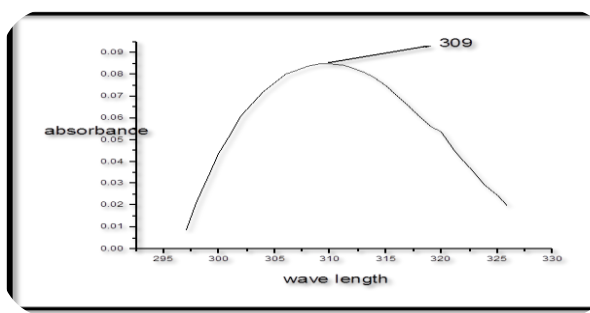


Figure (11): The λ_{max} of Schiff base (vanillin+valine) with Ni(II) Complex.

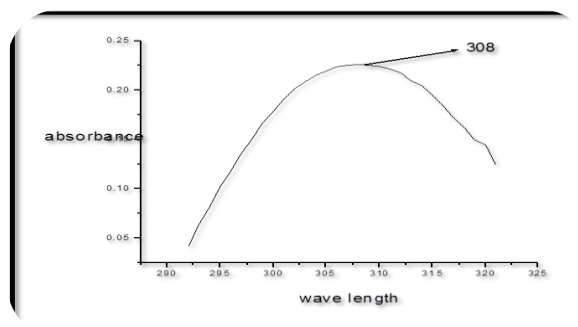


Figure (12): The λ_{max} of Schiff base (vanillin+valine) with pb(II) Complex.

Antibacterial activities of the valine Schiff base complex

Table (4) and Figures (13-19), show the inhibition zone of bacterial growth of the Schiff base valine of Co(II), pb(II), Ni(II) and Fe(II), complexes. Ni(II), Co(II) complexes have highest activity against staphylococcus aureus, Rizopus.

The results showed a reduction in the size of the inhibition zone in relation to a reduction in the compounds weight that was placed on the bacterial culture.

The effect Schiff base of valine complexes on bacteria was recorded only against staphylococcus aureus and Escherichia coli. No effect was observed against klebsiella. In contrast, no antibacterial effect was observed with Pb(II) and Fe(II) complexes against all bacteria tested.

Table (4):The effect Ni(II), Co(II) and valine Schiff base complexes on bacterial growth

sample	Schiff base valine		Ni(II)complex		Co(II)complex		Pb(II)complex		Fe(II) complex	
	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg
Bacterial	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg	0.1mg	0.2mg
Staphylococcus aureus	16mm	-	25mm	11mm	27mm	-	-	-	-	-
Rizopus	-	-	23mm	17mm	17mm	7mm	-	-	-	-
E.coli	19mm	-	-	-	20mm	-	-	-	-	-
klebsiella	-	-	-	-	-	-	-	-	-	-

Mean of inhibition zone millimetre

(-)No growth.

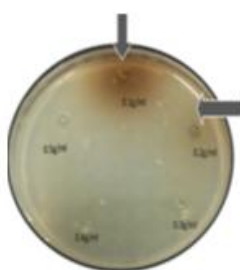


Figure (13): Effect (1,2) of Schiff base valine complex on Escherichia coli.



Figure (14): Effect (1) of Schiff base valine complex on Staphylococcus aureus.

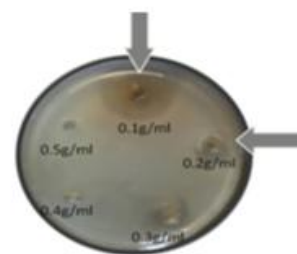


Figure (15): Effect (1,2) of Schiff base valine with Ni(II) Complex on Staphylococcus aureus.

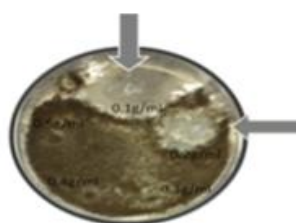


Figure (16):Effect (1,2) of Schiff base valine with Ni(II) complex on Rizopus.



Figure (17): Effect(1) of Schiff base valine with Co(II) complex on Staphylococcus aureus.

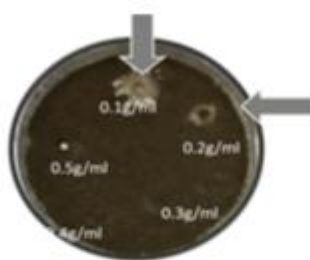
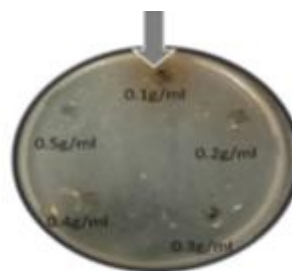


Figure (18): Effect(1,2) of Schiff base valine with Co(II) complex on Rizopus.



Figure(19): Effect(1) of Schiff base valine with Co(II) complex on Escherichia coli

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