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Research Article

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Synthesis and characterization of amino acid (phenylalanine) schiff bases and their metal complexes

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ABSTRACT

Schiff bases derived from the condensation of benzaldehyde or acetone and the amino acid phenylalanine in basic media using sodium hydroxide as a catalyst have been synthesized and their Co (II), Ni (II) and Cu (II) complexes have been prepared. The Schiff bases and their complexes that been prepared, were analyzed and characterized by using different techniques, such as elemental analysis, infrared and electronic spectra. The IR spectra, UV bands and atomic absorption analysis show that the Schiff base ligand forming chelates with 2 : 1 (ligand : Metal) stoichiometry. Some of prepared metal complexes were evaluated for in-vitro antibacterial activity against Negative and Positive Bacteria. The complexes showed significant anti bacterial activity.

Keywords: Characterization, Metal Chelate Complexes, Antibacterial, Amino Acids, Schiff Bases.

INTRODCTION

Amino acids are molecules containing an amine group, a carboxylic acid group and aside chain that varies between different amino acids. These molecules are particularly important in biochemistry (VOET D., 1993), where this term refers to amino acids with the general formula $H_2NCHRCOOH$, where R is an organic substituent. Amino acids containing uncharged amino groups, at physiological PH values, ay also undergo Schiff base formation, which presents another potential mechanism for metal complexes.

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also known as anils, imines or azomethines. Several studies (Kumar N., 2013 ,Gupta V. , 2013 ,Kumar L., 2011 , , ünve H., 2002) showed that the presence of alone pair of electrons in an SP^2 hybridized orbital of Nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility and the special property of C=N group, Schiff bases are generally excellent chelating agents especially when functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered-ring with the metal ion.

Schiff bases have been used extensively as ligands in the field of coordination chemistry, some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base compounds show, photochromosim and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms (Elerman Y.,2002).Schiff bases have appeared to be an important intermediate in a number of enzymatic, reactions involving interaction of enzyme with amino or carbonyl group of the substrate (Lehlinger L., , 1975).

Schiff base have been reported in their biological properties, such as, antibacterial and antifungal activities (Williams D., 1972, Adabiard Akani A., 2012)

Nowadays, the research field dealing with Schiff base coordination chemistry has been expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, biomedical application, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well-recognized and reviewed (Kumar N., 2013). Their metal complexes have widely studied because they have anticancer and herbicidal applications (Cozzi P, 2004, Kumar G, 2012). They serve as models for biologically important species.

EXPERIMENTAL SECTION

Materials and measurements

All chemicals used in this work were analytical analar grMade and used without further purification. Infrared spectra were recorded using KBR discs in the rang (4000-400 cm^{-1}) on(FT-IR ABB -MB 3000) spectrophotometer(mad in UK). Electrothermal melting point model SMP3 Stuart was used to determined melting point. Metal analysis were measured with (Phoenix-986) atomic absorption spectrophotometer(made in England). UV and Visible electronic spectra were recorded in the ג (190-1100nm) rang in DMSO solution using UV 1650 PC UV-Visible spectrophotometer Shimadzu.

Preparation of Schiff bases

The Schiff base were prepared by adding 10 ml of benzaldehyde or aceton ethanolic solution (0.01mol)gradually with stirring to the same volume of ethanolic solution of Phenylalanine (0.01mol) by gradual addition , adds sodium hydroxide ethanolic solution (0.01 mol) to the mixture during a period of 30 min. The mixture was heated under reflux for (5-6) hours . After cooling, the mixture was filtered, washed with ethanol several times and dried.

The prepared Schiff bases are soluble in water and in most organic solvents(Azzouz A.,2010).

Preparation of complexes

The the above solution of Schiff base (after reflux) , an ethanolic soluation (0.005 mol) of Co(II) , Ni(II), Cu(II) chloride salts was added gradually and the mixture were refluxed for 2 hours. Colored complexes precipitated out in each case , they were filtered and washed with ethanol several time then dried at about 50C°(Hadi M.,2009).

The prepared complexes are insoluble in most organic solvent and soluble in DMSO.

Antibacterial assay

The bacterial cultures for Gram positive *Staphylococcus aureus* and Gram negative *Escherichia Coil* were obtained from clinical laboratories in Ministry of Science and Technology .

The overnight Cultures (0.1ml) of each bacterium was dispensed into 10 ml of sterile nutrient broth and Nutrient agar was (3-5)hours to standardize the culture.Nuturient agar was prepared by suspend 28 gm in IL distilled water. After that the media were transferred to petri plates about (18 -20) ml for each petri plates . After that used 0.1 ml from each bacterium on the surface of petri plates by sterile swab in the different direction- Made a well about 0-6 mm in diameter in the petri plates culture ,

The number of well were equel to the numbers of the complex concentration , 0.1 ml from each concentration of complex was added to the wells while adding the distilled water and dimethyl sulphoxide DMSO to the control wells Petri plates culture in cubated under 37 C° to 24 hours and 48 hours(Muhammad A.,2012,Santosh K.,2010).

RESULTS AND DISCUSSION

This project describes synthesis of Schiff bases from benzaldehyde or acetone with the essential amino acid phenylalanine (L1,L2) respectively and their complexes with Co(II), Ni(II), and Cu(II). We used sodium hydroxide as anew catalyst on synthesis of Schiff bases under study (Azzuz A.,2010). The synthesis metal complexes give vary color crystals, depending on the nature of metal ions. All complexes insoluble in water and in common solvents, but they were soluble in DMSO.

Table (1) shows some physical and chemical properties of Schiff base ligands and their Co(II), Ni(II) and Cu(II) complexes. The results of metals analysis of the prepared complexes were in a good agreement with those required by the proposed formula. In all cases (2:1) ligand : metal solid complexes are isolated, that is agrees with the stoichiometric ratio found.

Infrared spectra of ligand (L_1/L_2) and their complexes

Selected Infrared absorptions of the ligands and their complexes are shown in table (2). Figures(1) and (5) are showing infrared spectra of Ligand (L1 ,L2) respectively. Infrared spectra of their metal complexes are shown in Figures (2-4) for L1 complexes, Figures(6-8) for L2 complexes. The spectra of free ligands show weak bands at 3027 cm^{-1} and 2870 cm^{-1} due to **υ** (C-H) aromatic. These bands are in stable in position in both ligands and chelate complexes.

The Infrared spectra of the synthesized compounds showed the presence of C=N stretching band at 1612 cm^{-1} for L1, this band was shifted to lower frequencies (1622-1592) cm^{-1} in the spectra of the chelate complexes, the C=N stretching band for L2 was appear at 1576 cm^{-1} and this band was shifted for metal complexes to (1594-1580) cm^{-1} , suggesting coordination of metal ion through nitrogen atom of azomethine group (Khander A. , 2005) .

A carboxyl group will give rise to two main absorption features in the infrared with energies that depend on the protonation state of the carboxyl. The protonated carboxylic acid in Schiff base yield absorption bands corresponding to a carboxyl stretch (**υ**C=O) at 1641 cm^{-1} for L1 and 1638 cm^{-1} for L2 and C-OH vibrations (**υ**C-OH) between 1300-1200 cm^{-1}.

On deprotonation, (**υ**C=O) shifted to lower energy as its vibrational mode becomes coupled to that of the other oxygen giving rise to as asymmetric feature (**υ**asy. COO) between (1403-1382) cm^{-1}. Similarly, the C-OH band shifted to higher energy on deprotonation, yielding a symmetric COO^- mode (**υ**asy.COO^-) between (1383-1333) cm^{-1}. This shifting indicated that the COO^- group was involved in bonding with metal ions (Hadi M.,2009,Socrates G.,2001).

The IR spectrum of L1 exhibits a broad band at 3424 cm^{-1} caused by **υ** (OH). This band disappeared in the spectra of complexes. A strong broad absorption band appeared around (3455-3437) cm^{-1} was associated of water molecules in these metal complexes. Coordinated H_2O appeared at (843-805) cm^{-1} in all complexes. New bands appeared in the range (558-473) cm^{-1} in all complexes assignable to **υ**(M-N), **υ** (M-O) vibrations. The appearance of these new bands supports the involvement of nitrogen and oxygen atoms in complexation with metal ions under investigation (Hadi M.,2009).

Electronic Spectra studies

The UV spectra of Schiff bases and their complexes are summarized in Table (2). The electronic spectrum of L1 (Fig.9) showed one band absorption at 250 nm this have been attributed to $\pi\rightarrow\pi^*$ transition. Band related to $n\rightarrow\pi^*$ which may be located at the same region are masked by such extension (Silverstein R., 1981).

The electronic spectra of the metal complexes Figs (10-14) showed the band corresponding to the intra-ligand $\pi \rightarrow \pi^*$ transition shifted to higher energy. This observation in the metal complexes relative to the free ligand have attributed to complexation.

Most of the transition metal complexes are colored and their colors are different from the transition metal salts and ligands, then this is an important indication of coordination. Therefore the colored complexes showed different characteristic absorption bands in their position and intensity (Gebbink R., 2002).

Complexation with metal ion was confirmed by the appearance of new bands in the visible and near IR regions which were assigned mainly to charge transfer and d-d transitions. The position and intensities of these bands are mainly dependent on electron configuration of metal ions stereochemistry of complexes and ligand field effects.

Cobalt complexes (CoL1, CoL2) gave light purple color and its electronic spectra exhibited one band appeared at 544 nm and 536 nm respectively which were assigned to the $T_1g\rightarrow A_2g$ transitions of Octahedral geometry. (Pemkumar T., 2003).

The electronic spectrum of Nickel (II) L1 complex showed two bands in the visible region at 565nm and 616nm which related to octahedral (Sultton O. 1968).

Copper complexes gave bands spectra in the visible region at 617nm (CuL1) and 619nm (CuL2) which support a tetrahedral configuration. (Cotton F.,1972).

Antibacterial activity of L1 complexes

Antibacterial activity of Cobalt and Copper complexes of L1 (10 mg/ml, 5mg/ml, 2.5mg/ml/ concentrations) were analyzed with several bacterial pathogens such as *Staphylococcus aureus* and *E. coli* [Figs.(15,16)] showed significant antibacterial activity against *Staphylococcus aureus* with cobalt complex (10mg/ml, 5mg/ml, and 2.5mg/ml concentrations) and with copper complex (2.5mg/ml concentration). While copper and complexes failed to show antibacterial activity with *E. coli* bacterium.

Table 1: Analytical and Physical data of Schiff bases (L1 and L2) and their metal complexes

Compound	Color	Yield, %	Melting Point, (C˚)	Metal, %
L1	White	-	255-260	---------
Co L1 Complex	Light purple	42	226-228	11.8
Ni L1 Complex	Light green	52	260	8.3
Cu L1 Complex	blue	65	210	13.3
L2	White	-	255-260	-
Co L2 Complex	Light purple	64	238-240	12.0
Ni L2 Complex	Light green	55	265-270	11.0
Cu L2 Complex	blue	70	205-210	14.4

Table 2: Some important infrared bands (cm^{-1}) and electronic data (nm) of Schiff bases (L1,L2) and their metal complexes

No.	Compound	ν C=O	ν C=N	ν(COO^-) asy.	H_2o aqua H_2O hydr.	ν(M-N)	ν(M –O)	λ max, (nm)
1	L1	1642	1612	1397	-			250
2	Co L1 Complex	1640	1592	1383	843 3437	496	563	680, 544, 289
3	Ni L1 complex	1640	1592	1403	838 3453	483	553	616, 565, 292
4	Cu L1 Complex	1738	1622	1382	430(w) 3453	473	558	617, 312
5	L2	1638	1576	1411	-	-	-	-
6	Co L2 Complex	1638	1588	1384	805 3476-3416	489	-	536, 268
7	Ni L2 Complex	1636	1594	1405	834 3358	473	549	-
8	Cu L2 Complex	1623	1580	1391	810(w) 3455-3416	500	558	619, 291

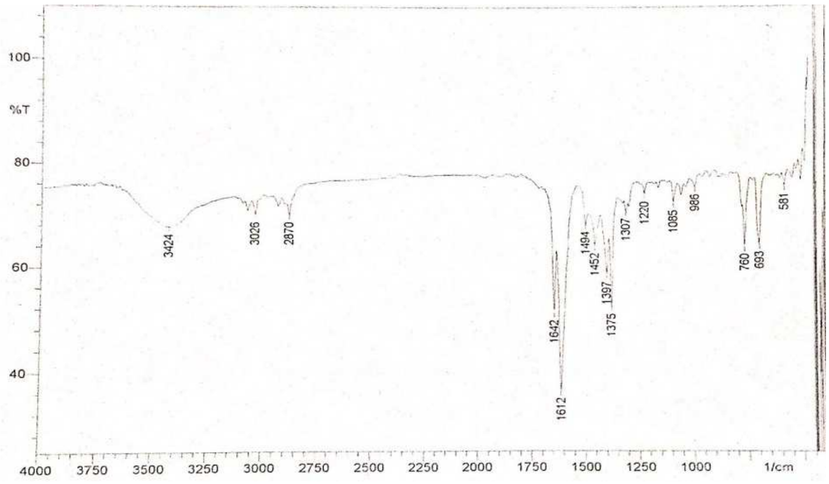

Figure (1): IR Spectrum of L1

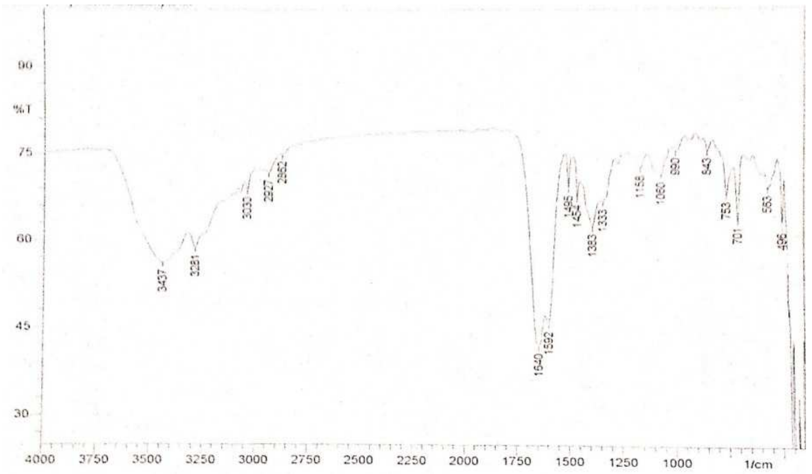

Figure (2): IR Spectrum of CoL1 Complex

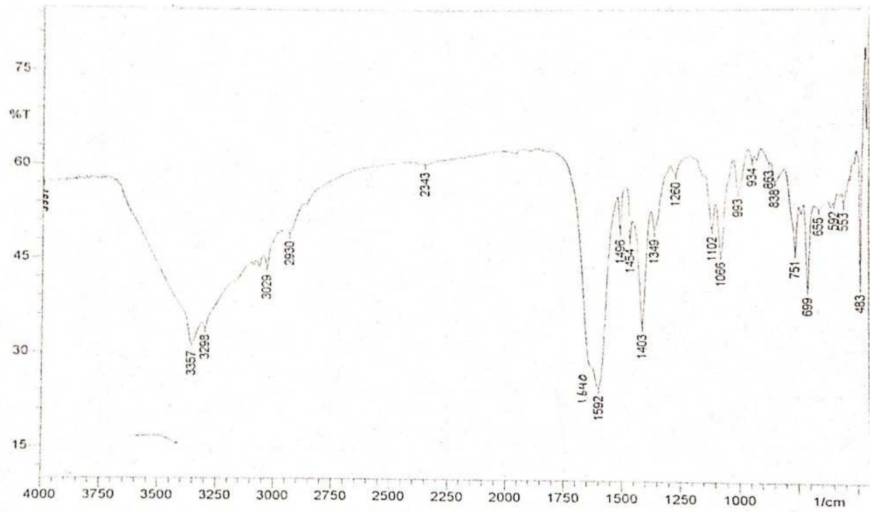

Figure (3): IR Spectrum of NiL1 Complex

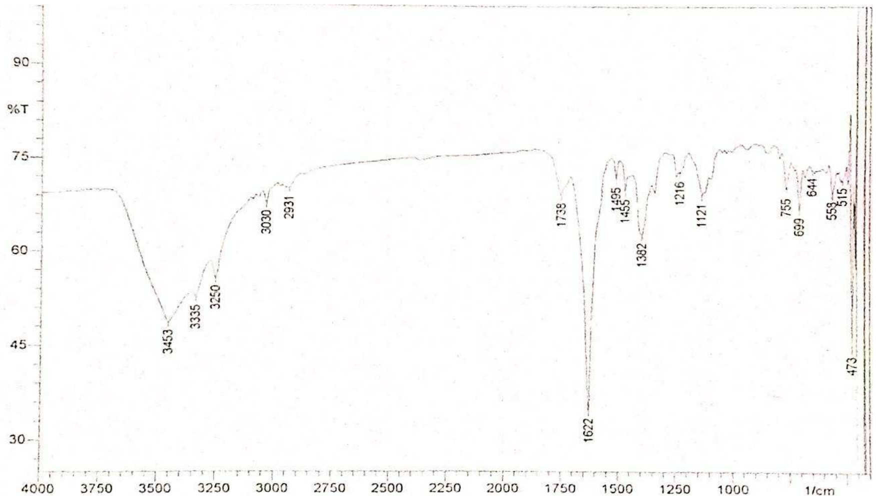

Figure (4): IR Spectrum of CuL1 Complex

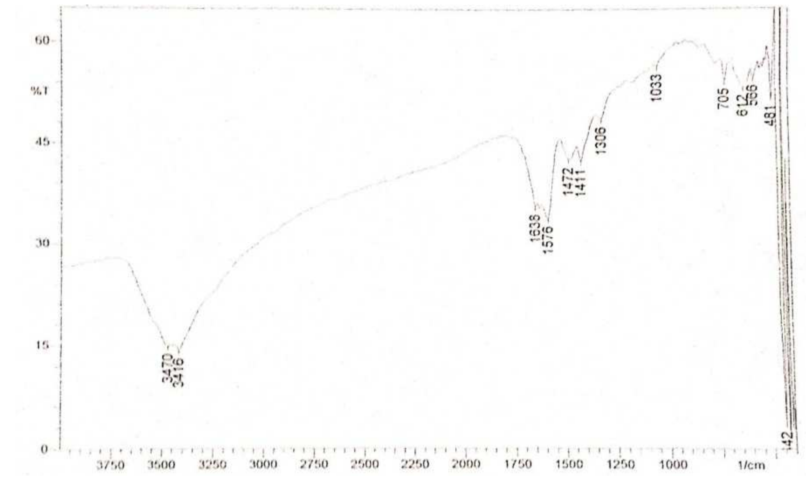

Figure (5): IR Spectrum of L2

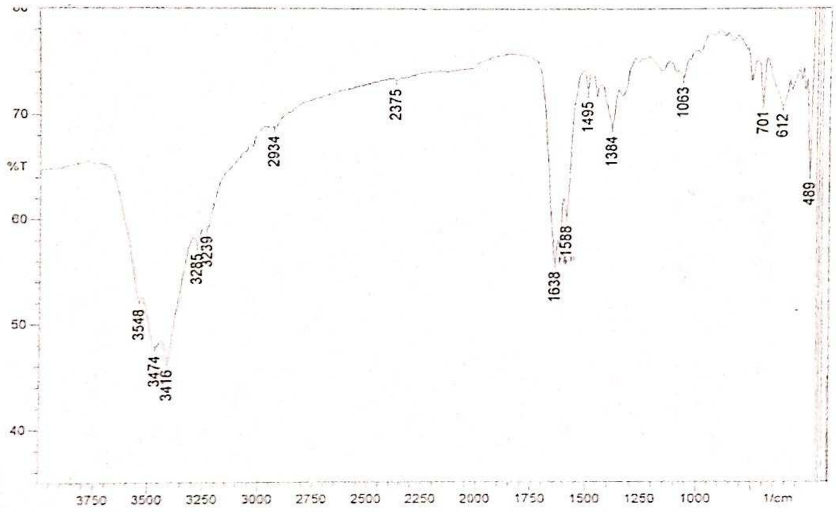

Figure (6): IR Spectrum of CoL2 Complex

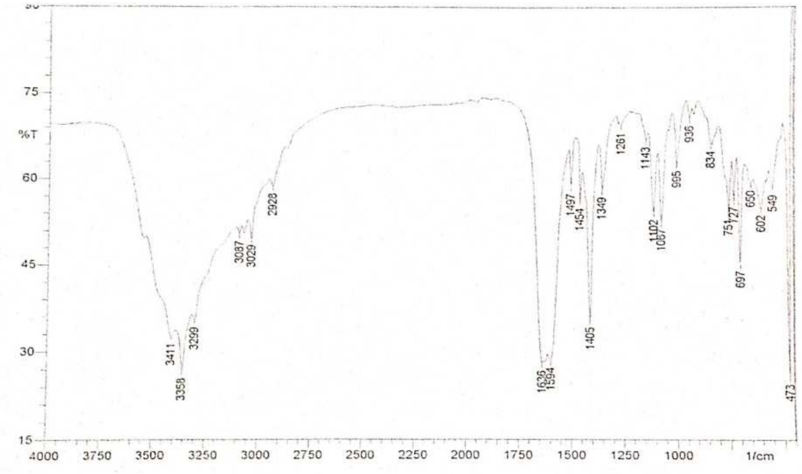

Figure (7): IR Spectrum of NiL2 Complex

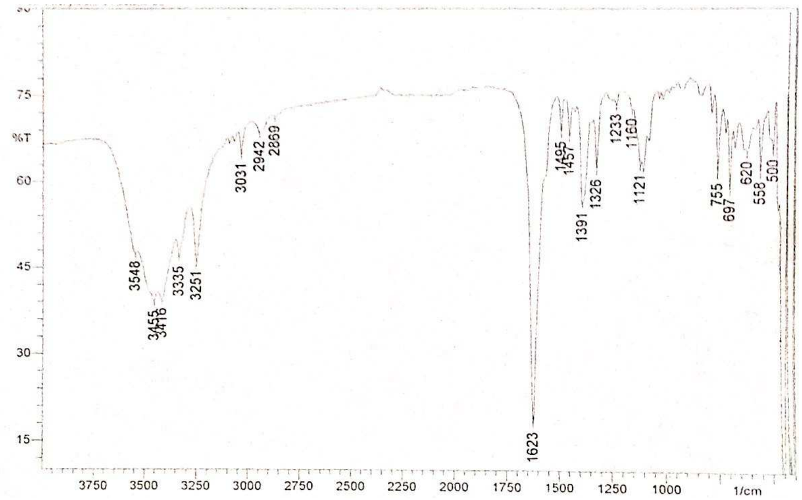

Figure (8): IR Spectrum of CuL2 Complex

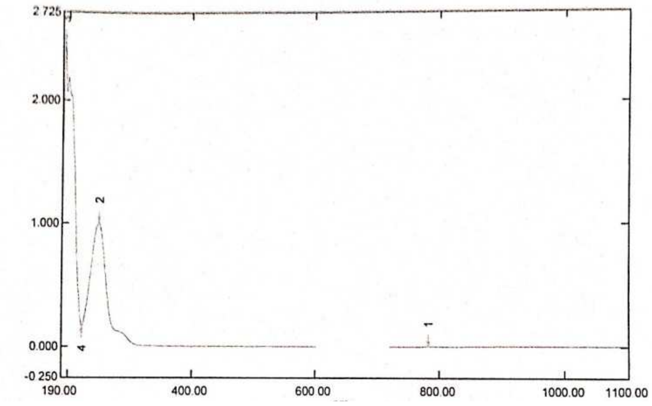

Figure (9): UV-Visible Spectrum of L1

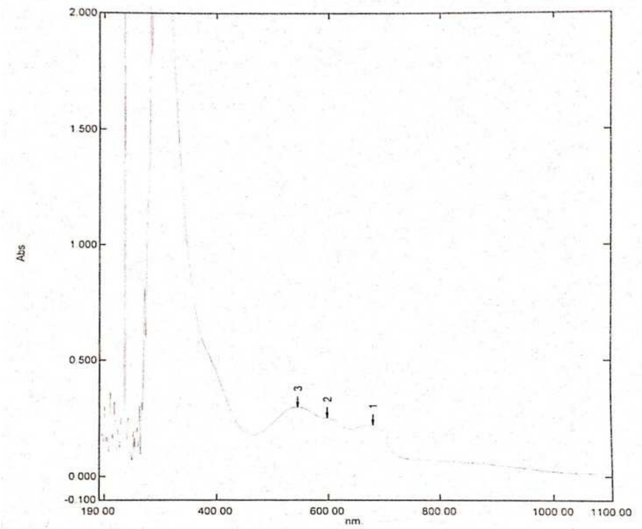

Figure (10): UV-Visible Spectrum of CoL1 Complex

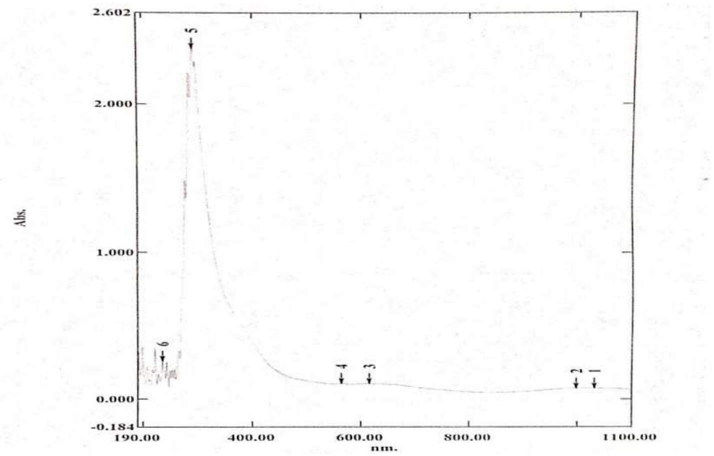

Figure (11): UV-Visible Spectrum of NiL1 Complex

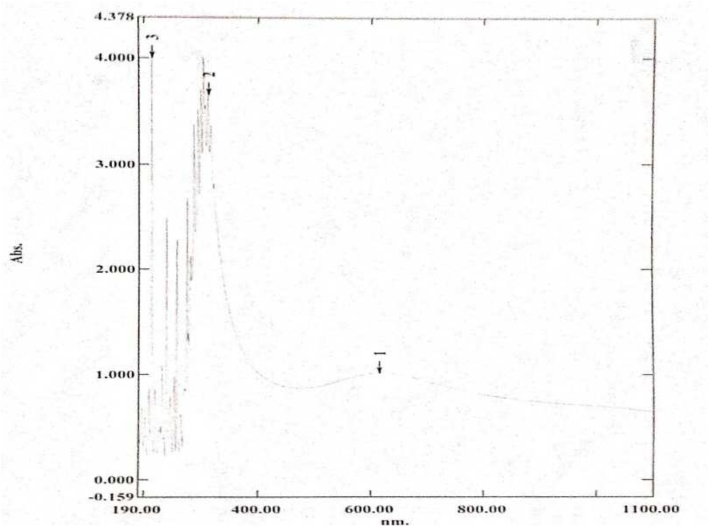

Figure (12): UV-Visible Spectrum of CuL1 Complex

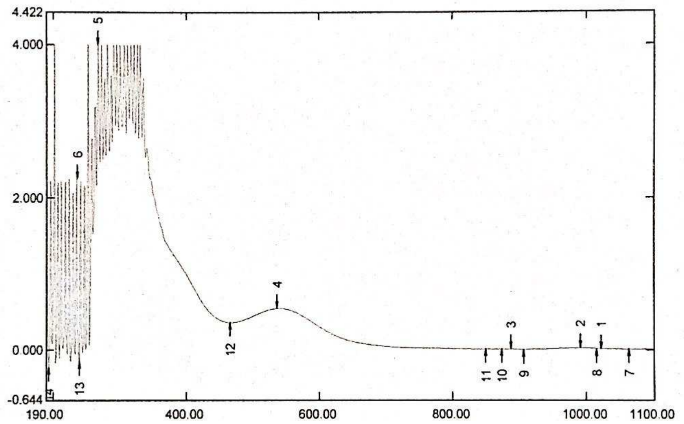

Figure (13): UV-Visible Spectrum of CoL2 Complex

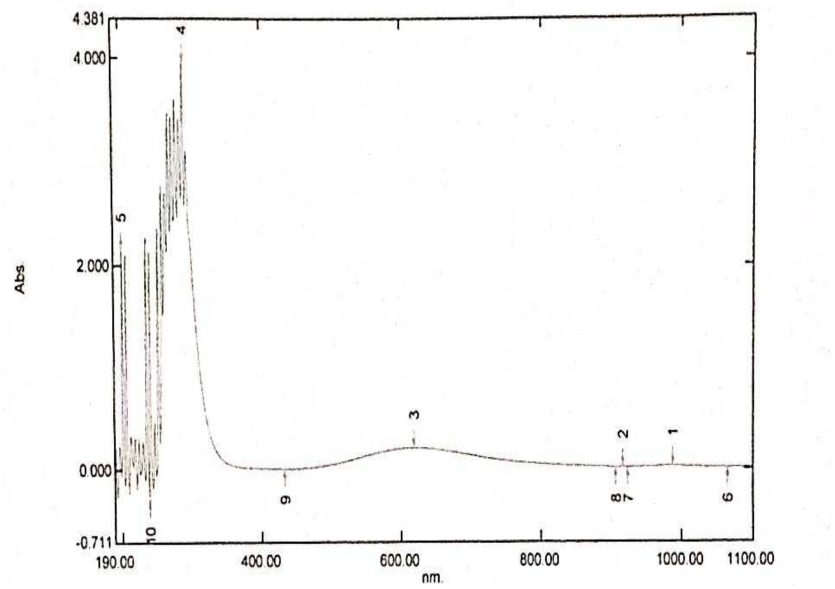

Figure (14): UV-Visible Spectrum of CuL2 Complex

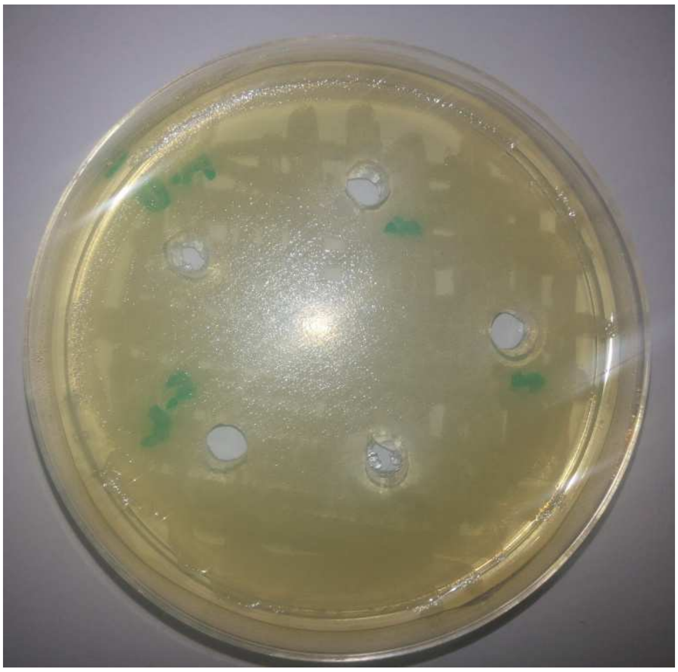

Figure 15: the effect of cobalt complex on *Staphylococcus aureus* bacteria in nutrient agar after 48 hours

Figure 16: the effect of copper complex on *Staphylococcus aureus* bacteria in nutrient agar after 48 hours

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