Article

Preparation and Characterization of Poly Dentate Amidic Ligand type NNSS and Complexes with Co(II), Ni(II) , Cu(II) and Biological Activity

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Abstract

A multi-dental amide ligand of the NNSS type consisting of nitrogen and sulfur donor atoms was prepared through one step, which is the reaction between one equivalent of hydrazine and another of sulfuric acetic acid. Coordination complexes were prepared by reacting the resulting ligand with a number of aqueous solutions of appropriate amounts of elemental chlorides. Transitivity of cobalt, nickel, and divalent copper in ethanol as a reaction medium, with a ratio (ligand: metal) equal to (1:1), The prepared compounds were characterized by the infrared spectrum technology , the visible ultraviolet spectrum and C.H.N analysis, in addition to the ^{1}H-NMR for ligand only and magnetic susceptibility , molar conductivity of the prepared complexes were shown to form octahedral for these complexes. Finally, a biological (bacterial) study was conducted for ligand and its complexes through Using two types of positive and negative bacteria concentrations of 250 ppm and 500 ppm, solutions of the complexes sensitivity to the two types of bacteria, while Ligand solutions are did not effective at both concentrations.

Key words: amidic ligand **,** hydrazine , complexes , biological activity

Introduction

The chemistry of complex compounds is of great importance, as the coordination or complex compound consists of a central ion or a central atom of the transition element atoms, surrounded by a number of negative ions or neutral molecules containing one or more donor atoms rich in unbounded electronic pairs, which are called with ligands, they bond with the partially empty d orbitals present in this type of elements through the coordination bond, forming this type of compounds (complexes).[1] Coordination complexes are gaining great importance in many fields such as medicine, agriculture, industry and engineering. N_2S_2 compounds are distinguished by special importance among other organic compounds, as it has been shown that they are used in

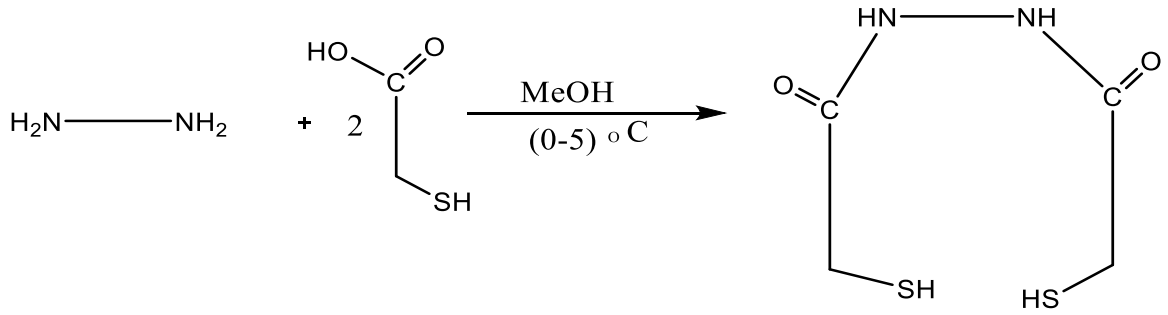
the biological field as an anti-tumor [2], anti-fever, anti-fungal, anti-bacterial, and others [3-6]. Studies conducted by many researchers also indicated that Prepared compounds containing electron-donating nitrogen and sulfur atoms are used as catalysts in some chemical reactions, as well as models for many biological systems, and are also used in radio pharmacy [7-9]. on the other hand, amides are considered organic chemical compounds that contain the amide group NH_2–C=O, which consists of the linkage of the primary amine group – NH_2 and the carbonyl group – C=O found in esters and carboxylic acids, with the loss of a water molecule [10]. This type of Compounds are divided into two main types: aliphatic and aromatic amides. They can also be classified into primary, binary and tertiary amides. [11-14] Aromatic amides are considered less effective than aliphatic ones due to the state of resonance that occurs between the electron double on the nitrogen atom and the pi electrons (π) For the carbonyl group, most amides are solids and have a low melting point, except for the simplest type, form amide, which is in the liquid state.

Materials and Methods

All chemicals used in this research are of high purity and from reliable international origins (Merck). The melting points of the ligand and prepared complexes were measured using an electrothermal device. The FT-IR spectra were also measured using a Shimadzu FT-IR-4800S device using KBr disks. The ultraviolet-visible spectra were measured using a UV-Visible spectrophotometer - 1800 Shimadzu, while the molar conductivity was measured using a Digital Conductivity meter - WT- 720 - inolab (Germany).

Preparation of H_2L Ligand

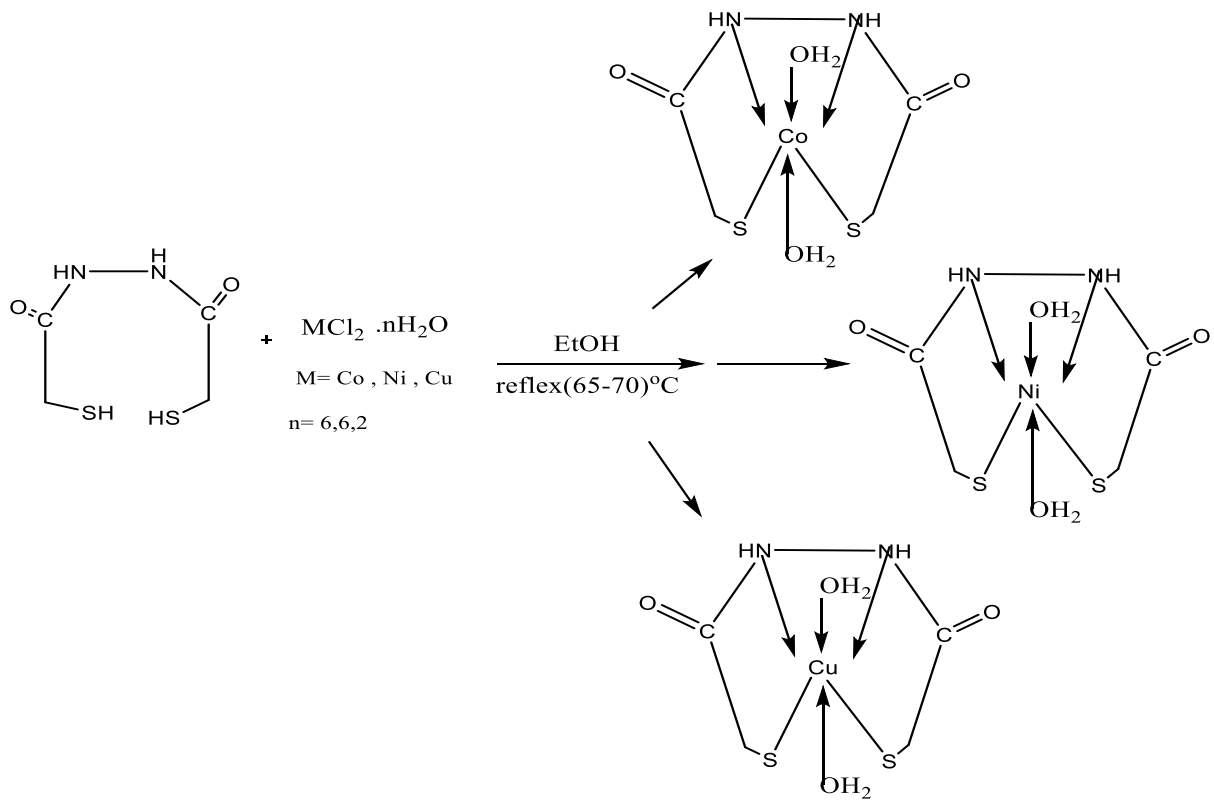
The ligand was prepared by adding (2.4×10^{-2} mol, 1.16 mL) of aqueous hydrazine to (3.2×10^{-2} mol, 2.2 mL) of mercepto acetic acid, in an ice bath at a temperature of (0-5) °C with continuous stirring. A compound with a gelatinous consistency is formed, then 30 ml of methyl alcohol is added, resulting in a light yellow precipitate. It is precipitated and recrystallized with cold distilled water, then filtered and dried. The precipitate weighed (2.751 gm) [15]. Its melting point was measured and it was (181-183) °C, its molecular formula is ($C_4H_8N_2S_2O_2$), and its molecular weight is (180.2) gm / mol according to the following Scheme (1):



Scheme.1 : Preparation of H_2L ligand

Preparation of Coordination Complexes

The three complexes $[CoL(H_2O)_2]$, $[NiL(H_2O)_2]$ and $[CuL(H_2O)_2]$ were prepared, respectively, by adding one equivalent of the divalent metal chlorides (cobalt, nickel, and copper) separately, each according to the appropriate weight (0.129, 0.130, 0.134) gm , to one equivalent (1×10^{-3} mol, 0.182 gm) of the ligand H_2L, in the presence of ethanol as the reaction medium, and reflexing in (65-70)ºC for three hours according to the following scheme (2).



Scheme.2: Preparation of H_2L ligand complexes

Table.1: Represents some properties and C.H.N. values for ligand and it's complexes

compound	Formula	M.wt	color	M.P °C	theoretical / found	C %	H %	%N	%M
H_2L	$C_4H_8N_2O_2S_2$	180.2	yellow	181-183	26.66 26.55		4.47 4.29	15.51 15.63	… ….
$CoL(H_2O)_2$	$C_4H_6N_2O_2S_2Co(H_2O)_2$	273.2	black	Dec.299	17.59 17.67		3.69 3.45	10.25 10.43	21.57 21.63
$NiL(H_2O)_2$	$C_4H_6N_2O_2S_2Ni(H_2O)_2$	272.9	green	280-283	17.60 17.55		3.69 3.77	10.26 10.63	21..50 20.99
$CuL(H_2O)_2$	$C_4H_6N_2O_2S_2Cu(H_2O)_2$	276.9	blue	250-253	17.29 17.45		3.63 3.59	10.08 10.21	22.87 22.73

Results and discussion

Infrared spectroscopy of the ligand and its complexes

Infrared spectroscopy of the ligand H_2L Figure.1, using a KBr disk, showed many stretching vibration frequencies such as 3362.04 cm^{-1} belonging to the υ (N-H) bond, a frequency of 2914.54 cm^{-1} belonging to the aliphatic υ ($-CH_2$) and a weak peak at 2760.23 cm^{-1} It represents υ(S-H) [16] in addition to a strong peak at 1587.47 cm^{-1} representing the carbonyl group belonging to the amide bond.

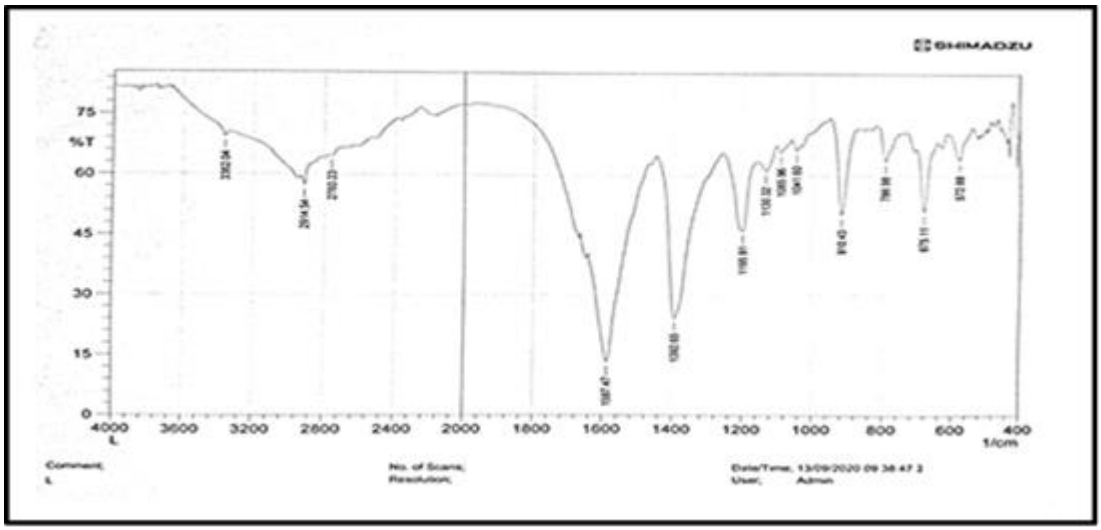


Figure.1: Infrared spectrum of H_2L ligand

While the FT-IR spectroscopy of the prepared complexes, as shown in Figures (2,3,4), respectively, shows the disappearance of the bond frequency υ(S-H) and the appearance of different shifts for the frequencies of the other bonds, as follows, for the bond υ(N-H) between (3309-3385) cm^{-1} , υ (-CH_2) between (2924-2937) cm^{-1}, υ(-C=O) between (1645-1510) cm^{-1}, and on the other hand, the spectra showed the appearance of new frequencies such as (3438-3470) cm^{-1}. It belongs to the bond υ (O-H) of coordinated water , and others at (412-434) cm^{-1} and (502-553) cm-1 belong to the frequencies of the bonds υ(M-S), υ(M-N), respectively, indicating the occurrence of coordination between the central metal and the ligand.[17-18] as in table No.2:

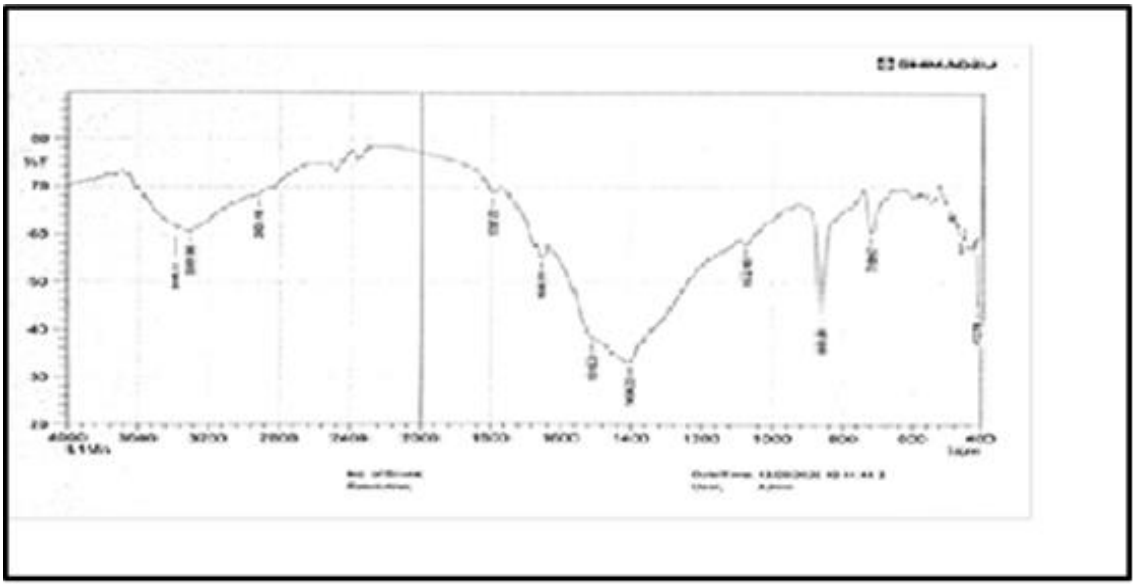


Figure.2: The infrared spectrum of the $CoL(H_2O)_2$ complex

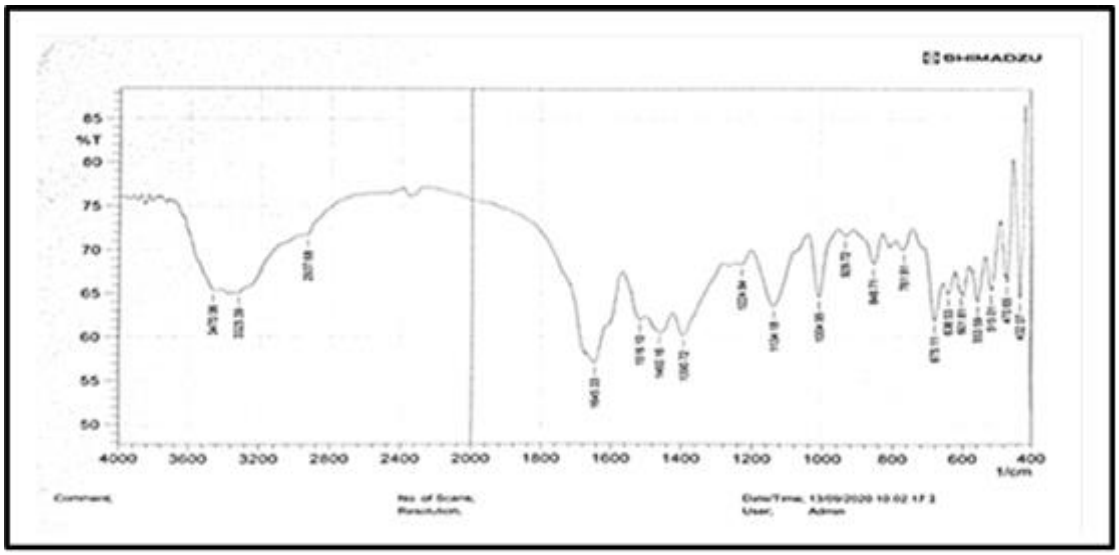


Figure.3: The infrared spectrum of the $NiL(H_2O)_2$ complex

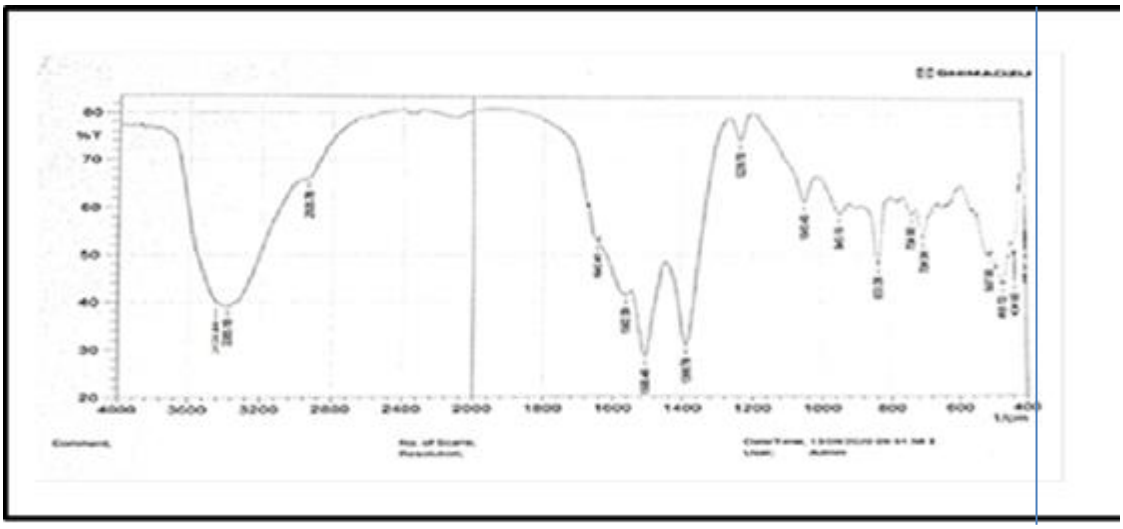


Figure. 4: The infrared spectrum of the $CuL(H_2O)_2$ complex

Table.2:FT.IR spectra for ligand and its complexes

Comp.	υ(-OH)	υ(-NH)	υ(-CH_2)	υ(S-H)	υ(C=O)	υ(M-N)	υ(M-S)
H_2L	…….	3362	2914	2760	1584	……	……
$[CoL(H_2O)_2]$	3438	3220	2987	……	1593	502	412
$[NiL(H_2O)_2]$	3470	3240	2987	…….	1594	553	425
$[CuL(H_2O)_2]$	3441	3237	2970	…….	1600	531	434

Ultraviolet–visible spectroscopy of ligand and its complexes

The ultraviolet- visible electronic spectra of the prepared ligand showed (Figure 5) a peak at (ʎ = 232) nm representing the π *π transition and at (ʎ =312) representing the n *π transition.[19]

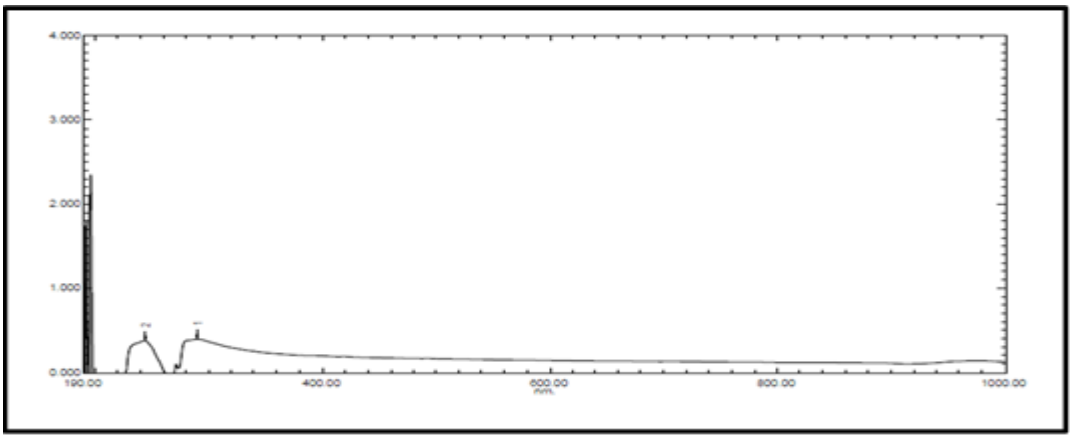


Figure.5 : UV-Vis spectrum of H_2L ligand

As for the spectra of the three prepared complexes shown in Figures (6,7,8), which belong to cobalt, nickel, and copper complexes, respectively, they showed peaks in the ultraviolet region representing Charge transfer bands disappear at this region these bands belong to $\pi \rightarrow \pi^*$ transition for ligand spectra (C.T.). At (ʎ =232,312) nm, (ʎ =222,311) and (ʎ=231,311) respectively. New peaks also appeared in the visible region at (ʎ = 656.5) nm for the cobalt complex, (ʎ = 665.5) nm for the nickel complex, and (ʎ = 799) nm for the copper complex, respectively. These represent d-d transitions in the three complexes, respectively, Indicates the occurrence of coordination between the central metal and the ligand.[20-21]

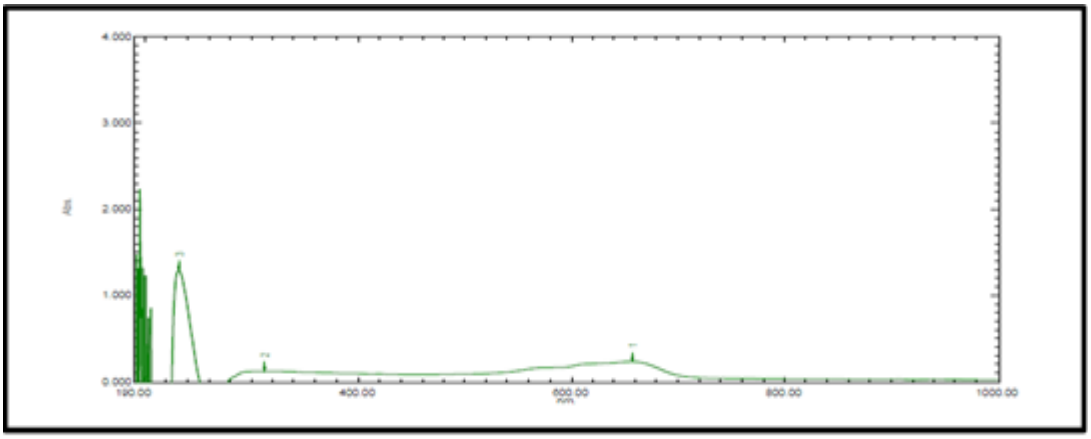


Figure.6 : UV-Vis spectrum of the $CoL(H_2O)_2$ complex

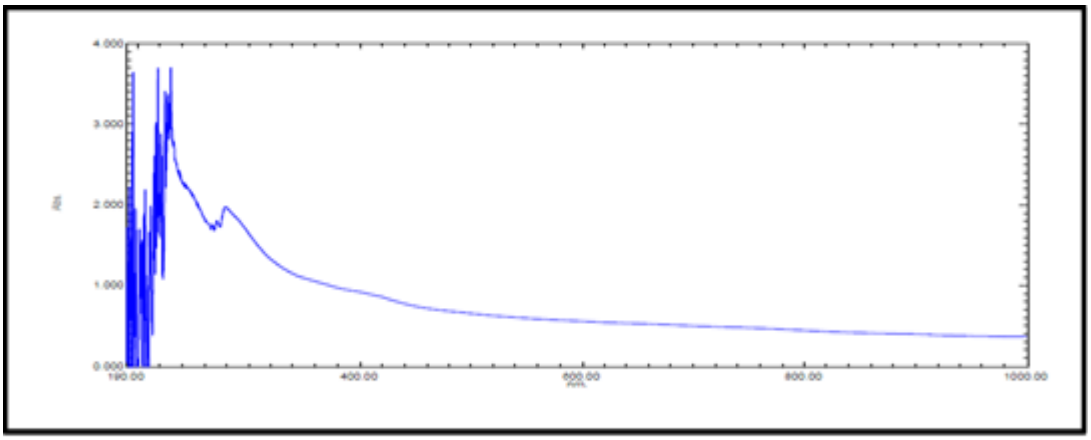


Figure.7 : UV-Vis spectrum of the $NiL(H_2O)_2$ complex

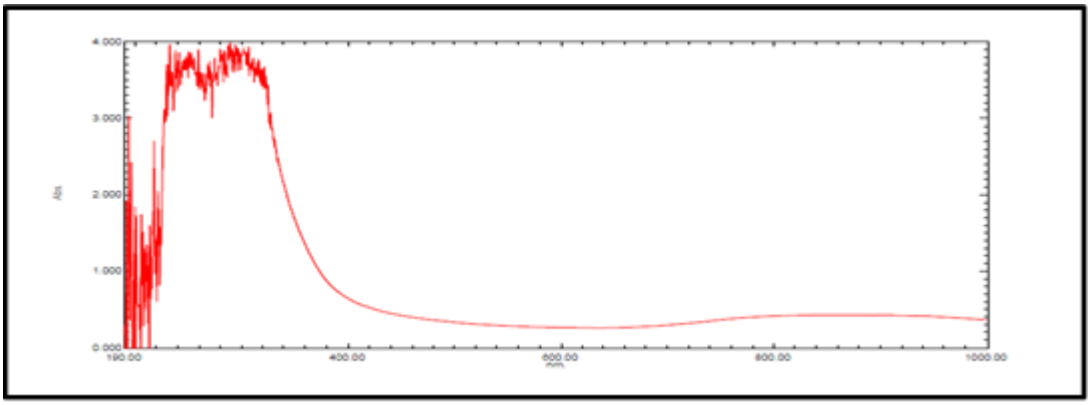


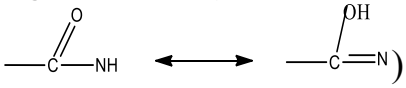
Figure.8 : UV-Vis spectrum of the $CuL(H_2O)_2$ complex

Measurements of the electrical conductivity of the complexes after dissolving them with dimethyl sulfoxide (DMSO) solvent showed that all of them are non-electrolytic [22], and as shown in Table No. 3 below:

Table.3: represents the electronic transitions, electrical conductivity, hybridization, and expected shapes of the complexes under study.

Comp.	Electronic spectra	Molar conductivity ($Ohm^{-1}.mol^{-1}.cm^2$)	magnetic susceptibility(B.M.)	hyperidization	Proposed structure
$CoL(H_2O)_2$	$^4T_1g \rightarrow {}^4T_2g$	9.3	3.99	Sp^3d^2	Octahedral
$NiL(H_2O)_2$	$^3A_2g \rightarrow {}^3T_2g$	7.2	2.84	Sp^3d^2	Octahedral
$CuL(H_2O)_2$	$^2Eg \rightarrow {}^2T_2g$	5.5	1.81	Sp^3d^2	Octahedral

^{1}H-NMR Spectroscopy of H_2L Ligand

The ^{1}H-NMR spectrum in DMSO – d^{6} (δ = 2.43-2.57 ppm) of the ligand Finger. 9 displays the chemical shift at (δ = 8.10 ppm, 2H) assigned to protons (N- H), the signals at (δ = 4.40 ppm, 2H) for tautomerrism in amide bond () , (δ = 3.40-2.88 ppm, 4H) belong to (-CH_2) protons, finally, (-SH) groups protons appear at (δ = 1.24 ppm, 2H) shifting .[23]

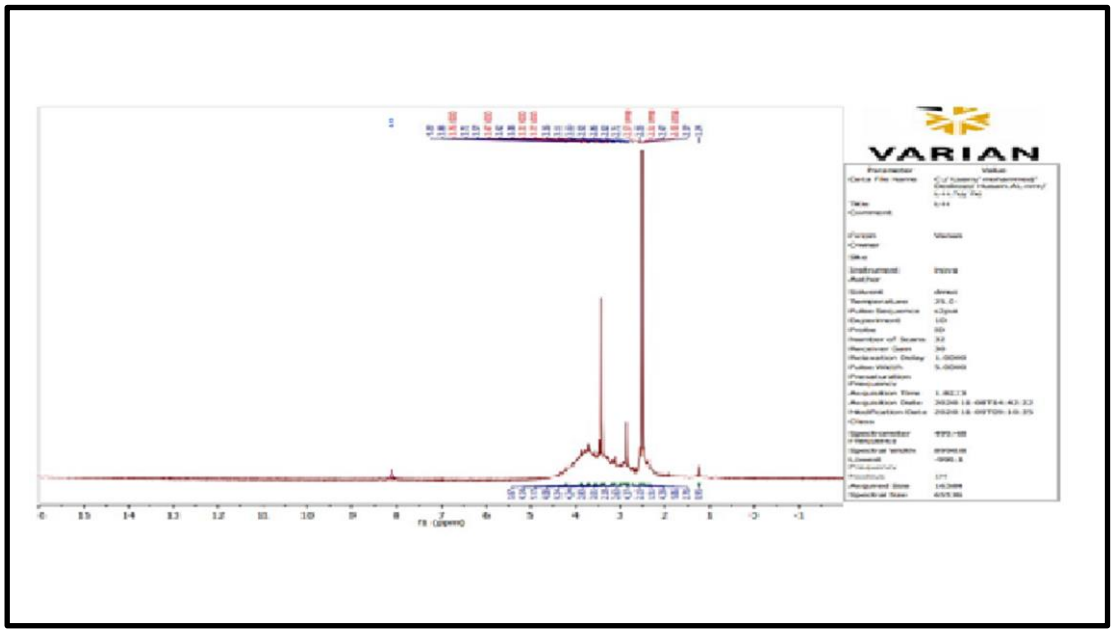


Figure.9 : ^{1}H-NMR spectrum of H_2L ligand

Bactericidal Activity of the prepared ligands and Complexes

In this research, the bacterial activity of the prepared compounds was measured against two types of gram-positive bacteria (*Staphylococcus aureus*) and gram-negative bacteria (*Escherichia coli*) with two concentrations (250)ppm and (500)ppm , *E.Coli* was show highest sensitivity for (500)ppm and (250)ppm in compound $[CoL(H_2O)_2]$, then $[NiL(H_2O)_2]$ and $[CuL(H_2O)_2]$ respectively. while, *Staphylococcu*s showed highest sensitivity for (500)ppm in $[NiL(H_2O)_2]$, and same activity in $[CoL(H_2O)_2$] and CuL , but (250)ppm showed highest sensitivity in $[CoL(H_2O)_2]$, then $[CuL(H_2O)_2]$ and $[NiL(H_2O)_2]$ respectively, with out any activity for ligand in both concentrations, [24] as show in Table No.4

Table.4: bacterial activity of the prepared compounds

Compound	*Staphylococcus*		*E. coli*	
	250	500	250	500
H_2L	R	R	R	R
CoL	15	11	17	20
NiL	11	14	15	14
CuL	14	11	13	13

R= Resistant(-ve)

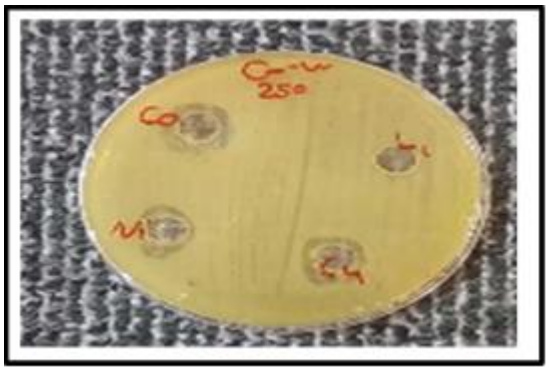


Figure .11: Sensitivity of E. coli to the ligand and its complexes in 250ppm

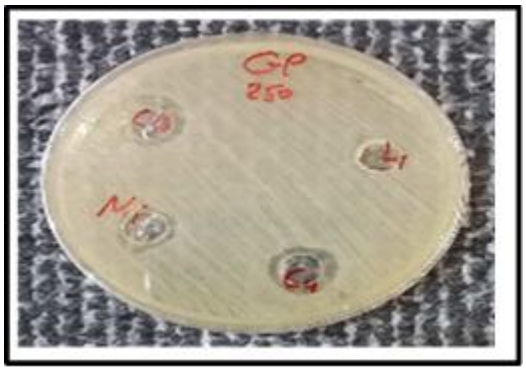


Figure. 10: Stapylococcal bacterial sensitivity to the ligand and its complexes in 250p pm

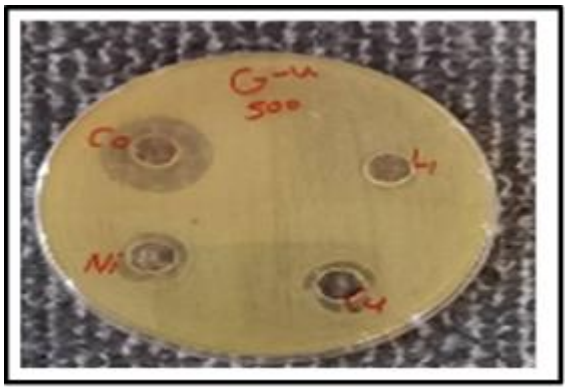


Figure .13: Sensitivity of E. coli to the ligand and its complexes in 500 ppm

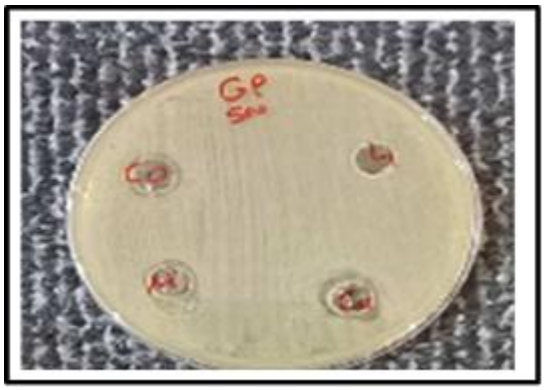


Figure .12: Stapylococcal bacterial sensitivity to the ligand and its complexes in 500 ppm

Conclusion

The multi-dental amide ligand of the NNSS done by condensation reaction between hydrazine and sulfuric acetic acid , ligand and complexes were colored and stable in temperature and air , measurements like ^{1}H-NMR, UV-Vis , FT-IR, C.H.N and magnetic susceptibility supported octahedral structure for all prepared di valance

(Cobalt, Nickel and Copper) complexes , while electric conductivity show the non-electrolytic property for all prepared complexes.

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