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SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY FOR COMPLEXES VO(II), MN(II), CO(II) AND NI(II) WITH NEW MULTIDENTATE LIGAND [2-((E)-4-((Z)-2-HYDROXY-1,2-DIPHENYLETHYLIDENEAMINO)-1,5- DIMETHYL-2-PHENYL-1H-PYRAZOL-3(2H)-YLIDENEAMINO)PROPANOIC ACID][H₂L] TYPE (N₂O₂)

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ABSTRACT

In this work, the precursor [(Z)-4-(2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one] was synthesised from 4-aminoantipyrine and Benzoin, this precursor has been used in the synthesis of new multidentate ligand [2-((E)-4-((Z)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)propanoic acid] [H₂L] type (N₂O₂). The ligand was refluxed in ethanol with metal ions [VO(II), Mn(II), Co(II) and Ni(II)] salts to give the complexes of general molecular formula: [M(H₂L)₂(X)(Y)].B, where: M=VO(II), X=0, Y=OSO₃⁻², B=2H₂O; M=Mn(II),Ni(II), X=H₂O, Y=H₂O, B=2Cl; M=Co(II), X=H₂O, Y=Cl, B=Cl. These complexes were characterised by atomic absorption(A.A), F.T.I.R., ultraviolet visible(U.V-Vis)spectroscopies (1H,13C NMR for ligand only), along with conductivity, elemental microanalysis (C.H.N), chloride content and melting point measurement. These studies revealed an octahedral geometries for VO(II), Mn(II), Co(II) and Ni(II) complexes. The ligand and its complexes exhibited biological activity against the *Staphylococcus aureus* (G+), *E-coli* (G-), *Pseudomonas* (G-) and *Proteus* (G-) except [Ni(H₂L)₂(H₂O)₂].2Cl with *Pseudomonase* has no biological activity.

KEYWORDS:4-aminoantipyrine, Benzoin, complexes.

INTRODUCTION

The Schiff bases have many various names⁽¹⁾, depending on the sources of carbonyl compound and primary amine, so its called Aldimines, if its derived from aldehydes and Ketimines, if it derived from ketones, while its called Aniles, Benzanils and Imines when the primary amine is aniline or one of its derivatives⁽²⁾. Heterocyclic compounds are important class of compounds in organic chemistry because of their biological activities^(3,4,5). Pyrazol is doubly unsaturated five membered ring compound having three carbon and two nitrogen atoms. Several pyrazoline substitution products are used in medicine⁽⁶⁾. In 1884, Knorr reported pyrazol derivatives in which called thermal descending for anti-inflammatory, that is called pyrazol chemistry, which has great importance in wide fields such as pharmaceutical as drug, in dyes synthesis and in biological activities⁽⁷⁾. Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects, antiviral, antibacterial activities^(8,9) and have

also been used as hair colour additives⁽¹⁰⁾, to potentiate the local anesthetic effect of lidocaine⁽¹¹⁾ and in spectrophotometric determination of metal ion, many of these reagents give intense colours with transition metal ions⁽¹²⁾.

MATERIALS AND METHODS

All chemicals used supplied from Fluka and Merck companies and used without any further purification. Infrared spectra were performed using a Shimadzu (FT-IR)-8400S spectrophotometer in the range (4000-400)cm⁻¹. Spectra were recorded as potassium bromide discs at Ibn-sina Company. The electronic spectra of the compounds were obtained using a (U.V.-Visible) spectrophotometer type Shimadzu 160, in range (200-900)nm using quartz cell of (1.0)cm length with concentration (10⁻³)mole L⁻¹ of samples in ethanol at 25°C. Electrical molar conductivity measurements of the complexes were recorded at (25°C) for (10⁻³)M solutions of the samples in ethanol using a PW 9526 digital conductivity meter.¹H,¹³C

NMR spectra were recorded using DMSO-d₆ at Bruker 400MHz spectrometer. The chloride content determined using potentiometric titration method on 686-Titro Processor-665 Dosim A-Metrohm/Swiss. The magnetic moments were measured with a magnetic susceptibility balance (Jonson Matty Catalytic system division). Melting points were obtained using an electrothermal apparatus Stuart, melting point and metals were determined with a Shimadzu (A.A.) 680G atomic absorption spectrophotometer, all measurements were obtained in Ibn Sina Company.

1- Preparation of precursor [(Z)-4-(2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one].

(1.0g, 4.9mmole) from 4-aminoantipyrine, was added to (1g, 4.7mmole) of benzoic acid in ethanol (30ml.) with stirring, then (0.3mL) HBr 48% was added and refluxed to 3hrs. (Orange precipitate was observed after refluxing for 1hr.). The reaction mixture was cooled in ice-bath, the orange product was isolated by filtration and washed by small portions of ethanol and dried to give an orange precipitate, yield (1.8g) (92%), m.p.(108-111°C).

2-Preparation of ligand[2-((E)-4-((Z)-2-hydroxy-1,2-diphenylethylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)propanoic acid]

A solution of precursor (1.0g, 2.5mmole) in (30mL) ethanol, was added to (0.2g, 2.2mmole) of 2-aminopropionic acid, then (0.3mL) HBr 48% was added and refluxed to 5hrs. (Orange-brown precipitate was observed after refluxing for 3 hrs.). The reaction mixture was cooled in ice-bath, the orange-brown product was isolated by filtration and washed by small portions of ethanol and dried to give an orange brown precipitate, yield (1.15g) (97%), m.p.(80-83°C).

3- Preparation of [VO(H₂L)₂(SO₄)₂·2H₂O (1)

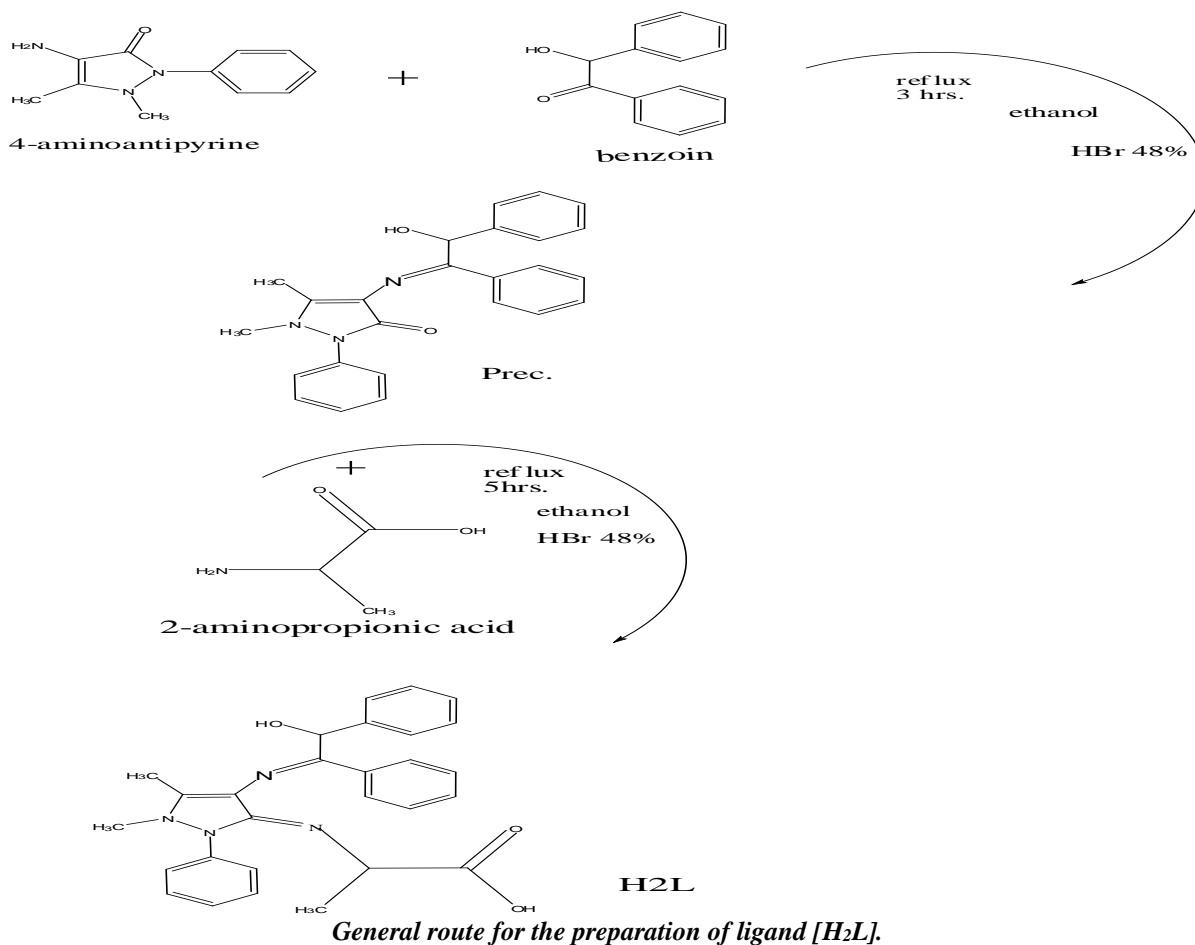
A solution of (0.035g, 0.21mmole) of Vanadium II Sulfate hydrate dissolved in (10mL) of ethanol was added drop wise to a solution of [H₂L] (0.2g, 0.21mmole) dissolved in (15 mL) ethanol. The reaction mixture was allowed to reflux for 3 hrs. A green precipitate was formed, which filtered off, washed several times with absolute ethanol and dried. Yield 0.18g, (78 %) of the title complex, m.p. (95 – 98°C).

4-Preparation of [Mn(H₂L)₂(H₂O)₂].Cl₂(2), [Co(H₂L)₂(H₂O)Cl].Cl (3), [Ni(H₂L)₂(H₂O)₂].Cl₂(4).

A similar method to that mentioned for the preparation of VO^{II} complex was used to prepare the complexes of [H₂L] with [Mn^{II}, Co^{II} and Ni^{II}] ions.

Results and Discussion

The ligand [H₂L] was obtained in high yield by the condensation reaction using one equivalent of precursor and one equivalent of 2-aminopropionic acid, which has N₂O₂ donor atoms. The ligand was prepared according to the general route shown in the Scheme below. It dissolve in MeOH, DMF and DMSO, some physical properties and elemental microanalysis C.H.N. of ligand [H₂L] were listed in table(1). The reaction of ligand [H₂L] and VOSO₄·H₂O or with metal chloride salt of Mn(II), Co(II) and Ni(II) were carried out in ethanol solvent under reflux. All prepared complexes (fig.1) are stable in solution and they dissolve in MeOH, DMF and DMSO. On the basis of elemental microanalysis, chloride content and atomic absorption(table1), the formula to be: [VO(H₂L)₂SO₄]₂·2H₂O, [Mn(H₂L)₂(H₂O)₂]₂·2Cl, [Co(H₂L)₂(H₂O)Cl].Cl and [Ni(H₂L)₂(H₂O)₂]₂·2Cl. Also the suggested molecular formula was supported by spectral measurements as well as molar conductivity.



NMR spectra for ligand [H₂L].

The ¹H and ¹³C correlated NMR analysis were used to characterise the ligand [H₂L]. The spectra were recorded in DMSO-d₆ solution.

¹H NMR spectrum for the ligand [H₂L].

In solution, as in the solid state, it is clear that an intramolecular hydrogen bonding between the hydrogens of the phenol group/carboxylic group and the nitrogens of the imine groups is occurred. This phenomenon has been confirmed by the IR and the NMR spectra. ¹H NMR spectrum for [H₂L], Fig.(2) in DMSO-d₆ displayed signal at chemical shift ($\delta_H = 7.29-7.94\text{ppm}$, 15H, m), (Ar-H), are assignable to protons of aromatic ring⁽¹³⁾. The appearances of these protons as a multi are due to mutual coupling. The resonance for methylene (N-CH) group is located at ($\delta_H = 3.88\text{ ppm}$) (1H, d, N-CH), the sharp singlet signals at ($\delta_H = 1.40\text{ ppm}$), (2.20 ppm) and (2.87 ppm) equivalent to nine protons (9H, S) is attributed to the protons of methyl group⁽¹⁴⁾, the signal at chemical shift ($\delta_H = 7.17\text{ ppm}$) is assignable to benzyl (-CH), while the signals at ($\delta_H = 8.16\text{ ppm}$, 1H) and ($\delta_H = 9.55\text{ ppm}$, 1H) are assignable to protons of (O-H) benzyl group

and (O-H) carboxylic group respectively⁽¹⁵⁾. The spectrum displayed chemical shifts at ($\delta_H = 2.50\text{ ppm}$, and $\delta_H = 3.36\text{ ppm}$) referred to the DMSO solvent, and the presence of water molecules in the solvent respectively. The results are summarised in Table (2).

¹³C NMR spectrum for [H₂L]

The ¹³C NMR spectrum of (H₂L), Fig.(3) in DMSO-d₆ solvent shows chemical shift at range ($\delta = 122.74-138.77\text{ ppm}$) assigned to aromatic carbon atoms (C_{7,8,9,10,11,12,17,18,19,20,21,22,23,24,25,26,27,28}). The chemical shifts at ($\delta = 47.84$ and 189.17 ppm) attributed to the benzyl and carboxylic carbon atoms (C₁, 16) respectively (COOH), while the chemical shifts at ($\delta = 164.02$ and 171.47 ppm) are assigned for imine carbon atoms (C₁₃, C₂)-(C=N-) respectively. The chemical shifts at ($\delta = 15.71$), (31.52) and (60.94 ppm) assigned to methyl group carbon atoms (C_{5,15,6}) respectively, while the chemical shift at ($\delta = 55.79\text{ ppm}$) is refer to carbon atom (C₁₄) (N-CH). At last the chemical shifts ($\delta = 105.75$ and 110.92 ppm) refer to C=C carbon atoms (C_{3,4}) respectively⁽¹³⁾. The results are listed in Table (3).

Molecular conductivity

The molar conductance of complexes (1) in ethanol lie in $(11.25)\text{S.cm}^{-1}.\text{mole}^{-1}$, indicating its non-electrolytic behavior, while the molar conductance of complexes (2 and 4) lie in $(110.51 \text{ and } 93.72)\text{S.cm}^{-1}.\text{mole}^{-1}$ respectively, indicating the 1:2 electrolyte nature, at last the molar conductance of complex (3) lie in $(63.60)\text{S.cm}^{-1}.\text{mole}^{-1}$, indicating the 1:1 electrolyte nature^(16,17).

Magnetic moment

The magnetic susceptibility for all prepared complexes were measured at room temperature and the effective magnetic moment values were listed in table(4). The observed magnetic moment values for $[\text{VO}(\text{H}_2\text{L})_2\text{SO}_4].2\text{H}_2\text{O}$ (1.84) B.M, $[\text{Mn}(\text{H}_2\text{L})_2(\text{H}_2\text{O})_2].2\text{Cl}$ (5.50) B.M, $[\text{Co}(\text{H}_2\text{L})_2(\text{H}_2\text{O})\text{Cl}].\text{Cl}$ (4.80) B.M and $[\text{Ni}(\text{H}_2\text{L})_2(\text{H}_2\text{O})_2].2\text{Cl}$ (2.80) B.M, suggested octahedral geometry around VO(II), Mn(II), Co(II) and Ni(II) central ion⁽¹⁸⁾.

FT-IR spectral data

I.R. spectral data for the ligand $[\text{H}_2\text{L}]$ and prepared complexes (1), (2), (3) and (4) were listed in table (5). The I.R. spectrum for $[\text{H}_2\text{L}]$ fig.(4) displayed two bands at $(1635 \text{ and } 1560)\text{cm}^{-1}$ whose referred to $\nu(\text{C}=\text{N})$ of imine groups in the free ligand were shifted to lower frequency and appeared at $(1616 \text{ and } 1541)\text{cm}^{-1}$ for complexes (1) and at $(1579 \text{ and } 1541)\text{cm}^{-1}$ for complex (2), and at $(1579 \text{ and } 1535)\text{cm}^{-1}$ for complex (3), and at $(1622 \text{ and } 1558)\text{cm}^{-1}$ for complex (4). The shift to lower frequency may be due to delocalisation of metal electron density into the ligand π -system (HOMO \rightarrow LUMO), (where HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital), the shift in $\nu(\text{C}=\text{N})$ confirming the coordination of the ligand through nitrogens atom to the metal ion^(19,20,21). On the other hand, the bands related to the carboxylato moiety at $1456 \text{ and } 1375\text{cm}^{-1}$, whose are assigned to $\nu_{\text{asy}}(\text{COO}^-)$ and $\nu_{\text{sy}}(\text{COO}^-)$ modes, respectively⁽²²⁾ in the free ligand. The shift of these bands to lower or higher frequencies in the (1), (2), (3) and (4) complexes may be attributed to Hydrogen-bonding^(23,24), the spectra showed bands at $(574, 570, 570 \text{ and } 578)\text{cm}^{-1}$ can be refer to $\nu(\text{M}-\text{N})$ for complexes (1),(2),(3)and(4) respectively. The new bands supported the coordination of the ligand to the central metal ion through two nitrogen atoms of iminic group⁽²⁵⁾, the spectrum of complex(1) fig.(5) showed bands at $[977, (1047,939),(615,466)]\text{cm}^{-1}$ may be refer to $\nu(\text{V}=\text{O})$, $\nu(\text{OSO})$ and $\delta(\text{OSO})$ respectively^(26,27). These results are supported by several reports⁽²⁸⁾. The characteristic bands are summarised in Table (5).

(U.V.-Vis) spectral data

(U.V.-Vis.) spectral data for ligand $[\text{H}_2\text{L}]$ and (1),(2),(3) and (4) complexes are shown in Table (4). The (U.V.-Vis) spectrum for $[\text{H}_2\text{L}]$ (fig.6) exhibits two intense absorption peaks, the first peak at $(244)\text{nm}$ $(40983)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=2349\text{molar}^{-1}\text{cm}^{-1}$) assigned to $(\pi \rightarrow \pi^*)$ electronic transition and the second peak at $(350)\text{nm}$ $(28571)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=150\text{molar}^{-1}\text{cm}^{-1}$) assigned to $(n \rightarrow \pi^*)$ electronic transition⁽²⁹⁾. The spectrum showed intense peak in the (U.V.) region at $(242)\text{nm}$ $(41322)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=2138\text{molar}^{-1}\text{cm}^{-1}$), $(244)\text{nm}$ $(40983)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=2344\text{molar}^{-1}\text{cm}^{-1}$), $(243)\text{nm}$ $(41152)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=2399\text{molar}^{-1}\text{cm}^{-1}$) and $(243)\text{nm}$ $(41152)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=2449\text{molar}^{-1}\text{cm}^{-1}$) for complexes (1), (2), (3) and (4) respectively assigned to intra ligand $(\pi \rightarrow \pi^*)$ electronic transition⁽³⁰⁾. Also the peaks at $(340)\text{nm}$ $(29411)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=500\text{molar}^{-1}\text{cm}^{-1}$) and $(350)\text{nm}$ $(28571)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=150\text{molar}^{-1}\text{cm}^{-1}$) for complexes (1) and (3) respectively can be assigned to intra-ligand. All intense absorption peaks of each complexes 1,2, 3 and 4 were shifted to higher or lower frequency in comparison with that of free ligand $[\text{H}_2\text{L}]$, that confirming the coordination of the ligand to the central metal ion. The spectra showed peaks at $(368)\text{nm}$ $(27174)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=250\text{molar}^{-1}\text{cm}^{-1}$), $(545)\text{nm}$ $(22067)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=10\text{molar}^{-1}\text{cm}^{-1}$) and $(518)\text{nm}$ $(12270)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=3\text{molar}^{-1}\text{cm}^{-1}$) which can be assigned to (d-d) electronic transition type $(^2\text{B}_{2g} \rightarrow ^2\text{A}_{1g})$, $(^2\text{B}_{2g} \rightarrow ^2\text{B}_{1g})$ and $(^2\text{B}_{2g} \rightarrow ^2\text{E}_g)$ respectively⁽¹⁸⁾. The spectrum of complex (2) showed peaks at $(355)\text{nm}$ $(28169)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=300\text{molar}^{-1}\text{cm}^{-1}$), $(400)\text{nm}$ $(25000)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=250\text{molar}^{-1}\text{cm}^{-1}$) and $(768)\text{nm}$ $(13021)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=6\text{molar}^{-1}\text{cm}^{-1}$) which can be assigned to (d-d) electronic transition type $(^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g})$, $(^4\text{E}_{g(G)})$, $(^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g(G)})$ and $(^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g(G)})$ respectively⁽³¹⁾. The spectrum of complex (3) showed peaks at $(400)\text{nm}$ $(25000)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=100\text{molar}^{-1}\text{cm}^{-1}$) and $(726)\text{nm}$ $(13774)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=4\text{molar}^{-1}\text{cm}^{-1}$) which can be assigned to (d-d) electronic transition type $(^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g(P)})$ and $(^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g})$ respectively⁽¹⁸⁾. At last spectrum of complex (4)fig.(7) showed peaks at $(355)\text{nm}$ $(28169)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=110\text{molar}^{-1}\text{cm}^{-1}$), $(475)\text{nm}$ $(21052)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=10\text{molar}^{-1}\text{cm}^{-1}$) and $(821)\text{nm}$ $(12180)\text{cm}^{-1}$ ($\epsilon_{\text{max}}=4\text{molar}^{-1}\text{cm}^{-1}$) which may be assigned to (d-d) electronic transition type $(^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g(P)})$, $(^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g})$ and $(^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g})$ respectively⁽³¹⁾. The (d-d) electronic transition for all prepared complexes (1), (2), (3) and (4) were a good agreement for octahedral geometry around VO(II), Mn(II), Co(II) and Ni(II) central ion⁽³⁰⁾.

Biological screening: The antibacterial activity test

In our study the synthesised compounds have been screened for their antibacterial activity against the

Staphylococcus aureus (G+), *E-coli* (G-), *Pseudomonas* (G-) and *Proteus* (G-) strains by the agar diffusion technique⁽³²⁾. Each of the compounds was dissolved in ethanol to give a final concentration of (0.001)mg/ml, and from the data shown in Table (6), and figs.(8,9,10,11), all compounds exhibited a biological activity against the 4 kinds of bacteria, except [Ni(H₂L)₂(H₂O)₂].2Cl with *Pseudomonase* has no biological activity [inhibition zone=0].

CONCLUSION

On the basis of elemental microanalysis, molar conductance, magnetic moment, chloride content and spectroscopic measurements[IR, UV-Vis, Atomic Absorption and ¹H ¹³C NMR], we suggest that the ligand [H₂L] behaves as bidentate on complexation with VO(II), Mn(II), Co(II) and Ni(II) via two N atoms of iminic group forming octahedral geometry around metal central ion.

Table (1) Results of elemental analysis and physical properties of [H₂L] complexes

Empirical formula	m.wt	yield %	colour	m.p.	Microanalysis found , (Calc.) %				
					C	H	N	metal	Cl
C ₂₈ H ₂₈ N ₄ O ₃	468	97	Orange-brown	80-83	71.62	5.79	11.80		
					71.79	5.98	11.96		
[VO ^{II} C ₅₆ H ₅₆ N ₈ O ₆ SO ₄]2(H ₂ O)	1118.94	78	Green	95-98	59.93	5.12	9.87	4.29	Nil
					(60.05)	(5.36)	(10.00)	(4.55)	Nil
[Mn ^{II} C ₅₆ H ₅₆ N ₈ O ₆ (H ₂ O) ₂]Cl ₂	1096.94	86	Red	89-92	61.00	5.29	10.09	4.92	6.40
					(61.26)	(5.46)	(10.21)	(5.00)	(6.47)
[Co ^{II} C ₅₆ H ₅₆ N ₈ O ₆ (H ₂ O)Cl]Cl	1082.93	82	Dark green	91-93	61.87	5.07	10.17	5.12	6.49
					(62.05)	(5.35)	(10.34)	(5.44)	(6.55)
[Ni ^{II} C ₅₆ H ₅₆ N ₈ O ₆ (H ₂ O) ₂]Cl ₂	1100.69	91	Dark green	96-99	60.67	5.18	10.03	5.14	6.30
					(61.05)	(5.45)	(10.17)	(5.33)	(6.45)

Table (2) ¹H NMR data for [H₂L] measured in DMSO-d₆ and chemical shift in ppm(δ)

Compound	Funct. Group	δ (ppm)
[H ₂ L]	Ar-C-H	(7.29-7.94) (15H, m)
	-CH ₃	(1.40)(2.20)(2.87) (9H, s)
	N-CH	(3.88, 1H, s)
	-CH	(7.17, 1H,s)
	-OH	(8.16)(9.55) (2H, s)

s= singlet m=multi

Table (3) ^{13}C NMR data for $[\text{H}_2\text{L}]$ measured in DMSO-d^6 and chemical shift in ppm (δ)

Compound	Func. Group	δ_c (ppm)
[H ₂ L]	Ar-C _{7,8,9,10,11,12,17,18,19,20,21,22,23,24,25,26,27,28}	(122.74-138.77)
	C _{1,16}	(47.84)(189.17)
	C _{13,2}	(164.02)(171.47)
	C _{5,15,6}	(15.71)(31.52)(60.94)
	C ₁₄	(55.79)
	C _{3,4}	(105.75)(110.92)

Table (4) (U.V.-Vis.) spectral data, molar conductivity and magnetic susceptibility in ethanol solution

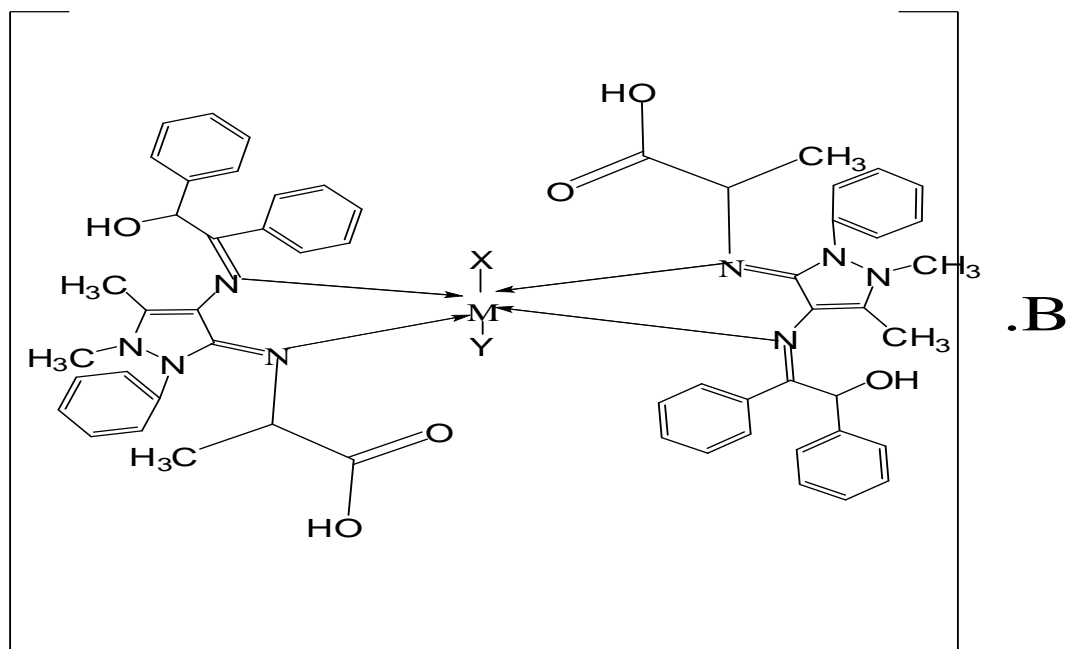
compound	λ nm	ϵ Cm ⁻¹	assignments	χ_m S.cm ² .mole ⁻¹	μ_{eff} (μB)	Suggested structure
[H ₂ L]	244 350	40983 28571	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
[VO(H ₂ L) ₂ (SO ₄).2H ₂ O]	242 340 368 454 815	41322 29411 27174 22067 12270	Intra-ligand Intra-ligand (² B _{2g} → ² A _{1g}) (² B _{2g} → ² B _{1g}) (² B _{2g} → ² E _g)	11.25	1.84	octahedral
[Mn (H ₂ L) ₂ (H ₂ O) ₂].Cl ₂	244 355 400 768	40983 28169 25000 13021	Intra-ligand (⁶ A _{1g} → ⁴ A _{1g} , ⁴ E _{g(G)}) (⁶ A _{1g} → ⁴ T _{2g(G)}) (⁶ A _{1g} → ⁴ T _{1g(G)})	110.51	5.50	octahedral
[Co(H ₂ L) ₂ (H ₂ O)Cl].Cl	243 350 400 726	41152 28571 25000 13774	Intra-ligand Intra-ligand (⁴ T _{1g} → ⁴ T _{1g(P)}) (⁴ T _{1g} → ⁴ T _{2g})	63.60	4.80	octahedral
[Ni(H ₂ L) ₂ (H ₂ O) ₂].Cl ₂	243 350 475 821	41152 28169 21052 12180	Intra-ligand (³ A _{2g} → ³ T _{1g(P)}) (³ A _{2g} → ³ T _{1g}) (³ A _{2g} → ³ T _{2g})	93.72	2.80	octahedral

Table (5) I.R. spectral data of the synthesized compounds

Compounds	ν (OH)	ν (C=N)	ν (C=C)	ν (C=O)	$\nu_{\text{asy}}(\text{COO})^-$ $\nu_{\text{sy}}(\text{COO})^-$	ν (M-N)	Additional peaks
[H ₂ L]	3404 _(br)	1635 _(w) 1560 _(w)	1593 _(m)	1660 _(s)	1456 _(s) 1375 _(m)	—	δ (OH)1313 _(m)
[VO(H ₂ L) ₂ (SO ₄)] ₂ .2H ₂ O	3410 _(br)	1616 _(w) 1541 _(w)	1559 _(m)	1660 _(s)	1450 _(s) 1338 _(m)	574 _(w)	δ (OH)1325 _(m) , ν (V=O)977 _(m) , ν (OSO)1047,939, δ (OSO)615,466
[Mn(H ₂ L)(H ₂ O) ₂].Cl ₂	3441 _(br)	1579 _(m) 1541 _(w)	1595 _(w)	1624 _(m)	1450 _(s) 1327 _(m)	570 _(w)	δ (OH)1292 _(w) , (H ₂ O)939 _(w) coordinated
[Co(H ₂ L)(H ₂ O)Cl].Cl	3429 _(br)	1579 _(w) 1535 _(m)	1595 _(w)	1633 _(s)	1473 _(w) 1325 _(m)	570 _(w)	δ (OH)1317 _(m) , (H ₂ O)939 _(w) coordinated
[Ni(H ₂ L)(H ₂ O) ₂].Cl ₂	3373 _(br)	1622 _(m) 1558 _(m)	1595 _(m)	1670 _(m)	1450 _(s) 1325 _(s)	578 _(w)	δ (OH)1379 _(w) , coordinated(H ₂ O)910

Table (6) the biological activity of the synthesised compounds

compound	<i>Staphylococcus aureus</i> (G+)	<i>E-coli</i> (G-)	<i>Pseudomonas</i> (G-)	<i>Proteus</i> (G-)
[H ₂ L]	3	2	2	3
[VO(H ₂ L) ₂ (SO ₄)] ₂ .2H ₂ O	35	30	37	32
[Mn (H ₂ L) ₂ (H ₂ O) ₂].Cl ₂	17	7	15	9
[Co(H ₂ L) ₂ (H ₂ O)Cl].Cl	12	7	16	8
[Ni(H ₂ L) ₂ (H ₂ O) ₂].Cl ₂	5	4	0	3
Control	2	7	11	5



M=VO⁺, X=O, Y= OSO₃, B=2H₂O
 M= Mn⁺, Ni⁺, X=H₂O, Y=H₂O, B=2Cl
 M= Co⁺, X= H₂O, Y= Cl, B= Cl

Fig.(1) Chemical structure of complexes

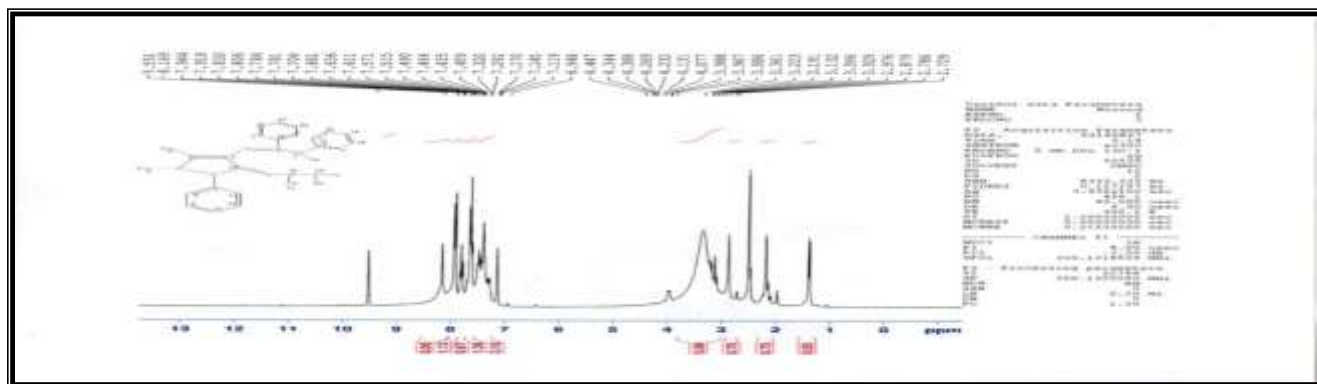


Fig.(2) ¹H NMR spectrum for the ligand [H₂L] in DMSO-d₆

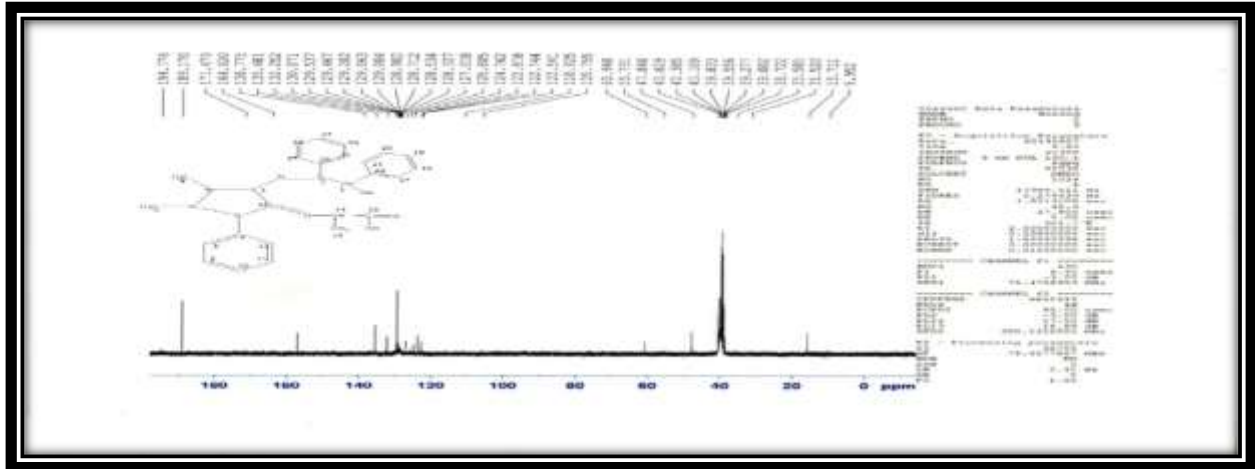


Fig. (3) ¹³C NMR spectrum for [H₂L] in DMSO-d⁶

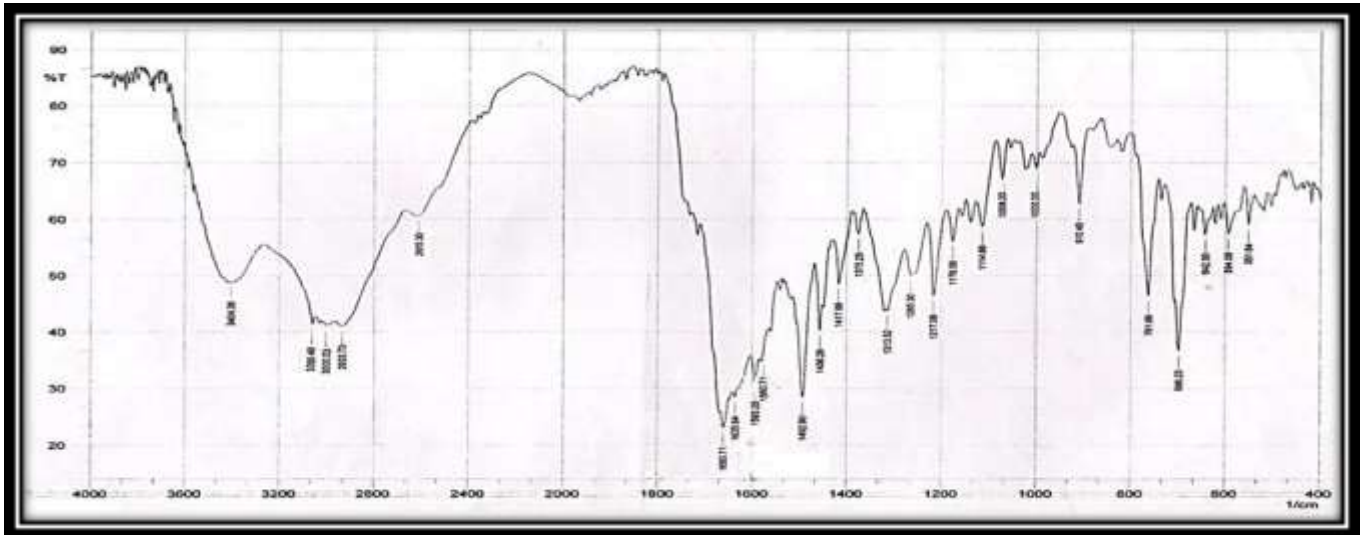


Fig.(4) the I.R. spectrum of the ligand [H₂L]

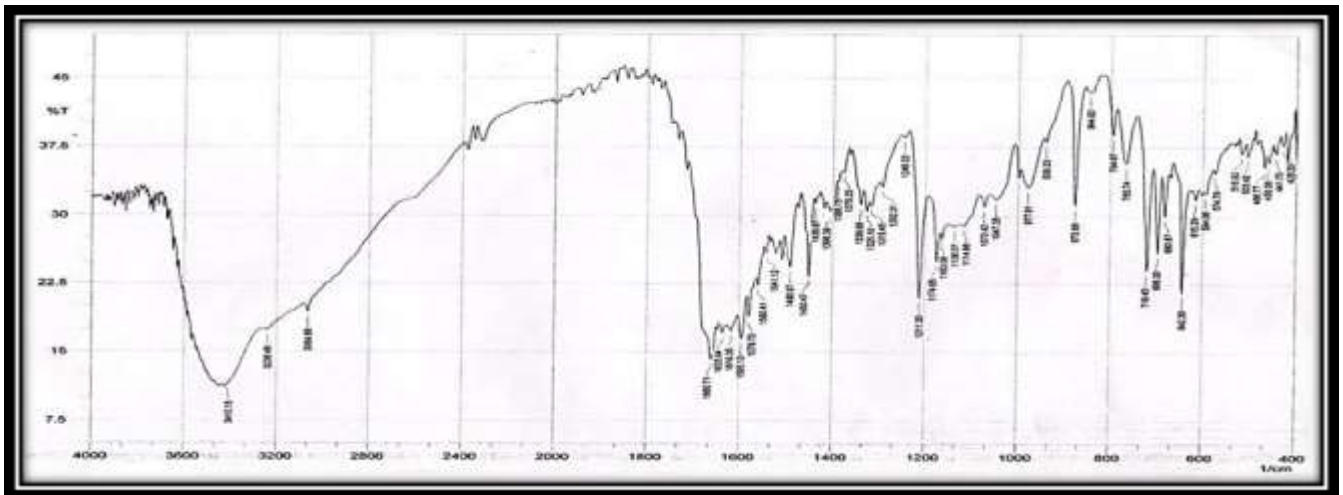


Fig.(5) the I.R. spectrum of [VO(H₂L)₂(SO₄)].2H₂O

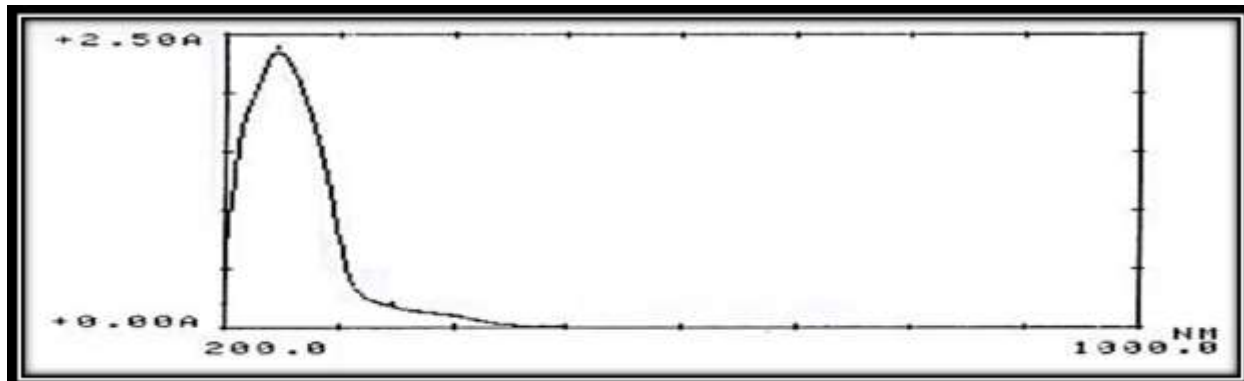


Fig.(6) Electronic spectrum of ligand [H₂L]

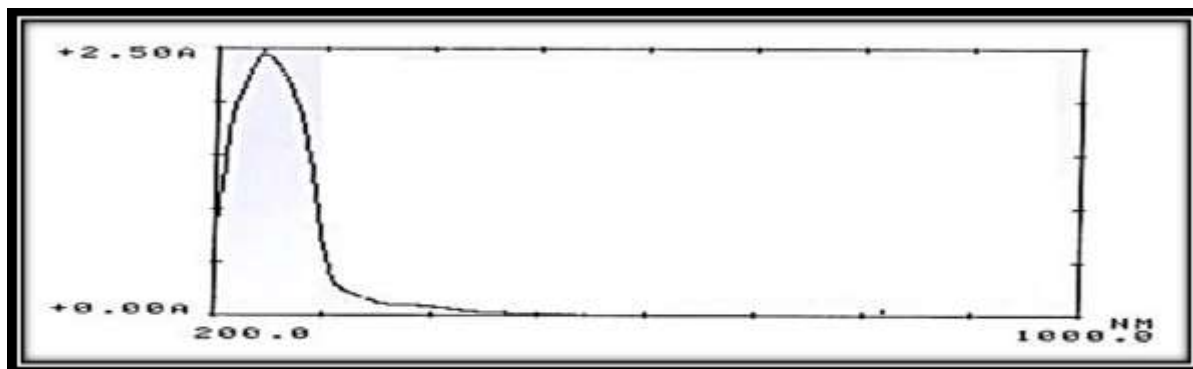


Fig.(7) Electronic spectrum of [Ni(H₂L)₂(H₂O)₂].Cl

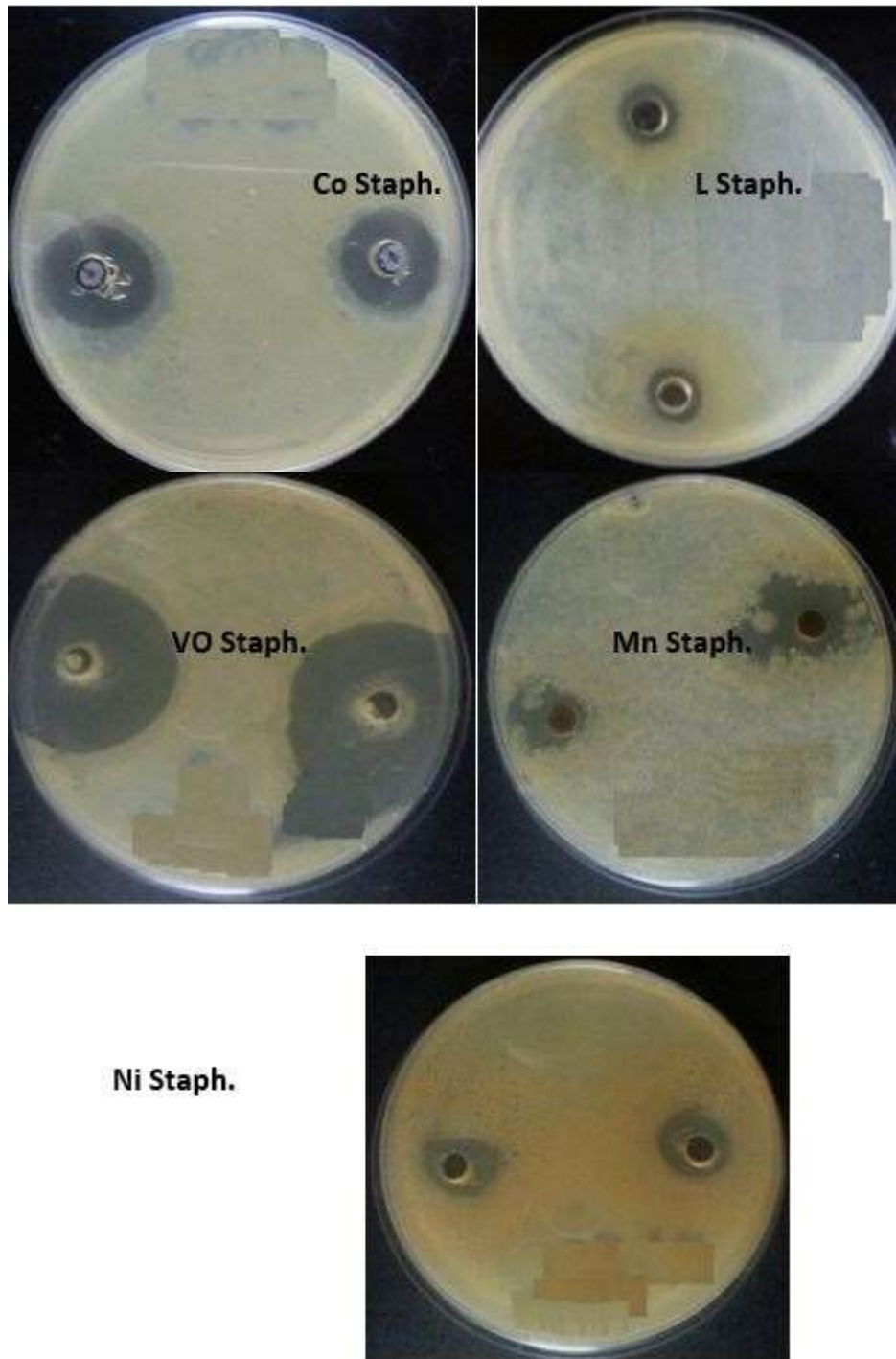


Fig.(8) Effect of the ligand and complexes towards the Staphylococcus aureus

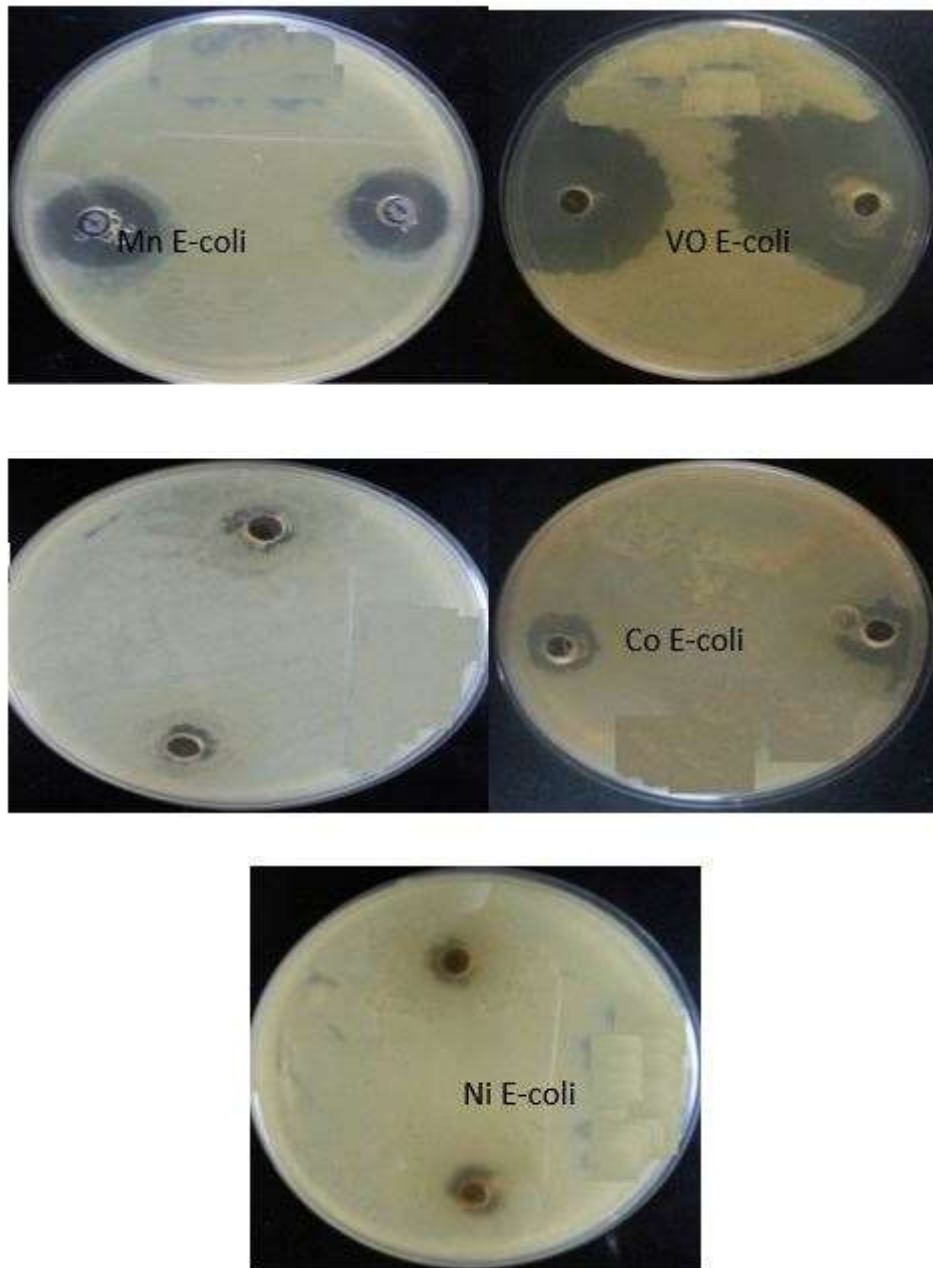


Fig.(9) Effect of the ligand and complexes towards the E-coli

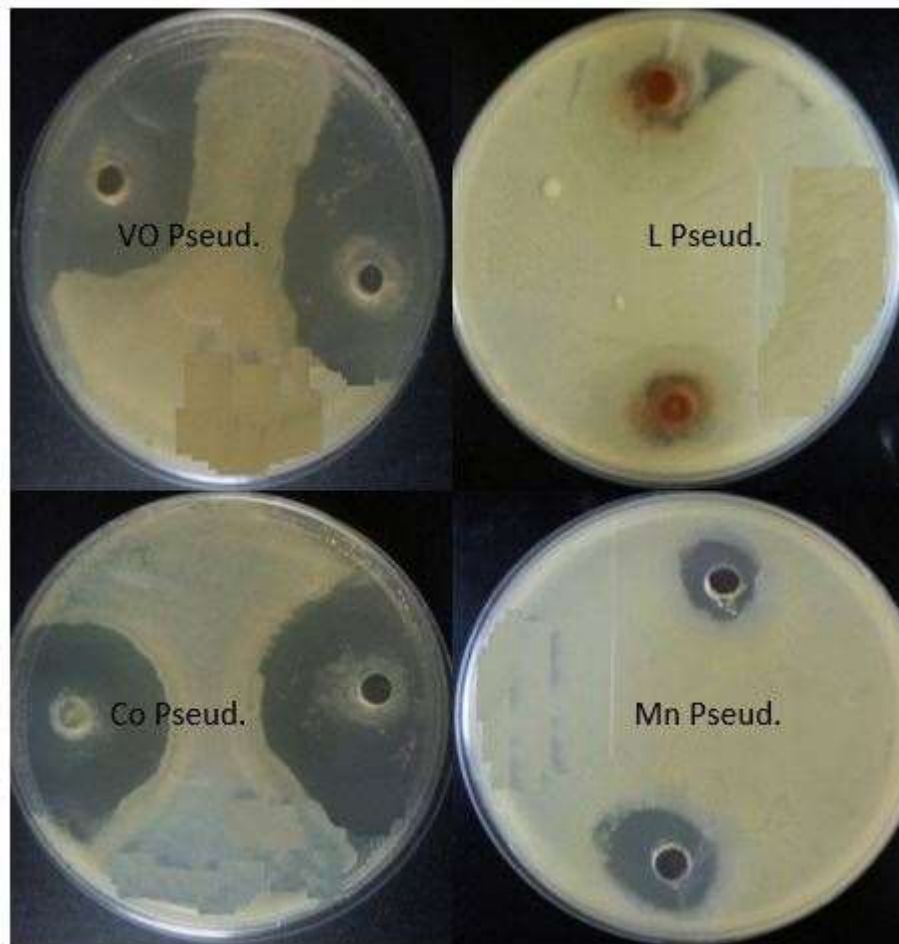


Fig.(10) Effect of the ligand and complexes towards the Pseudomonas

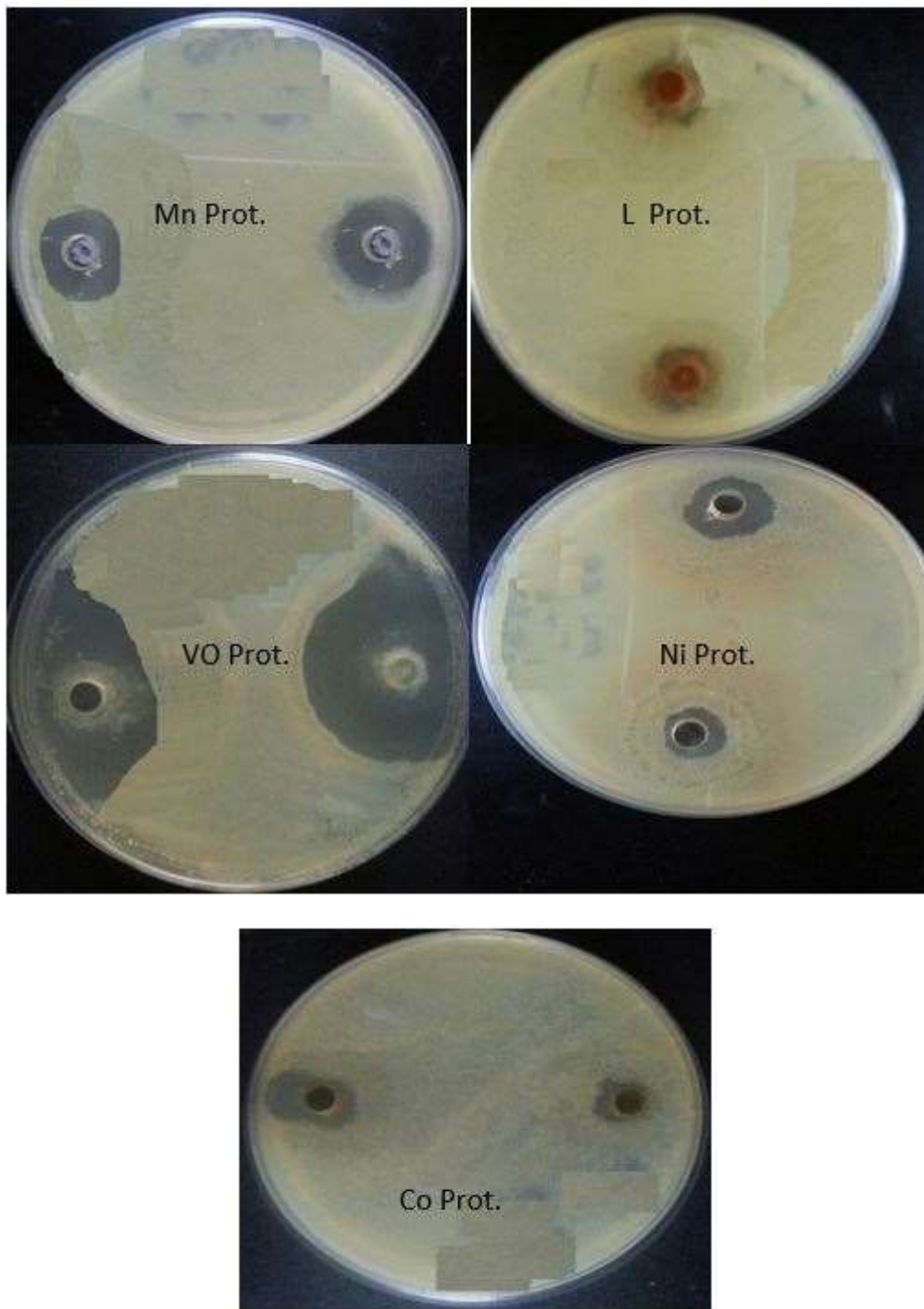


Fig.(11) Effect of the ligand and complexes towards the Proteus

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