Synthesis, Characterization and Biological Activity for Complexes VO(II), Mn(II), Co(II) and Ni(II) with new multidentate ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid][H_2L] type (N_2).

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Received 15 February 2015 ; Accepted 9 April 2015

Abstract

In this work, the precursor [2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid] was synthesised from 4-aminoantipyrine and glyoxylic acid, this precursor has been used in the synthesis of new multidentate ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid][H_2L] type (N_2O_2). The ligand was refluxed in ethanol with metal ions [VO(II), Mn(II), Co(II) and Ni(II)] salts to give complexes of general molecular formula:$[M(H_2L)_2(X)(Y)].B$, where: M=VO(II), X=0, $Y=OSO_3^{-2}$, $B=2H_2O$; M=Mn(II),Co(II) ,X=Cl, Y=Cl, B=0; M=Ni(II), X=H_2O, Y=Cl, B=Cl. These complexes were characterised by atomic absorpition(A.A), F.T-I.R., (U.V-Vis)spectroscopies (^1H,^{13}C NMR for ligand only), along with condectivity, 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 $[Ni(H_2L)_2(H_2O)Cl].Cl$ with *Pseudomonase* has no biological activity.

Keywords: 4-aminoantipyrine, glyoxilic acid, complexes.

تحضير و تشخيص و دراسة الفعالية البيولوجية لمعقدات Ni(II), Co(II), Mn(II),VO(II) مع الليكاند متعدد السن الجديد [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid][H_2L] type (N_2).

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الخلاصة

في هذا البحث, المشتق [2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid] تم تحضيره من 4-امينوانتي بايرين مع حامض الكلايوكسلك حيث المشتق الناتج تم استعماله في تحضير الليكاند المتعدد السن الجديد [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid][H_2L] type (N_2O_2).

تم تصعيد الليكاند باستعمال الايثانول مذيبا مع املاح الايونات VO(II), Mn(II), Co(II), Ni(II) ذوات الصيغة الجزيئية العامة $[M(H_2L)_2(X)(Y)].B$, where: M=VO(II), X=0, $Y=OSO_3^{-2}$, $B=2H_2O$; M=Mn(II),Co(II) ,X=Cl, Y=Cl, B=0; M=Ni(II), X=H_2O, Y=Cl, B=Cl. شخصت المعقدات بالطرائق الطيفية (الاشعه تحت الحمراء والاشعة فوق البنفسجية-المرئية مع الامتصاص الذري, وقياسات التوصيلية الكهربائية والتحليل الدقيق للعناصر(C.H.N.) ومحتوى الكلوريد ودرجات الانصهار وكذلك قياسات الرنين النووي المغناطيسي (^1H,^{13}C) لليكاند. هذه الدراسات بينت ان الشكل الهندسي هو ثماني السطوح لمعقدات Ni(II), Co(II), Mn(II),VO(II) أما قياسات الفعالية البيولوجية فأظهرت ان الليكاند ومعقداته فعالة تجاه انواع من البكتريا وهي *Staphylococcus aureus* (G+), *E-coli* (G-), *Pseudomonas* (G-), *Proteus* (G-) ماعدا معقد النيكل ضد بكتريا الـ *Pseudomonas* (G-) .

الكلمات المفتاحية: 4-امينو انتي بايرين، كلايوكسيلك ، المعقدات.

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 member ring compound having three carbon and two nitrogen atoms. Several pyrazoline substitution products are used in medicine[6]. In 1884, Knoor 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 spectrophtometric determination of metal ion, many of these regents 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 25ºC. Electrical molar conductivity measurements of the complexes were recorded at (25ºC) for (10^{-3})M solutions of the samples in ethanol using a PW 9526 digital conductivity meter.^{1}H,^{13}C NMR spectra were recorded using DMSO-d6 at Brucker 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[2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid].

(2.0g, 9.8mmole) from 4-aminoantipyrine, was added to (0.72g, 9.7mmole) of glyoxylic acid in ethanol (30ml.) with stirring, then (0.3mL) HBr 48% was added and refluxed to 5hrs. (Light brown precipitate was observed after refluxing for 3hrs.). The reaction mixture was cooled in ice-bath, the light brown product was isolated by filtration and washed by small portions of ethanol and dried to give a light brown precipitate, yield (2.3g) (90%), m.p.(178-180°C).

2- Preparation of ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic acid].

A solution of precursor (1.0g, 3.8mmole) in (30mL) ethanol, was added to (0.3g, 2.7mmole) of *O*-aminophenol, then (0.3mL) HBr 48% was added and refluxed to 7hrs. Dark brown precipitate was observed after refluxing for 4hrs., the reaction mixture was cooled in ice-bath, the dark brown product was isolated by filtration and washed by small portions of ethanol and dried to give a dark brown precipitate, yield (1.09g) (85%), m.p.(115-120°C).

3- Preparation of $[VO(H_2L)_2(SO_4)].2H_2O$ (1)

A solution of (0.045g, 0.27mmole) of Vanadium (II) Sulfate monohydrate($VOSO_4.H_2O$) dissolved in (10mL) of ethanol was added dropwise to a solution of [H_2L](0.21g, 0.28mmole) dissolved in (15 mL) ethanol. The reaction mixture was allowed to reflux for 3hrs.

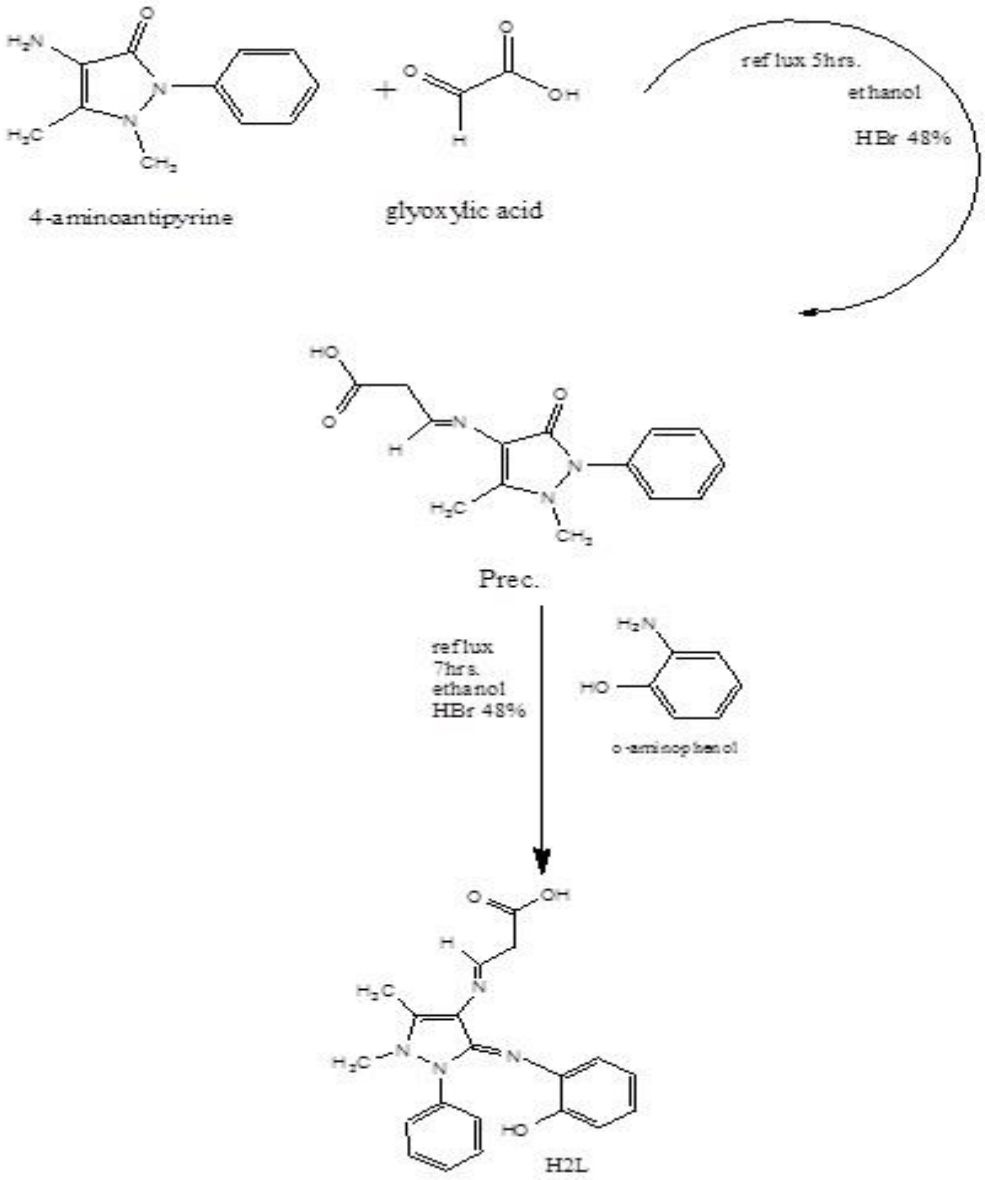
A dark brown precipitate was formed, which filtered off, washed several times with absolute ethanol and dried. Yield 0.19g, (86 %) of the title complex, m.p. (151 – 153ºC).

4-Preparation of [$Mn(H_2L)_2Cl_2$](2), [$Co(H_2L)_2Cl_2$](3) and [$Ni(H_2L)_2(H_2O)Cl$].Cl (4)

A similar method to that mentioned for the preparation of VO(II) complex was used to prepare the complexes of [H_2L] with [Mn(II), Co(II) and Ni(II)] ions.

Results and Discussion

The ligand [H_2L] was obtained in high yield by the condensation reaction using one equivalent of precursor and one equivalent of *O*-aminophenol, which has N_2O_2 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 [H_2L] were listed in table(1). The reaction of ligand [H_2L] and $VOSO_4.H_2O$ 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: [$VO(H_2L)_2SO_4$].$2H_2O$, [$Mn(H_2L)_2Cl_2$], [$Co(H_2L)2Cl_2$] and [$Ni(H_2L)_2(H_2O)Cl$]Cl. Also the suggested molecular formula was supported by spectral measurements as well as molar conductivity.



General route for the preparation of ligand [H_2L]

(NMR) spectra for ligand [H_2L].

The ^{1}H and ^{13}C correlated NMR analysis were used to characterise the ligand [H_2L]. The spectra were recorded in DMSO–d^6 solution.

^{1}H NMR spectrum for the ligand [H_2L].

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.^{1}H NMR spectrum for [H_2L], Fig.(2) in DMSO-d^6 displayed signal at chemical shift (δ_H = 7.90 ppm, 1H, s) attributed to the proton of the azomethine group (N=C-*H*) [13]. The resonances at chemical shift (δ_H = 6.17-7.23ppm, 9H, m), (Ar–H), are assignable to protons of aromatic ring. The appearances of these protons as a multi are due to mutual coupling. The sharp singlet signals at (δ_H = 2.30 and 1.95 ppm) equivalent to six protons (6H, S) is attributed to the protons of methyl group[14]. The broaden hump signal at (δ_H = 8.75 ppm, 1H) and (δ_H = 9.38 ppm, 1H) are assignable to protons of (O–*H*) phenolic group and (O–*H*) carboxylic group respectively. The broadness of these signals could be related to hydrogen bonding (N…..H—O)[15] and the ion pairs of nitrogen atoms of azomethine groups. The spectrum displayed chemical shifts at (δ_H = 2.50 ppm, and δ_H = 3.05 ppm) referred to the DMSO solvent, and the presence of water molecules in the solvent respectively. The results are summarised in Table (2).

^{13}C NMR spectrum for [H_2L]

The ^{13}C NMR spectrum of (H_2L), Fig.(3) in DMSO-d^6 solvent shows chemical shift at range (δ= 114.85-129.02 ppm) assigned to aromatic carbon atoms ($C_{7,8,9,10,11,12,14,15,16,17,18,19}$). The chemical shift at (δ= 170.82 ppm) attributed to the carboxilic carbon atom (C_1) (COOH), while the chemical shifts at (δ= 135.72 and 144.24 ppm) are assigned for imine carbon atoms (C_{13}, C_2) (-C=N-) respectively. The chemical shifts at (δ= 13.93 and 60.75 ppm) assigned to methyl group carbon atoms ($C_{5,6}$) respectively. At last the chemical shifts (δ=110.88 and 113.58 ppm) refer to C=C carbon atoms ($C_{3,4}$) respectively[13]. The results are listed in Table(3).

Molar conductivity

The molar conductance of complexes (1,2 and 3) in ethanol lie in the (14.50- 28.52)S.cm^{-1}.mole^{-1} range, indicating their non-electrolytic behavior, while the molar conductance of complex (4) lie in (31.50)S.cm^{-1}.mole^{-1}, indicating 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 [$VO(H_2L)_2SO_4$].2H_2O (1.86)B.M, [$Mn(H_2L)_2Cl_2$] (5.52) B.M, [$Co(H_2L)_2Cl_2$] (4.81) B.M and [$Ni(H_2L)_2(H_2O)Cl$]Cl (2.81) 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 [H_2L] and prepared complexes (1), (2), (3) and (4) were listed in table (5). The I.R. spectrum for [H_2L] fig.(4) displayed two bands at [(1515), (1496)]cm^{-1} assigned to the iminic υ(C=N) group and these bands were shifted to higher frequencies in complexes, the shift to higher frequency may be due to the weak bonding nature between the metal ions and the iminic (C=N)group. The shift in υ(C=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 1458 and 1369 cm^{-1}, whose are assigned to $\upsilon_{asy}(COO^{-})$ and $\upsilon_{sy}(COO^{-})$ 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, 551, 592 and 543)cm^{-1} can be refer to υ(M-N) for complexes (1),(2),(3)and(4) respectively. This new bands supported the coordination of the ligand to the central metal ion through two nitrogen atoms of iminic group[25].The IR spectrum of complex (1) fig.(5) showed bands at (927), (1055,923),(613,495)cm^{-1} maybe refer to υ(V=O), $\upsilon(OSO_3)$ and $\delta(OSO_3)$ 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 [H_2L] and (1),(2),(3) and (4) complexes are shown in Table (4). The (U.V.-Vis) spectrum for [H_2L](fig.6) exhibits three intense absorption peaks, the first peak at (241)nm (41493)cm^{-1} (ε_{max}= 2429 $molar^{-1}cm^{-1}$) assigned to ($\pi \rightarrow \pi^*$) electronic transition, the second peak at (348) nm (28735)cm^{-1} (ε_{max}= 615 $molar^{-1}cm^{-1}$) assigned to ($n\rightarrow\pi^*$) electronic transition, and the third peak at (412) nm (24271)cm^{-1} (ε_{max}= 384 $molar^{-1}cm^{-1}$) assigned to ($n\rightarrow\pi^*$) electronic transition[29]. The spectrum showed intense peak in the (U.V.)region at (241)nm (41493)cm^{-1} (ε_{max}= 2441)$molar^{-1}cm^{-1}$, (241)nm (41493)cm^{-1} (ε_{max}=2418) $molar^{-1}cm^{-1}$, (239)nm (41841)cm^{-1} (ε_{max}= 2045)$molar^{-1}cm^{-1}$ and (242)nm (41322)cm^{-1}, (ε_{max}=2264) $molar^{-1}cm^{-1}$ for complexes (1), (2), (3) and (4) respectively assigned to intra ligand ($\pi\rightarrow \pi^*$) electronic transition[30]. Also the peaks at (350)nm (28571)cm^{-1}(ε_{max}=750) $molar^{-1}cm^{-1}$, (350)nm (28571)cm^{-1} (ε_{max}=700)$molar^{-1}cm^{-1}$ and (349)nm (28653)cm^{-1}, (ε_{max}=450) $molar^{-1}cm^{-1}$ for complexes (1), (3) and (4) 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 [H_2L], that confirming the coordination of the ligand to the central metal ion.

The spectrum of complex (1) showed peaks at (416)nm (24038)cm^{-1} (ε_{max}=1026)$molar^{-1}$ cm^{-1}, (545)nm (18349)cm^{-1}(ε_{max}=230)$molar^{-1}$ cm^{-1} and (786)nm (12723)cm^{-1} (ε_{max}=21)$molar^{-1}cm^{-1}$ which can be assigned to (d-d) electronic transition type ($^2B_2g\rightarrow{}^2A_1g$), ($^2B_2g\rightarrow{}^2B_1g$) and ($^2B_2g\rightarrow{}^2Eg$) respectively[18]. the spectrum of complex (2) showed peaks at (355)nm (28169)cm^{-1}(ε_{max}=900)$molar^{-1}cm^{-1}$, (433)nm (23095)cm^{-1} (ε_{max}=1189)$molar^{-1}cm^{-1}$ and (610)nm (16393)cm^{-1} (ε_{max}=10)$molar^{-1}cm^{-1}$ which can be assigned to (d-d) electronic transition type ($^6A_1g\rightarrow{}^4A_1g$, $^4Eg_{(G)}$), ($^6A_1g\rightarrow{}^4T_2g_{(G)}$) and ($^6A_1g\rightarrow{}^4T_1g_{(G)}$) respectively[31]. The spectrum of complex (3) fig.(7) showed peaks at (430)nm (23256)cm^{-1}(ε_{max}=881)$molar^{-1}cm^{-1}$, (572)nm (17482)cm^{-1} (ε_{max}=25)$molar^{-1}cm^{-1}$ and (747)nm (13387)cm^{-1} (ε_{max}=43)$molar^{-1}$ cm^{-1} which can be assigned to (d-d) electronic transition type ($^4T_1g\rightarrow{}^4T_1g_{(P)}$), ($^4T_1g\rightarrow{}^4A_2g$)

and ($^4T_1g \rightarrow {}^4T_2g$) respectively[18]. At last spectrum of complex (4) showed peaks at (431)nm (23202)cm^{-1}(ε_{max}=609)$molar^{-1}cm^{-1}$, (829)nm (12062)cm^{-1} (ε_{max}=12)$molar^{-1}cm^{-1}$ and (968)nm (10330)cm^{-1} (ε_{max}=5)$molar^{-1}$ cm^{-1} which can be assigned to (d-d) electronic transition type ($^3A_2g \rightarrow {}^3T_1g_{(P)}$), ($^3A_2g \rightarrow {}^3T_1g$) and ($^3A_2g \rightarrow {}^3T_2g$) 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-), *Pseudomonase*(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 $[Ni(L)_2(H_2O)Cl].Cl$ 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 ^{13}C NMR], we suggest that the ligand [H_2L] 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 [H_2L] Complexes

Empirical formula	m.wt	yield %	colour	m.p.	Microanalysis found , (Calc.) %				
					C	H	N	metal	Cl
H_2L*	350	85	Dark brown	115-120	65.10	5.06	15.92	-	-
					(65.14)	(5.14)	(16.00)		
$[VO^{II}(H_2L)_2SO_4](H_2O)$	782.94	86	Brown	151-153	58.08	4.96	14.21	6.38	0
					(58.24)	(5.10)	(14.30)	(6.50)	0
$[Mn^{II}(H_2L)_2Cl_2]$	824.94	91	Brown	129-132	55.18	4.23	13.44	6.54	8.49
					(55.27)	(4.36)	(13.57)	(6.65)	(8.60)
$[Co^{II}(H_2L)_2Cl_2]$	828.93	91	Dark green	255-257	54.78	4.14	13.45	7.00	8.49
					(55.01)	(4.34)	(13.51)	(7.10)	(8.56)
$[Ni^{II}(H_2L)_2(H_2O)Cl]$ Cl	846.69	83	Brown	130-133	53.73	4.31	12.87	6.84	8.13
					(53.85)	(4.48)	(13.22)	(6.93)	(8.38)
					(53.54)	(4.46)	(13.15)	(7.46)	(8.33)

*H_2L: $C_{19}H_{18}N_4O_3$

Table (2) ^{1}H NMR data for [H_2L] measured in DMSO-d^6 and chemical shift in ppm(δ)

Compound	Funct. Group	δ (ppm)
[H_2L]	*Ar-C-H*	(6.17-7.23) (9H, m)
	-CH_3	(1.95)(2.30) (6H, s)
	N=C-H	(7.90, 1H, s)
	-OH	(8.75)(9.38) (2H, br)

Table (3) ^{13}C NMR data for [H_2L] measured in DMSO-d^6 and chemical shift in ppm (δ)

Compound	**Func. Group**	**δ_c (ppm)**
[H_2L]	Ar–$C_{7,8,9,10,11,12,14,15,16,17,18,19}$	(114.85-129.02)
	C_1	(170.82)
	$C_{13,2}$	(135.72)(144.24)
	$C_{5,6}$	(13.93)(60.75)
	$C_{3,4}$	(110.88)(113.58)

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

compound	λ nm	ύCm^{-1}	assignments	Λ_mS.cm^2.mole^{-1}	μ_{eff}(μB)	Suggested structure
[H_2L]	241 348 412	41493 28735 24271	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
[$VO(H_2L)_2(SO_4)$].2H_2O	241 350 416 545 786	41493 28571 24038 18349 12723	Intra-ligand Intra-ligand ($^2B_2g \rightarrow {}^2A_1g$) ($^2B_2g \rightarrow {}^2B_1g$) ($^2B_2g \rightarrow {}^2Eg$)	18.52	1.86	octahedral
[$Mn(H_2L).Cl_2$]	241 355 433 610	41493 28169 23095 16393	Intra-ligand ($^6A_1g \rightarrow {}^4A_1g, {}^4Eg_{(G)}$) ($^6A_1g \rightarrow {}^4T_2g_{(G)}$) ($^6A_1g \rightarrow {}^4T_1g_{(G)}$)	14.50	5.52	octahedral
[$Co(H_2L).Cl_2$]	239 350 430 572 747	41841 28571 23256 17482 13387	Intra-ligand Intra-ligand ($^4T_1g \rightarrow {}^4T_1g_{(P)}$) ($^4T_1g \rightarrow {}^4T_2g$) ($^4T_1g \rightarrow {}^4T_1g$)	28.52	4.81	octahedral
[$Ni(H_2L)_2(H_2O)Cl$].Cl	242 349 431 829 968	41322 28653 23202 12062 10330	Intra-ligand Intra-ligand ($^3A_2g \rightarrow {}^3T_1g_{(P)}$) ($^3A_2g \rightarrow {}^3T_1g$) ($^3A_2g \rightarrow {}^3T_2g$)	31.50	2.81	octahedral

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

compound	*Staphylococcus aureus* (G+)	*E-coli* (G-)	*Pseudomonas* (G-)	*Proteus* (G-)
$[H_2L]$	3	2	2	3
$[VO(H_2L)_2(SO_4)].2H_2O$	5	3	6	3
$[Mn(H_2L)_2\ Cl_2]$	17	7	15	9
$[Co(H_2L)_2\ Cl_2]$	8	4	9	7
$[Ni(H_2L)_2(H_2O)Cl].Cl$	5	4	0	3
Control	2	7	11	5

Table (6) the biological activity of the synthesised compounds

Compounds	ν (OH)	ν(C=N)	ν(C=C)	ν(C=O)	$\nu_{asy}(COO)^-$ $\nu_{sy}(COO)^-$	ν(M-N)	Additional peaks
$[H_2L]$	$3419_{(w)}$	$1515_{(s)}$ $1496_{(s)}$	$1589_{(s)}$	1624 (carbox.)	$1458_{(s)}$ $1369_{(m)}$	———	$\delta(OH)1450_{(w)}$
$[VO(H_2L)_2(SO_4)].2H_2O$	$3442_{(br)}$	$1541_{(w)}$ $1521_{(m)}$	$1558_{(m)}$	$1635_{(m)}$	$1508_{(w)}$ $1319_{(w)}$	$574_{(w}$	$\delta(OH)1338_{(m)}$, $\nu(V=O)927_{(m)}$, $\nu(OSO)1055,923$, $\delta(OSO)613,495$
$[Mn(H_2L).Cl_2]$	$3383_{(br)}$	$1541_{(w)}$ $1500_{(m)}$	$1560_{(w)}$	$1624_{(s)}$	$1490_{(w)}$ $1317_{(w)}$	$551_{(w}$	$\delta(OH)1338_{(m)}$
$[Co(H_2L).Cl_2]$	$3398_{(br)}$	$1541_{(m)}$ $1521_{(w)}$	$1558_{(m)}$	$1616_{(s)}$	$1490_{(m)}$ $1313_{(m)}$	$592_{(m)}$	$\delta(OH)1338_{(m)}$
$[Ni(H_2L)_2(H_2O)Cl].Cl$	$3483_{(br)}$	$1541_{(w)}$ $1520_{(m)}$	$1577_{(w)}$	$1624_{(s)}$	$1489_{(w)}$ $1319_{(w)}$	$543_{(w)}$	$\delta(OH)1338_{(m)}$, coordinated$(H_2O)923$

Synthesis, Characterization and Biological Activity for Complexes VO(II), Mn(II), Co(II) and Ni(II) With New Multidentate Ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic Acid][H_2L] type (N_2).

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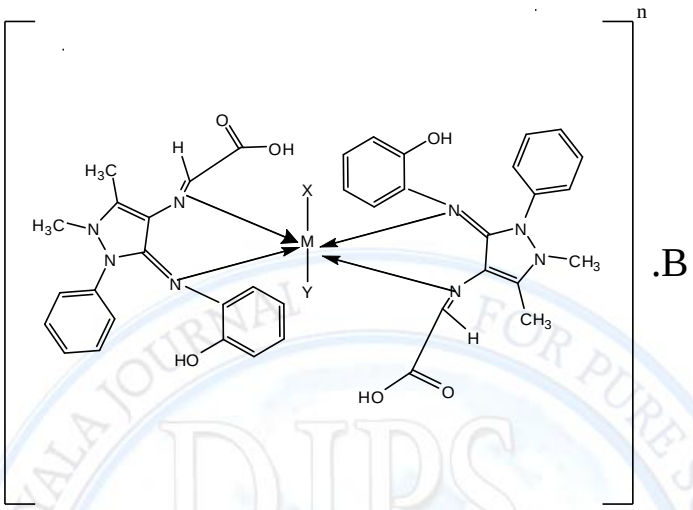

M=VO(II),X=0,Y= OSO_3^{-2}, B=2H_2O; M= Mn(II), Co^{+2}, X=Cl, Y=Cl, B=0; M=Ni(II), X=H_2O,Y= Cl,B=Cl

Fig. (1) Chemical structure of prepared complexes

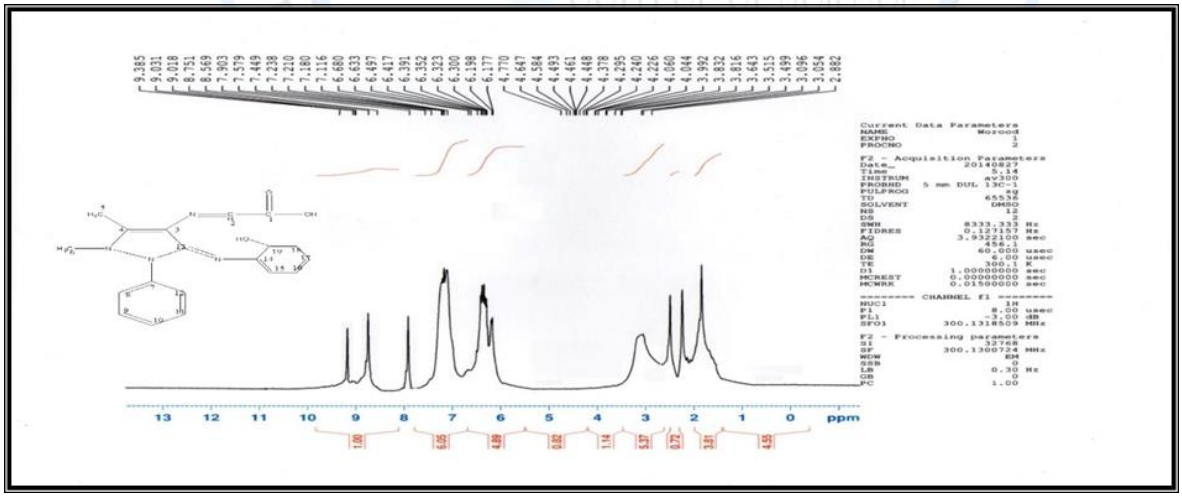

Fig.(2) ^{1}H NMR spectrum for the ligand [H_2L] in DMSO-d^6

Synthesis, Characterization and Biological Activity for Complexes VO(II), Mn(II), Co(II) and Ni(II) With New Multidentate Ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic Acid][H_2L] type (N_2).

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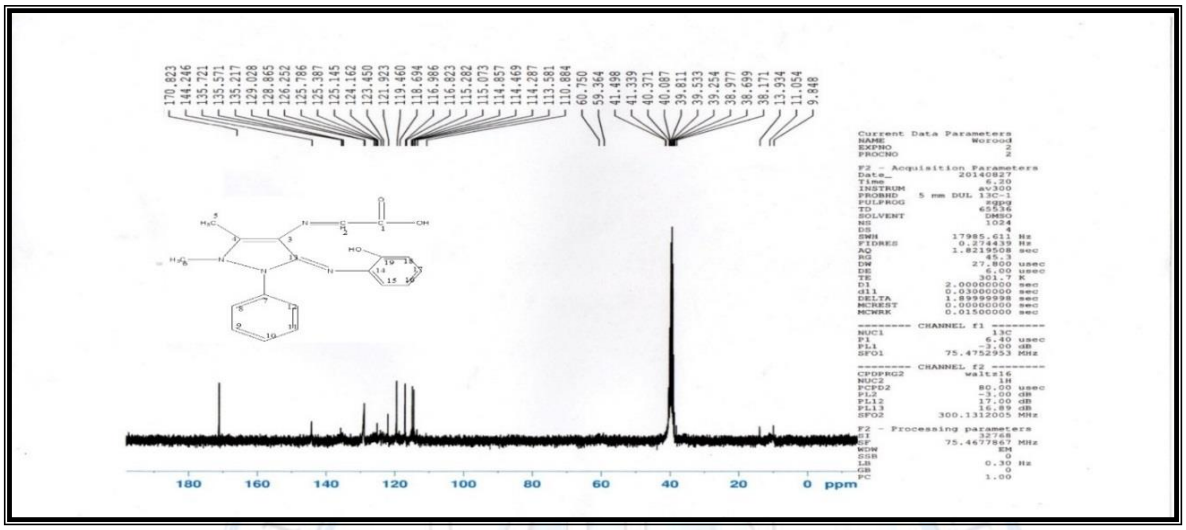

Fig.(3) ^{13}C NMR spectrum for [H_2L] in DMSO-d^6

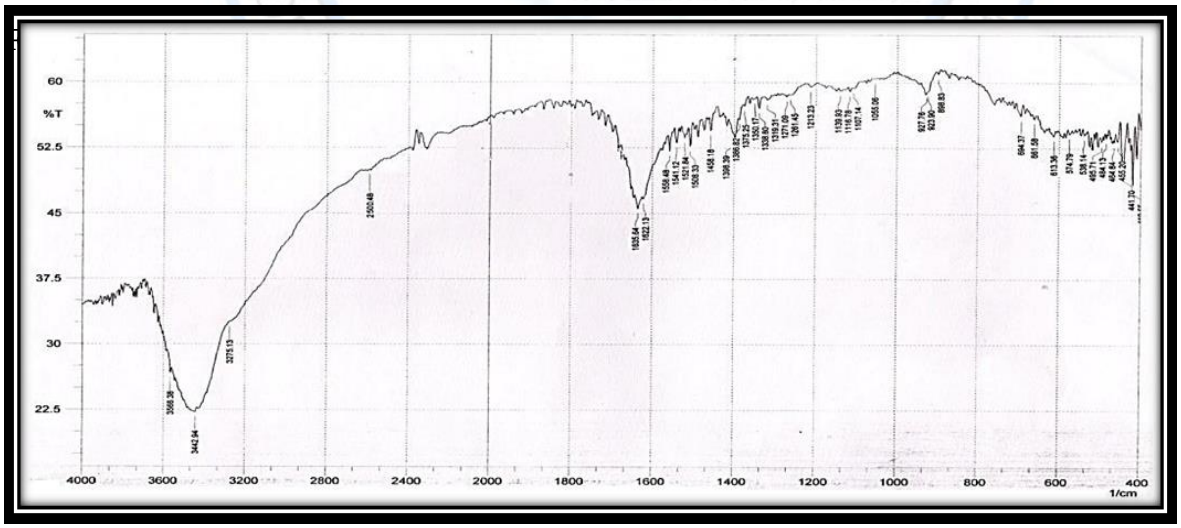

Fig.(4) the I.R. spectrum of the ligand [H_2L]

Synthesis, Characterization and Biological Activity for Complexes VO(II), Mn(II), Co(II) and Ni(II) With New Multidentate Ligand [2-((E)-3-(2-hydroxyphenylimino)-1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)acetic Acid][H_2L] type (N_2).

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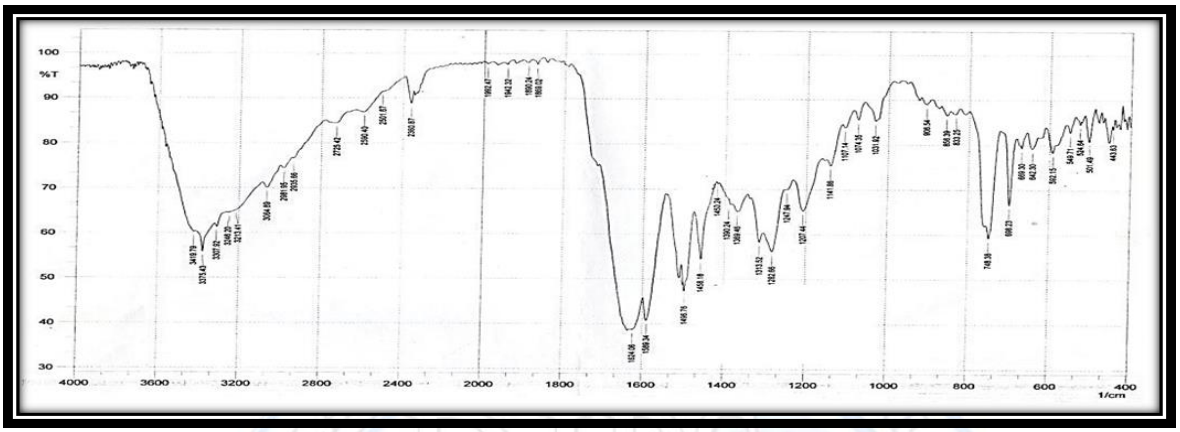

Fig(5) the I.R. spectrum of [$VO(H_2L)_2(SO_4)$].$2H_2O$

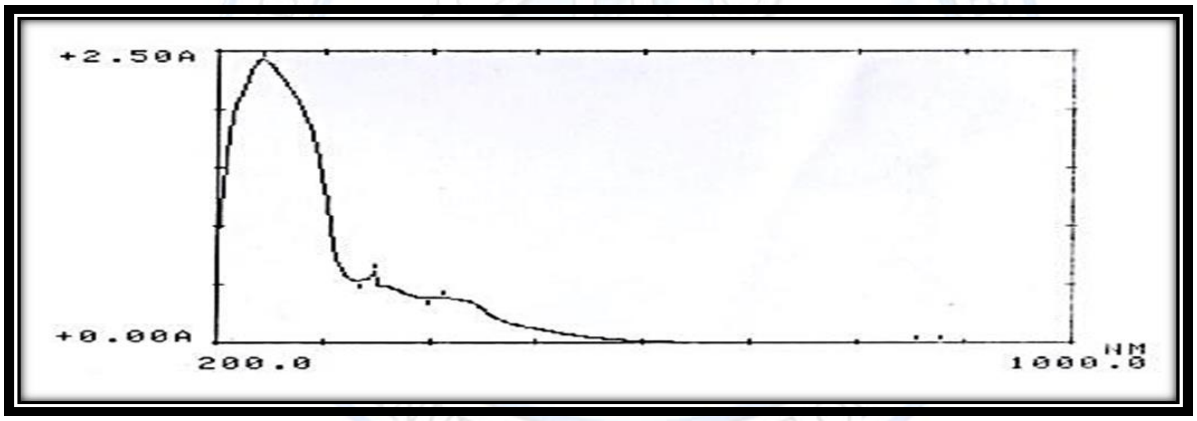

Fig.(6) Electronic spectrum of ligand [H_2L]

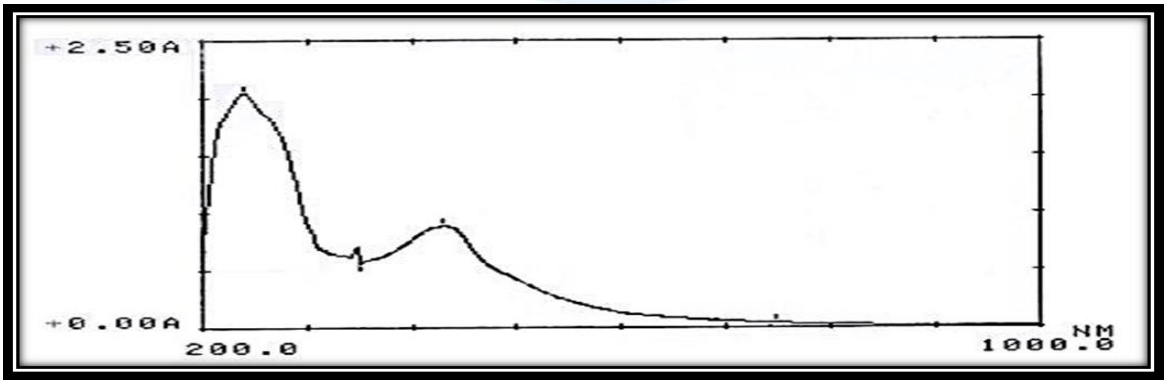

Fig.(7) Electronic spectrum of [$Co(H_2L)_2Cl_2$]

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